

VŠB – Technical University of Ostrava



ADVANCED MATERIALS

textbook

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1. NICKEL ALLOYS



Time needed to study: 2 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- Define basic properties of nickel and nickel alloys
- Describe basic classification of nickel alloys
- Explain differences of nickel alloys
- Explain influence of microstructure on the properties of nickel alloys
- Distinguish selected application of nickel alloys considering their properties



Lecture

1.1 Generalities

1.1.1 Physical properties of nickel

Atomic weight	58.71 g/mol
Crystal structure	FCC
Lattice parameter	0.35168 nm
Density	$8.908.10^3 \text{ kg/m}^3$
Melting point	1453 °C
Latent heat of fusion	309 kJ/kg
Electrical resistivity	6.844 μΩ.cm (20°C)
Curie point	357 °C

- heavy metal
- ductile and malleable (can be drawn into a wire and rolled into a sheet)
- stable on air
- resistant to bases, not well resistant to acids
- ferromagnetic
- weldable
- CAUTION: carcinogenic, mutagenic, teratogenic and allergenic (it is therefore restrained in some applications)

1.1.2 Effect of alloying elements on the properties of nickel alloys

Nickel is able to dissolve larger amounts of alloying elements in it than iron, especially chromium, molybdenum and tungsten which allows for its application in much more aggressive environments than stainless steels. In the following enumeration of selected additives, specific effects on nickel alloys are stated.

Copper improved the resistant to non-oxidizing acids; addition of 30-40 % of Cu increases resistance to deoxygenated H_2SO_4 and HF; 2-3% of Cu increases resistance to HCl, H_2SO_4 and H_3PO_4 .

Chromium increases resistance to oxidizing environments (HNO₃, H_2CrO_4), but also to H_3PO_4 , as well as high temperature oxidation (formation of a passivation coating on the surface). Amounts of Cr are up to 50%, common number is around 15-30 % of Cr.

Iron primarily decreases cost and price of the alloy but it does not improve and anti-corrosive properties of nickel. An exception is an amount more than 50 % of Fe, which is a cause for increased resistance to H_2SO_4 . Iron also increases solubility of carbon in nickel and therefore the resistance against high-temperature carburizing.

Cobalt increases solubility of carbon in nickel, similar to Fe, which increases resistance to high-temperature carburizing; it also increases resistance against high-temperature sulfurization (with the melting temperature of Co sulfide is higher than Ni sulfide).

Molybdenum increases resistance against non-oxidizing acids. With 28 % of Mo (Hastelloy B alloy) the alloys resist the environment of HCl, HF, H_3PO_4 and H_2SO_4 with up to 60 % concentration. Molybdenum increases resistance against pitting and crevice corrosion. Molybdenum is an important strengthening element for alloys with increased firmness at high-temperature applications.

Tungsten increases resistance to non-oxidizing acids and local corrosion, similar to Mo. It is also a significant strengthening element, however it has higher atomic mass and is more expensive, therefore Mo is chosen if necessary, or a combination of W and Mo.

Silicon is contained in nickel only in small amounts either as a trace element from the deoxidation process or as an additive to improve the resistance to high-temperature oxidation. In alloys with higher content of Fe, Co, Mo, W and other metals difficult to melt, their amounts are rigorously checked, because Si stabilizes carbides and harmful intermetallic phases. On the other hand, Si as the main alloying element increases the resistance to hot concentrated H_2SO_4 , in which case nickel alloys with higher amounts of Si (9-11 wt.%) are only cast and are not further mechanically processed.

1.1.3 Mechanical properties

Mechanical properties of nickel depend on its purity and further alloying. Commercially pure nickel (Nickel 200) achieves the yield strength of 148 MPa and tensile strength of 462 MPa at 47 % ductility. The elasticity module (Young's module) is close to steels (204 GPa). Comparison of mechanical properties of various treatments of nickel is given in Table 1.1. An advantage for nickel application is not only good processability in hot and cold, but especially that nickel and its alloys keep their strength characteristics up to relatively high temperatures (400-550°C for common alloys, up to 800°C for some superalloys).

1.1.4 Corrosive properties

Nickel alloys are used in various reductive or oxidizing corrosive environments, as will be stated later on in the description of selected alloys. According to the nature of these environments and specific processes which occur within them, the following corrosion tests are performed for various types of nickel alloys:

- 1. Atmospheric corrosion;
- 2. Corrosion in water: flowing seawater, stale, mild current, co-interaction of sea organisms, etc.;
- 3. Corrosion in acids: H₂SO₄, HCl, HF, H₃PO₄, HNO₃ and in selected organic ones;
- 4. Corrosion in bases: NH₄OH, KOH, NaOH;
- 5. Corrosion in salts: halides (especially chlorides), nitrides, carbides, sulfides, octanes;

Somewhat about corrosion

Let us review that the term reductive and oxidizing is related to the nature of reaction at cathode locations during corrosion. Due to the influence of reductive solutions (for example HCl acid) hydrogen development occurs on the cathode, oxidizing solutions (HNO₃ acid) cause cathode reaction with higher potential.

Corrosive tests are performed at various temperatures and concentrations of solutions and agents in gaseous environment. Depending on the effects of the environment on the material, various types of corrosion are defined: general, pitting, crevice, intercrystalline, stress corrosion cracking.

1.1.5 Fields and examples of nickel use

Despite *toxic properties* have been confirmed in nickel recently, it is still widely used in many industry (nickel consumption by first use), the following material productions cannot be imagined without nickel (Source: metalpedia.asianmetal.com):

₽	stainless steel	66 %
₽	alloy steels	5 %
₽	alloys based on Ni, Cu, other nonferrous metals	12 %
₽	electroplating	7 %
₽	castings	3 %
₽	batteries	2 %
₽	other (including chemicals)	5 %

Due to the aforementioned materials applications, nickel can be found in the following fields (end-use consumption) (Source: http://www.nipera.org/):

0	transport (automotive, railway, aerospace, shipbuilding, containers, atc.)	19 %
0	building and construction (lifts, ascalators, chimney liners, air cond., sinks, etc.)	12 %
0	engineering (heat exchangers, chemical/petrochemical, food and beverage, packaging,	etc.) 23 %
0	tubular products (seamless, welded, flanges, fittings, etc.)	9 %
۲	electro and electronics	14 %
0	metal goods (cutlery, tableware, medical applications, wires, catering, etc.)	16 %
۲	others	7 %

1.2 Classification of nickel alloys

Nickel alloys can be divided into several basic groups; in some sources is the group of materials based on Ni-Mo further divided based on the presence of a ternary element and its amount.

- 1) technical nickel and low-alloyed nickel
- 2) Ni-Cu alloys
- 3) Ni-Mo alloys
- 4) Ni-Cr alloys

5) alloys with specific properties - magnetic and other physical properties

(Fe-Ni-Cr, Ni-Cr a Ni-Cr-Fe(-Mo) alloys)

6) nickel superalloys

In the following paragraphs we will state examples, properties and use of the individual groups of nickel alloys. It is necessary to note that a significant characteristic in alloys in items 1-5 is that they are usually alloys with monophase structure and their strengthening is ensured by a solid solution of additive atoms (these are atoms dissolved in a solid solution). In contrast with group 6. (superalloys), thermal processing is performed in order to dissolve unwanted secondary phases and is followed by hardening in water. In some cases (as for example the Duranickel 301 or Alloy K-500), alloys undergo precipitation hardening.

Currently, the main worldwide producers of Ni alloys are **Haynes International** and **INCO Alloys International** and their names also appear in the names of some alloys, as shown on the schematic division of nickel alloys on Figure 1.1.

In Table 1.1, the mechanical properties of selected nickel alloys are given from the aforementioned six groups, which are presented in detail in latter chapters.



Fig.1.1 Classification of nickel alloys and their trade names from the worldwide producer INCO Alloys International

	Yield strength	Ultimate tensile stress	Elongation	Young	Hardness
Alloy	(MPa)	(MPa)	(%)	(GPa)	
Nickel 200	148	462	47	204	109HB
Duranickel 301*	862	1170	25	207	30-40HRC
Ni-Cu					
Alloy-400	240	550	40	180	110-150HB
Alloy R-405	240	550	40	180	110-140HB
Alloy K-500*	790	1100	20	180	300HB
Ni-Cr-Fe-Mo					
Alloy 600	310	655	40	207	75HRB
Alloy-718*	1036	1240	12	211	36HRC
Alloy 800	295	600	44	193	138HB
Alloy 925*	815	1210	24	-	36.5HRC
Alloy B – cast N-12MV	275	525	6		
Ni-Al-Cr superalloys					
Inconel 718	1100	1375	25		
Haynes 230	390	860	47.7	211	
Nimonic 80A	780	1250	30		
Inconel 600	310	655	45		

Table 1.1 Properties of selected nickel alloys at room temperature

*- alloy with precipitation hardening

1.2.1 Technical nickel and low-alloyed nickel

Technical nickel is used under various names based on the amount of nickel and impurities or small amounts of additives:

93-99.9 wt.% Ni, 0.01- 0.25 wt.% Cu, 0.05-0.75 wt.% Fe, 0.003-5.25 wt.% Mn, 0.02-0.3 wt.% C, 0.005-1 wt.% Si, 0.008-0.015 wt.% S, and others (Mg, Ti, Al)

- Examples: A-nickel (nickel 200, nickel 205-electronic form), nickel 201, nickel 220, duranickel (with Al, Ti)
- Properties: combination of good mechanical and electronic properties with good corrosion and oxidation resistance
- Use: Depending on the composition, nickel is used as a component in food industry devices, transport containers for chemicals, electronic components (Ni 205 and 220), parts in airline and space industry, battery cases, electrodes in glow lamps, high-temperature parts and environments with high amounts of sulfur, stamping component for extrusion of plastics, forms for glass production....

1.2.2 Ni-Cu alloys

Alloys of nickel and copper can be divided into two big groups based on the majority amount of Ni or Cu as is evident from the following subchapters. Binary system given on Figure 2.1 is characteristic for mutual perfect solubility in solid state which means that no secondary phases are created and a microstructure in the whole volume is formed by only one phase, which is solid solution of copper in nickel or nickel in copper. This type of microstructure allows for good formability of cold alloys and adds to high corrosion resistance. From certain Ni concentration, spinodal decomposition of the solid solution occurs, which is presented binary diagram on Figure 1.2.



Fig.1.2 Equilibrium phase diagram of binary system Cu-Ni with perfect solubility in solid state and spinodal decomposition at temperatures below 345.5°C. The dotted line T_c represents Curie temperature of Ni transformation from paramagnetic to ferromagnetic state.

Prevalence of Ni (so called Monels)

Alloys under the name of **Monel** (registered trademark of Special Metals Corporation) have been used since the beginning of the 20th century. The first alloy was produced in 1901 by R.C. Stanley and named after the then-president of the company International Nickel Company (INCO) Ambrose Monel.

Properties: Monels, which contain 63-66 % of Ni, up to 34 % of Cu + Fe, Mn, Si, Al, Ti are materials with great mechanical properties and chemical resistance in difficult environments. Originally they were meant for slightly reductive environments but are currently used because of their high anti-corrosive resistance against seawater, acids HF, H₂SO₄ and bases where the properties of stainless steels are not good enough, e.g. in long-term contact with salt water but also in chemical industry (see Table 1.2)

Examples: Monel alloy 400, Monel alloy R-405, Monel alloy K-500

Use: Monels are used in shipbuilding industry (ship screw-propeller), equipment for chemical and carbohydrates production, sheets, pipes, valves, pumps, shafts, scrapers, armatures, heat exchangers, rivets, screws...

> Prevalence of Cu

1) constantan - 45 % Ni

Properties: high electrical resistivity of 0.49 μΩ·m, very low temperature coefficient of electrical resistivity at 20 °C 0.00001, low coefficient of thermal expansion 0.000015/K

Use: thermocouples

nickeline - 31 % Ni, 56 % Cu, 13 % Zn

Properties: high electrical resistivity, very low temperature coefficients of electrical resistivity Use: resistance elements

2) nickel silver – 55- 65 % Cu, 10-30 % Ni, balance Zn

Alloys know under other names as well: *argentan* or most commonly *alpacca*, got to Europe from China in 18th century but coins have been minted from it in bigger amounts after the 2nd World War. Alpacca contains 10-20 % of Ni, 40-70 % of Cu and 5-40 % of Zn.

Properties: white colour, good formability, medium strength, very good corrosive resistance even against seawater, high content of Ni prevents dezincification - it replaces brass in corrosive environment of salt water, favorable coloration (similar to Ag).

Example of composition: The most common alloys are 65Cu-18Ni-17Zn and 55Cu-18Ni-27Zn

- Use: Alloys are used in plating, valves, armatures, various parts of common equipment, decorative and architecture elements, coins.
- 3) *cupronickel* -10 30 % Ni + do 1.5 % Fe, balance Cu

amount of Ni/Cu: 30/70 wt.% + Fe, Mn, Zn, Pb, Sn (S, C)

90/10 wt.% + Fe, Mn, Zn, Pb, Sn (S, C)

Two main Cu-Ni alloys used for forming and use in seawater contain 10 or 30 % of Ni. Both are alloyed by significant amounts of Fe and Mn, which are necessary to keep good corrosion resistance. Their development was based on the understanding of these alloying elements, especially Fe on the property of alloys. Research work started in the 1930s on the request of British Navy to improve the material for coolers, because then used 70-30 brass could not sufficiently resist the velocity of the seawater current.

Properties: It has been discovered that properties of 70-30 Cu-Ni alloys change based on the content of Fe and Mn and therefore such composition has been sought that would give optimal resistance against velocity effects, corrosion due to deposits and pitting. In the end, a typical composition of 0.6 % Fe and 1.0 % Mn has been prepared. In an alloy composition of 10 % Ni, the optimal content of Fe is higher and of Mn lower than in the case of 70-30 alloys, for example 1.5 % Fe and 0.8 % Mn.

From the comparison of composition of both alloys of Cu-Ni (Table 1.3) labeled according to international norms can be deduced that the content of elements is slightly changed. These changes have little use on the overall function of the alloys in practice. Iron is an important element in both alloys, because it improved the resistance against turbulent corrosion caused by the speed of a current. Optimal amount of Fe is determined by the solubility of copper in solid state. Until Fe stays in a solid solution, its increasing amount can be counted on to improve corrosion resistance of an alloy. Limiting

conditions were adjusted based on experimental results. Manganese is essential element in deoxidation during the melting process but its effect on the corrosion resistance is less researched than in the case of Fe. At lower amounts of Fe, higher amount of Mn improve resistance against turbulent corrosion.

Elements	Cu	Ni	Fe	Mn	Sn	С	Pb	Р	S	Zn	Other impurities	Total impurities
Alloy 90-10 Cu-Ni												
ISO CuNi10Fe1Mn	bal.	9.0- 11.0	1.2-2.0	0.5- 1.0	0.02	0.05	0.03	-	0.05	0.5	0.1	-
BS CN 102	bal.	10.0- 11.0	1.0-2.0	0.5- 1.0	-	0.05	0.01	-	0.05	0.5	-	0.3
ASTM C70600	bal.	9.0- 11.0	1.0-1.8	- 1.0	-	0.05	0.03	0.02	0.02	0.5	-	-
DIN CuNi10Fe2.0872	bal.	9.0- 11.0	1.0-1.8	0.5- 1.0	-	0.05	0.03	-	0.05	0.5	0.1	-
Alloy 70-30 Cu-Ni												
ISO CuNi30Mn1Fe	bal.	29.0- 32.0	0.4-1.0	0.5- 1.5	- 0.02	0.06	0.03	-	0.06	0.5	0.1	-
BS CN 107	bal.	30.0- 32.0	0.4-1.0	0.5- 1.5	-	0.06	0.01	-	0.08	-	-	0.3
ASTM C71500	bal.	29.0- 33.0	0.4-1.0	- 1.0	-	0.05	0.02	0.02	0.02	0.5	-	-
DIN CuNi30Fe2.0882	bal.	30.0- 32.0	0.4-1.0	0.5- 1.0	-	0.06	0.03	-	0.05	0.5	0.1	-

 Table 1.3 Element contents in various Cu-Ni alloys (Maximum values, except where stated)

Table 1.4	Physical and	mechanical	properties	of 90-10	and 70-30	Cu-Ni alloys
	2					2

Alloy	90 - 10	70 – 30
Physical properties		
Density (g/cm ³)	8,9	8,95
Specific heat (J/kg.K)	377	377
Melting range (°C)	1100-1145	1170-1240
Heat conductivity (W/m.K)	50	29
Coefficient of linear expansion	13	12
-180 to 10 °C 10 ⁻⁶ /K	15	12
10 to 300 °C 10 ⁻⁶ /K	17	16
Electrical resistivity ($\mu\Omega$.cm)	19	34
Coefficient of electrical resistivity (10 ⁻⁶)	70	50
Young modulus (GPa) annealed	135	152
cold worked	127	143
Modulus of rigidity (GPa) annealed	50	56
cold worked	47	53
Mechanical properties		
Yield strength (MPa)	140	170
Ultimate tensile stress (MPa)	320	420
Elongation (%)	40	42

The content of impurities also has to be checked in alloys, since elements such as Pb, S, C and P can influence strength at higher temperatures, weldability and formability at higher temperature even though they have minimal influence on corrosion resistance. World renowned suppliers are aware of this effect and try to produce material with decreased amount of impurities in accordance with the norms. Alloys are processed by forming in hot and cold temperatures.

Alloys exhibit advantageous resistance against fatigue, high thermal conductivity, good strength and plasticity, resistance against corrosion and attack by sea organisms in seawater (seaweed, crustaceans) and related environments, which predetermines it especially for long-term exploitation in maritime industries.

Table 1.4 gives the typical physical and mechanical properties in annealed state of both Cu-Ni alloys. Both types of alloys have good mechanical strength and toughness, though the alloys with higher amount of Ni exhibits increased firmness. Both alloys are monophase solid solutions and can not be solidified by heat processing. Their strength can be increase by deformation solidification. While pipelines from 90-10 Cu-Ni can have tensile yield strength of 100-160 MPa in annealed state, in drawn state they can achieve 345-485 MPa.

In terms of use for heat exchangers and coolers, heat conductivity and expansion is very important. Conductivity of both alloys is good, higher values are achieved by the 90-10 alloy. This partly explains the higher popularity of this alloy for heat exchangers and coolers, where strength is not the deciding factor.

The 70-30 alloy is virtually non-magnetic and its magnetic permeability is close to one. 90-10 alloy with higher Fe content is also non-magnetic, if the Fe during preparation is kept dissolved in solid solution. For ensuring low permeability of the 90-10 alloys, used in minesweeper pipes, the precipitation of secondary phase with amount of Fe is sufficiently suppressed by air-cooling after the final annealing.

Examples: Alloy 450, CuNi10Fe, CuNi10Fe1Mn

Use: Alloys are used for coolers, condensers, condenser plates, distillation pipes, vaporizers and heat exchangers, seawaters pipes in commercial and military ships. While the 90-10 alloy is more often used for surface ships, the 70-30 alloy finds use in submarines, because its greater strength allows it to endure higher surrounding pressures. These alloys are also used for coolers in power plants and coast pipelines on oil rigs (oil/natural gas), for desalination industry and for plating and coating of naval constructions and equipment.

1.2.3 Ni-Mo alloys

Alloys are designated for strongly reductive environments. Their corrosive properties are stated, in comparison with two other alloys, in Table 1.5.

	Average corrosion rate (mm/year)						
Acid Alloy	B-3	B-2	316L	Monel 400			
50% acetic acid	0.005	0.010	0.005	-			
40% formic acid	0.013	0.018	41.01	0.053			
50-55% phosphoric acid	0.076	0.152	0.457	0.114			
50% sulphuric acid	0.043	0.030	above 500	4.699			
20% hydrochloric acid	0.305	0.381	above 500	40.310			

Table 1.5 Comparison of corrosion resistances of three Ni alloys- B-3, B-2, Monel 400 and stainless steel 316L

Composition: 68.5 wt.% Ni- 28.5 wt.% Mo, + Fe, Cr, Co, W, Si

Properties: resistant to stress corrosion cracking, pitting even in HCl environment at high temperature and high concentrations

Example: Hastelloy B, Hastelloy B-2, Hastelloy B-3, (or also Alloy B) Use: in environments containing HCl (release of hydrogen on cathodes)

1.2.4 Ni-Cr- (+Si, Mo, Fe) alloys

Alloys designated for strongly oxidizing environments.

Composition: 65 wt.% Ni-20 wt.% Cr-5 wt.% Si + Mo, Fe, Cu;

78.1 wt.% Ni -7.9 wt.% Cr-4.2 wt.% Si + B, Cu, Mo, Nb

Properties:	resistant to high corrosive potentials and stress corrosion cracking
Example:	Hastelloy D-205, Colmonoy 98
Use:	for NaOH environments, salt water and H ₂ SO ₄ environments

1.2.5 Electromagnetic purpose alloys

Fe-Ni-Cr, Ni-Cr and Ni-Cr-Fe based alloys are designed for multi-purpose use. They can be divided based on their specific properties as follows:

Soft Magnetic materials

Composition: 35 - 79 wt.% Ni, up to 21 wt.% Fe, + possibly Mo, Cr

Properties: soft magnetic materials, high initial permeability, low coercitivity, low eddy-current losses, magnetic characteristic susceptible to cooling rate (addition of Cr, Mo decrease this sensitivity), hot and cold workable (improvement of formability is achieved by a small addition of manganese).

Magnetic properties in soft magnetic fields depend on chemical composition, thermal and mechanical processing, additives contained, careful adherence to melting procedure (in vacuum) and annealing (in hydrogen). The highest maximum initial permeability is achievable at a cooling rate of 20°C/s. If this rate is increased 4 times, maximum permeability is achieved. Thermal treatment is performed after finishing mechanical treatment. Magnetization curve is very steep, which is because the permalloy is saturated at relatively low magnetic fields.

Example: 50 permalloy, 36 permalloy, Magnetic compensating alloy, Superpermalloy, etc.

- Permalloy A 78.5% Ni and 21.5% Fe, susceptible to thermal treatment
- Permalloy C 18.5% Ni, 18% Fe, 3% Mo, 0.5% Mn, replacement of Permalloy A, magnetically softest material. It is used in communication technology for small transformers, chokes, relays, magnetic shielding, magnetic probes.
- Hypernik, Conpernik, Invariant approximately 50% Ni, lower sensitivity to thermal treatment, higher resistivity; these alloys have lower $\mu_{init} = \mu_{max}$, but higher constancy of permeability in range of weak magnetic fields. They achieve high saturation values which allows for smaller cross-sections of transformer cores.
- Mumetal 76% Ni, 17% Fe, 5% Cu, 1% Mn, has higher electrical resistance than Permalloy and is less sensitive to mechanical and thermal treatment.
- Megaperm 65%Ni, 10% Mn, balance Fe
- Supermalloy 79% Ni, 5%Mo, 0,5% Mn, balance Fe, μ_{max} =180000
- Use: cores of magnetic heads, tachometers, magnetic sensors, floppy disks, video recorders, videocameras...

Alloys with controlled expansion

Composition:30-36 wt.% Ni, 53-64 wt.% Fe, possibly 17 %CrProperties:expansion coefficient - similar to glass or porcelain, coefficient is controlled within
certain temperature limitsExamples:Kovar, Invar, 42 alloy, 52 alloy and others
magnetrons, solar collectors, TV electron gun, Guarts oscillator, bimetals, screens...

Alloys with high resistivity

Composition: 80-90 wt.% Ni, 10-19 wt.% Cr, + Fe, Mn, Si

Properties: high electrical resistivity at elevated temperatures

Examples: Super Alloy Nichrome V(tm), Chromel A, Chromel C Use: heating elements

1.2.6 Nickel based superalloys

Composition: 50-70 wt.% Ni, 15-20 wt.% Cr, + Ti, Al, Mo, Co, Nb, Zr, V.....

Properties: retain good mechanical properties (strength) and resistance to oxidation up to high temperatures, good corrosion resistance, creep resistance (precipitation strengthening)
 Examples: Inconel 718, Inconel 600, Inconel X-750, Inconel 625
 Haynes 230, Haynes 625, Hastelloy S, Hastelloy X, Waspaloy Nimonic 75, Nimonic 90

Use:

- engine components in cars,
- in nuclear energy (reactors, pumps, ..),
- containers for chemical industry,
- pressure vessels,
- protection tubes of thermocouples,
- aircraft, reactive engines, combustion systems,
- maritime construction,
- components in furnace systems, ...

Nickel superalloys represent important material for most of current high-temperature applications, therefore we will discuss characteristics and properties of all these alloys in detail in the next chapter.



Important terms

Corrosion environment, monels, magnetic alloys, cupronickels, nickel silver, constantan, superalloys.



Questions

- 1. What is basic classification of nickel alloys?
- 2. Define differences between cupronickels and monels?
- 3. What properties are characteristic for Kovar and Invar alloys?
- 4. What alloys are used in strong reduction environment?
- 5. Can you name the basic properties of superalloys?
- 6. What phase transformation proceeds in binary system of Cu-Ni?

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2. SUPERALLOYS



Time needed to study: 4 hours



Learning objectives

After careful study of this chapter you should be able to do the following:

- Define basic properties of superalloys
- Specify structure composition of superalloys
- Conclude influences of alloying on mechanical properties
- State basic diferences between Co, Fe-Ni and Ni based superalloys
- Discuss mechanisms of strengthening of Co, Fe-Ni and Ni based superalloys
- Determinate harmful phases in the microstructure of Ni superalloys
- Divide application of Co, Fe-Ni and Ni based superalloys



20

Lecture

2.1 Generalities

2.1.1 Classification of superalloys

Superalloys are alloys based on nickel, iron-nickel or cobalt for use at over 540°C. First generation superalloys was designed for temperatures up to 700°C, generation four superalloys are prepared and used as single crystal material and are alloyed by special elements, such as ruthenium and can be used at temperatures up to 1100°C.

Based on the main element, superalloys can be divided into following groups

- 1. based on Fe-Ni (density of 7.9-8.3 $\cdot 10^3$ kg/m³)
- 2. based on Co (density of $8.3-9.4 \cdot 10^3 \text{ kg/m}^3$)
- 3. based on Ni (density of $7.8-8.9 \cdot 10^3 \text{ kg/m}^3$)
- 4. based on Ni and Al containing Ir and Rh (density of $8.5-12.4 \cdot 10^3 \text{ kg/m}^3$) (4th generation)

2.1.2 Development of superalloys

Now we will discuss the historical development of superalloys, which started in 30s and 40s.

Somewhat about the superalloys development

Among the first so called superalloys were in the early 40s alloys based on Fe, which were formed cold. The method of exact casting allowed for alloy preparation based on cobalt with higher operation temperatures. Using vacuum melting, chemical composition of superalloys could be directed more closely and contamination could be decreased; this technology was also used in directed crystallization and preparation of single crystals. Currently, superalloys are used on gas turbines in semicrystal as well as single crystal form (since the late 70s and early 80).

Disks of high-pressure turbines are made from semicrystal material prepared by powder metallurgy or casting. Turbines of the blades can be either of semicrystal microstructure with directed crystallization as well as of single crystal microstructure. Polycrystalline blades with columnar structure are prepare by casting into ceramic forms, where grains grown during the directed crystallization parallel to the main axis of tension. If the modified method of direct crystallization is used, superalloys with single crystal structure can be formed, i.e. there are no other grain boundaries in the material.

Mechanical strengthening in most alloys depends on the grain boundaries which is however participating in creep at higher temperature and their effect on the strengthening has to be replaced by some other mechanism. In most of these superalloys, the structure is formed by areas with precipitates of ordered intermetallic phase in a disordered matrix, as you will learn later on.

2.1.3 Basic properties of superalloys

Density of alloys is influenced by additive elements (Table 2.1): Al, Ti, Cr, which decrease it or W, Re, Ta, which increase it. Corrosive properties are influence by additives as well as the nature of the working environment.

Based on Fe-Ni												
Element	Ni	Fe	Ti	Al	M	0	Со	Cr	Nb	١	N	С
Wt.%	9-44	29-67	0-3	0.3-1	L 0-3	3	0-20	0-25	0-5	0-2	2.5	<0.35
Based on Co												
Element	Со	Ni	Ti	Al	M	0	Fe	Cr	Nb	\ \	N	С
Wt.%	do 62	0-35	0-3	0-0.2	2 0-1	.0	0-21	19-30	0-4	0-	15	0-1
Based on Ni												
Element	Ni	Ti	Al		Мо		Со	Cr	Nb	v	V	С
Wt.%	37-79.5	0-5	0-6		0-28	(0-20	5-22	0-5.1	0-3	15	<0.30

Table 2.1 Contents of main elements in superalloys

+ other elements such as Zr, La, Mn, Si, Cu, B, Ce, Mg, V, Ta, Hf

Modulus of elasticity reaches values of 172-241 GPa in polycrystalline alloys, after directional solidification from 124 to 310 GPa. Electric, thermal conductivity as well as thermal expansion depends on transition metals and on the presence of high-melting metals, it is rather lower in comparison with other metallic systems.

The upper temperature limit of alloy use is determined by the temperature of solution of the strengthening phase and the beginning of the matrix melting (Table 2.2 and 2.3). Unlike relatively good formability of Fe-Ni and Ni based superalloys, cobalt based superalloys are less formable.

Table 2.2 Critical temperatures of melting and precipitation for selected Ni based superalloys

Alloy	Melting temperature (°C)	Precipitation temperature (°C)
Alloy X	1260	760
Alloy 718	1260	845
Waspaloy	1230	980
Alloy 901	1200	980
Alloy X-750	1290	955
M-252	M-252 1200 1010	
Alloy R-235	1260	1040
René 41	1230	1065
U500	U500 1230 1095	
U700	1230	1120
Astroloy	1230	1120

 Table 2.3
 Microstructure phases with controlled presence in the alloy and ranges of operational temperatures for selected superalloys

	Controlled microstructure	Range of operational
Alloy	phase	temperatures (°C)
Ni based alloys		
Waspaloy	γ' -Ni $_3$ (Al,Ti)	955-1025
Astroloy	γ′ -Ni₃(Al,Ti)	1010-1120
IN-100	γ′ -Ni₃(Al,Ti)	1040-1175
René 95	γ′ -Ni₃(Al,Ti)	1025-1135
Fe-Ni based alloys		
Alloy 901	η -Ni₃Ti	940-995
Alloy 718	δ -Ni₃Nb	915-995
Pyromet CTX-1	η -Ni $_3$ Ti, δ -Ni $_3$ Nb or both	855-915

2.1.4 Phase structure of superalloys

The constitution of superalloy microstructure depends on the alloying elements, which influence the strength of the matrix, feature of the precipitate, precipitation of carbide particles, resistance to oxidation or hydrogen environment, etc. The effects of various additives are given in Table 2.4. The structure is composed of austenitic matrix γ with face centered cubic lattice (FCC) and other secondary phases:

- γ' FCC structure Ni₃(Al,Ti)
- γ'' D0₂₂ structure (tetragonal body centered) Ni₃Nb
- $\eta D0_{24}$ structure (hexagonal ordered) Ni₃Ti
- ★ δ orthorhombic structure Ni₃Nb
- \diamond carbides (MC, M₂₃C₆, M₆C a M₇C₃)

Table 2.4 Role of alloying elements in superalloys

	Fe-Ni based	Co based	Ni based			
Effect(s)	Element					
Solid solution strengtheners	Cr, Mo	Nb, Cr, Mo, Ni, W, Ta	Co, Cr, Fe, Mo, W, Ta, Re			
FCC matrix stabilizers	C,W,Ni	Ni				
Carbide formers						
MC	Ti	Ti	W, Ta, Ti, Mo, Nb, Hf			
M ₇ C ₃		Cr	Cr			
M ₂₃ C ₆	Cr	Cr	Cr, Mo, W			
M ₆ C	Мо	Mo, W	Mo, W, Nb			
Carbonitrides: M(CN)	C, N	C, N	C, N			
Promotes general carbide precipitation	Р					
γ′ -Ni₃(Al,Ti) formers	Al, Ni, Ti		Al, Ti			
Retards formation of hexagonal η -Ni₃Ti	Al, Zr					
Raises solvus temperature of γ'			Со			
Hardening precipitates and/or intermetallics	Al, Ti, Nb	Al,Mo, Ti, W, Ta	Al, Ti, Nb			
Oxidation resistance	Cr	Al, Cr	Al, Cr, Y, La, Ce			
Improving hot corrosion resistance	La, Y	La, Y, Th	La, Th			
Sulfidation resistance	Cr	Cr	Cr, Co, Si			
Improving creep properties	В		В, Та			
Increasing rupture strength	В	B, Zr	В			
Grain-boundary refiners			B, C, Zr, Hf			
Facilitates working		Ni ₃ Ti				

Creep resistance depends on the decrease of the velocity of dislocation motion inside the crystal lattice. In Ni based superalloys, γ' -Ni₃(Al,Ti) phase acts as a coherent obstacle for dislocation movement, which allows precipitation strengthening. In Table 2.4, alloying elements and their effects on superalloy structure are stated. The influence of (Al + Ti) content on creep resistance is shown on Fig. 2.1, on which we can observe beneficial effects of increasing amount of these two elements on creep strength in both cast and wrought nickel based superalloys.

Fe-Ni and Ni based superalloy strengthening is ensured using alloying elements (Cr, Co, Mo, W, Ta, Al, Ti, Zr, Nb, Re, C, B or Hf), which strengthen the solid solution using dissolved atoms, precipitation of γ' and γ'' phases or cause formation of carbides. The carbides can have limited strengthening effect, either direct (precipitation strengthening) or indirect (they stabilize the grain boundaries against excessive slide in wrought alloys). Precipitation of γ' and γ'' phases can be controlled by thermal treatment. Most superalloys are submitted to the two-step thermal treatment due to which γ' particles are precipitated as primary rectangular and secondary fine spherical (Fig. 2.2). Important phases that are controlled during the processing of wrought superalloys are η and δ .

Strengthening can also be improved by alloying elements: B, Zr and Hf. If the alloy contains higher amounts of B, borides can be formed.

In Co based superalloys, strengthening is ensured by elements soluted in solid solution and carbides, γ' precipitates are not present in the alloys and if so, they are dissolved at 815-1050°C.



Fig.2.1 Influence of (Al+Ti) content on creep strength in wrough and cast Ni-superalloys after 100 h at 870°C.



Fig.2.2 Wrought Ni based superalloys with a) spheroidal morphology in alloys with low amounts of γ' phase and b) bimodal morphology with higher amount of cuboidal and spheroidal γ' phase.

2.1.5 Mechanical properties of superalloys

Mechanical properties depending on temperature are listed for selected types of superalloys in Table 2.5, where we can clearly observe high values of yield strength even at 760°C for example in René 95 alloy, Astroloy or Udimet 720. Nickel superalloys are used at temperatures of 760 up to 890°C, while Fe-Ni superalloys are designed for lower temperatures of 650-815°C (depending on the amount of Ni) and achieve lower strength characteristics at both lower as well as higher temperatures. Cobalt based alloys have lower values than Ni superalloys at medium and lower temperature because they do not contain the γ' phase. These alloys find their use in high-temperature / low-pressure components with high durability such as industrial turbine blades. Comparison of creep strength for all three types of superalloys with different type of strengthening can be found on Fig.2.3.

Alloy	UTS (MPa) at temperature			Y.S. (MPa) at temperature			Tensile elongation (%) at temperature			
	21 °C	540 °C	760 °C	21 °C	540 °C	760 °C	21 °C	540 °C	760 °C	
Ni based										
Astroloy	1415	1240	1160	1050	965	910	16	16	21	
Inconel 587©	1187	1035	830	705	620	605	28	22	20	
Inconel 600	660	560	260	285	220	180	45	41	70	
Inconel 718	1435	1275	950	1185	1065	740	21	18	25	
Nimonic 75	745	675	310	285	200	160	40	40	67	
Nimonic942©	1405	1300	900	1060	970	860	37	26	42	
René 95	1620	1550	1170	1310	1255	1100	15	12	15	
Udimet 720	1570		1455	1195		1050	13		9	
Fe-Ni based										
A -286	1005	905	440	725	605	430	25	19	19	
Alloy 901	1205	1030	725	895	780	635	14	14	19	
Incoloy 801 ©	785	660	325	385	310	290	30	28	55	
Incoloy 909	1310	1160	615	1020	945	540	16	14	34	
Co based										
Haynes 188	960	740	635	485	305	290	56	70	43	
MP159	2025			1620			10			

Table 2.5 Mechanical properties depending on temperature for selected Fe-, Ni- and Co based superalloys



Fig.2.3 Stress-rupture characteristics of wrought Ni-, Fe-Ni- and Co- based superalloys depending on the strengthening mechanism

2.1.6 Processing of superalloys

Superalloys are usually processed so that some properties are optimized while others are not. In general, superalloys are either only cast or at favorable composition are further formed by forging, rolling or pressing. Their properties can be further optimized so that with the same chemical

composition, cast or wrought alloys can be processed by different thermal or thermo-mechanical processes. For selected composition the superalloys can also be prepared in single crystalline form (Table 2.6). Thus, for the same wrought product with the same nominal composition we can then obtain significantly different properties due to optimized thermal treatment. Depending on microstructure (Fig.2.4) and technology of preparation, the differences in yield strength and creep resistance are especially achieved (Fig.2.5).

Cast alloys have more coarse-grained microstructure, segregation of alloying elements and higher creep and fracture resistance, they can be further only welded or soldered. Generally, wrought superalloys are more homogeneous with more fine-grained structure and higher tensile and fatigue properties. Single crystal alloys are able to work for 100 h at 140 MPa pressure and at temperature higher by 50°C than common polycrystalline forms. Characteristic differences between polycrystalline, directionally solidified or single crystal microstructures are given on Fig.2.4.

Table 2.6	Composition of	Ni superalloys,	which are	prepared by	directional	solidification	or in s	ingle crystal
	form							

Alloy	Composition (wt.%)											
	Cr	Со	W	Мо	Та	Nb	Ti	Al	Hf	В	Zr	С
			Co	olumna	r grain	ed alloy	/s					
MAR-M200+Hf	9	10	12			1	2	5	2	0.015	0.08	0.14
MAR-M246+Hf	9	10	10	2.5	1.5							0.15
MAR-M247	8.4	10	10	0.6	3							0.15
Rene 80H	14	9.5	4	4								0.08
Single crystal alloys												
PWA 1480	10	5	4		12		1.5	5				
PWA 1484 (3% Re)	5	10	6	2	8.7			5.6	0,1			
CSMX-2	8	5	8	0.6	6		1	5.5				
CSMX-3	8	5	8	0.6	6		1	5.5	0.15			
SRR99	8.5	5	9.5		2.8		2.2	5.5				



Fig.2.4 Comparison of three types of microstructure in turbine blades: a) polycrystalline equiaxed grains, b) directionally solidified with columnar grains and c) single crystal.



Fig.2.5 Comparison of creep strength, thermal fatigue resistance and corrosion resistance for three types of superalloy structure: polycrystalline, columnar crystalline and single crystal.

2.1.7 Use of superalloys

Due to the aforementioned properties, superalloys are designed for applications at high temperatures in various aggressive environments such as parts of aircraft engines, reactive engines, combustion systems, turbines in energetics, maritime constructions, parts of furnace systems, reactors and pumps in nuclear energetics, containers for chemical industry, pressure vessels, protection tubes of thermocouples etc.

One of common applications are exhaust turbines of turbochargers in combustion or injection (TSI) engines in cars (@ *see video1 -superalloys* **@**).

2.2 Ni-Fe based superalloys

Part of the more expensive nickel is replaced by iron in these superalloys therefore it is possible to use them just at lower temperatures (650-815°C). As a high-temperature material, their properties are somewhere between martensitic steel and Ni or Co based superalloys. The composition and selected properties of Fe-Ni based superalloys have already been given in Table 2.1, 2.3 through 2.5.

Their microstructure is formed of γ matrix and γ' precipitates. Due to the fact that iron content fluctuates between 18-55%, some superalloys can be evaluated as wrought austenitic steel alloyed by γ' , γ'' or carbides (nitrides, carbonitrides) formers (such as alloys A-286 or Inconel 718). Solid solution strengthening is achieved by alloying of Cr, Mo, W, Ti, Al and Nb, where the last three elements promote precipitation of intermetallic compounds γ' , γ'' and η in conjunction with Ni.

2.3 Co based superalloys

Co based superalloys exhibit great resistance to high temperature corrosion and strength up to 980-1100°C. They are sometimes used at lower temperatures (750°C) instead of Ni superalloys, which are more expensive due to their preparation in vacuum metallurgy whereas Co superalloys can be cast on air or under argon.

Cobalt has an HCP (hexagonal close packed) structure at room temperature, which changes into FCC lattice at 417°C. As was stated above, Co superalloys are not strengthened by precipitates but only by solid solution and carbide particles. The alloying elements that strengthen the solid solution are in this case W, Mo, Ta, Nb, Ni and Cr, with W being the most effective. However, if tantalum is replaced by tungsten for example in Mar-M918 alloy, oxidation resistance is increasing without

decrease of the strength. Carbide particles, which are present in a Co based superalloy are MC, M_7C_3 , $M_{23}C_6$ and M_6C . The character of carbide precipitate can be controlled by the Cr to C ratio and amount of Mo, Nb, Ta, Zr and Ti. Typical composition of a Co based superalloy is 50-60% Co, 20-30% Cr, 5-10% W and 0.1-1% C. Absence of γ' - Ni₃(Al,Ti) phase leads to lower strength at medium temperatures.

Even though Co superalloys are not as widely used at high temperatures as Fe-Ni or Ni superalloys, they still play an important role due to their great resistance to sulfurization, high-temperature corrosion and conserving their strength at temperatures higher then temperatures at that the solution of γ' and γ'' precipitates is provided in Fe-Ni or Ni superalloys.



Fig.2.6 Tensile properties of superalloy MP35N after cold drawing and subsequent aging

For high temperature applications, it is necessary to ensure the stability of FCC lattice and increase high temperature strength and resistance to corrosion and oxidation, which is performed by Ni, Fe, Mn, Ti, Zr, Cu, B, C and other elements alloying. Co based superalloys which exhibit high temperature strength contain 10% of Ni or more. Alloys MP35N and MP159, which belong to the group of multiphase (MP) alloys are thermally treated, contain higher percentage of Ni and Fe as stabilizers of the FCC lattice so that the alloys can be cold worked. These aforementioned multiphase alloys are useful in applications such as fasteners in aircrafts and spacecraft for their high strength, toughness and resistance to corrosion including stress corrosion cracking (SCC). The principle of strengthening these alloys during thermal treatment is based on the transition of the FCC structure into an HCP structure during cold forming. This transformation occurs with high contents of Co in alloy and is called as multiphase reaction. It is precisely the coexistence of two types of solid solution structure which represents an obstacle for dislocation motion and therefore yield strength increases, as is shown on Fig. 2.6, comparing two states: after drawing and drawing with aging for 4h at 538°C.

Corrosion and oxidation resistance of these superalloys depends on the amount of Cr in the alloy, which is much higher when compared to Ni superalloys. The addition of La, Y or Th can increase cohesion of the surface protective coating and therefore resistance to oxidation and corrosion. In general, solubility of alloying elements in Co based superalloys is lower than in Ni based superalloys, and so optimization of composition is important to prevent precipitation of unwanted intermetallic phases.

2.4 Ni based superalloys

Within the most important properties of superalloys, as we already have learned, lies resistance to high-temperature creep, oxidation and corrosion, fatigue life and phase stability. High-temperature strength is in Ni based superalloys ensured by strengthening of the solid solution γ (austenitic phase) and precipitation strengthening of the precipitated γ' - Ni₃(Al,Ti) phase, then further by dispersion strengthening by carbide particles. Fig.2.7 represents basic physico-metallurgical characteristics: apart from typical cuboidal form of γ 'phase precipitates (TEM image in Fig.2.7a), phase equilibrium diagram of binary system Ni-Al is shown with areas of appearance of solid solution of γ and γ' phase (Fig.2.7b) and a schematic of γ' phase coherence and γ solid solution (Fig.2.7c).

Oxidation and corrosion resistance in Ni superalloys is based on aluminum and chromium alloying, which form a protective layer of Cr_2O_3 and Al_2O_3 oxides immediately after contact with an environment with oxygen. Other alloying elements may be: Co, Fe, W, V, Nb, Ta, B, Zr, Mg, Ti, Mo. Phase stability of Ni superalloys is related to high occupation of 3d orbital by electrons in Ni atoms.

2.5 Principles of strengthening of superalloys

As stated in chapter 2.1.3, strengthening of nickel superalloys can be performed by adding alloying elements which can affect:

- strengthening of γ matrix (by solid solution strengthening)
- precipitation of γ' phase (or eventually γ'' phase) and its stability
- precipitation of carbide particles on the grain boundaries
- properties of grain boundaries



Fig.2.7 Basic characteristics of Ni based superalloys: a) TEM image of typical γ matrix microstructure and γ' precipitates; b) Ni-Al binary diagram and c) schematic illustration of coherency between ordered γ' particle with positive lattice misfit and disordered γ matrix

In the following paragraphs, we will focus on the strengthening mechanisms in terms of physical metallurgy.

2.5.1 Strengthening of γ matrix

Basic solid solution γ (FCC) is strengthened by the addition of atoms of Co, Cr, Mo, Fe, W, V, Ti, Al. The difference in atomic radii *a* of additives and Ni ($\Delta a = 1-13$ %) allows to preserve the strengthening up to 810° C (0.6 T_m).

Important parameter in superalloy strengthening is also the difference in number of electron vacancies \overline{N}_V in both the additives and nickel. All has the highest values (7.6) followed by Ti (6.6). The influence of \overline{N}_V for selected additives on increasing yield strength are given on Fig.2.8, the greater \overline{N}_V , the higher is its influence on its increase. The value of \overline{N}_V is determined by:

$$\overline{N}_V = \sum_{i=1}^n m_i (N_V)_i \tag{2.1}$$

where m_i is atomic fraction of ith element with N_V electron vacancies and *n* is the number of elements in the alloy. Stability of γ phase is limited by the value $\overline{N}_V \approx 2.5$.

Additives influence strength levels as well as stacking fault energy (SFE) of the basic solid solution γ . With the decreasing SFE cross slip of dislocations in γ matrix is limited which increases creep resistance. Fig.2.9. compares the alloying elements in terms of their influence on the decrease of SFE with the higher effect exhibited by Mo, W, Cr, Fe and Co.



Fig.2.8 Decrease of yield strength of the superalloy depending on the \overline{N}_{V} change for 1 % of an additive.

Fig.2.9 Change of stacking fault energy in γ solid solution depending on \overline{N}_V change for 1 % of an additive.

2.5.2 Strengthening effect of γ' phase

Precipitation of phase γ' -Ni₃(Al,Ti) is conditioned by high content of Ni in the basic matrix and supported by low compressibility of Ni atoms which is related to high density of electrons on the 3d orbital. On the other hand, Fe atoms have increased number of electron vacancies N_V, which allows for γ' phase precipitation. In terms of basic characteristics of γ' phase:

- homogeneous nucleation of γ' precipitates with low interphase energy and high stability occurs due to γ' coherence with γ phase (Fig.2.7c)
- γ' is an intermetallic phase with highly ordered structure L1₂ (FCC) (compare structures on Fig.2.10), strengthening is supported especially by the effect of stacking faults formation (APB-antiphase boundary, SISF, SESF, and others; more detailed theories and basics of formation will be discussed for Ni₃Al in chapter 4), where the increasing temperature enhances the strengthening effect

γ' has high inner plasticity so any potential embrittlement effect of this phase can be ignored for Ni alloys.



Fig.2.10 FCC structure of γ matrix (left) and L1₂ γ' phase (right).

Stacking faults

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The most dense occupied planes if FCC or HCP lattices are ordered with various stacking. If we label the most dense plane as *A*, then the layer above it can be placed in two positions - B or C, the next layer can again be in two position, etc. In a perfect HCP crystal, the stacking of planes is *ABABABA*, in an FCC crystal, the planes are stacked in order of *ABCABCABCA*. Random change in this ordering of planes is called *stacking fault*.

The total energy of the crystal with regular ordering of atomic planes is lower than in a crystal with a stacking fault. The difference in the energies is called stacking fault energy (SFE). If the atomic planes slip one after the other, the stacking fault energy increases up to its maximum value, which corresponds to an unstable configuration with two identical planes neighboring (i.e. *ABCCAB* stacking). If another yield of atomic planes occurs, the SFE decreases to the minimum in the spot where the lattice is stable but not with perfect stacking volume. This stable configuration is called *superlattice intrinsic stacking fault (SISF)*, as for example in an FCC crystal with plane sequence *ABCBCABCABC*. . . (i.e. one plane is removed of a regular stacking order). This stacking fault can be viewed as one layer of HCP ordering in an FCC layer or vice versa - an FCC layer within an HCP lattice.

In FCC metal the slip in the $[\overline{1} \ 1 \overline{2}]$ direction is common, because this direction has the lowest energy of unstable configuration. In crystals, *superlattice extrinsic stacking fault* can appear, which is created by inserting an extra layer into the stacking of planes.

SFE influences plastic deformation. A metal with low SFE (stacking fault is wide) strengthens much faster and twins (annealing or mechanical twins) are formed much more easily, while in metals with SFE stacking faults are narrow or they don't occur at all. Fig. 2.11 represents a schematic of stacking fault formation in precipitates during creep.



Fig.2.11 Schematic illustration of shearing of the particle during primary creep, dissociation of dislocations and formation of SISF, SESF and APB stacking faults. Action of the precipitated phase can be evaluated in terms of:

- ⇒ stacking fault energy modification
- \Rightarrow effect of APB in coherent ordered γ' phases in an disordered γ solution
- ⇒ strengthening due to coherent deformation
- \Rightarrow differences in moduli of elasticity of γ and γ' phases
- \Rightarrow modifications of strengthening dependent on the volume fraction (f_V) and size (h) of the γ' particles

 \downarrow

the contributions are not additive

2.5.3 Theory of strengthening (by Gleiter and Hornbogen)

Effect of APB

Two full dislocations of type $b = \frac{a}{2} \langle 1 \overline{1} 0 \rangle$, which get into the precipitate from solid solution γ ,

move through the precipitate only as a pair. The first dislocation from the pair has to form an APB fault in a highly ordered structure (superlattice), which limits its yield. The second dislocation of the pair moves behind it and can annihilate this APB fault. To return to an ordered structure, superdislocation is necessary: $b = a \langle 1 \overline{1} 0 \rangle$ with the Burgers vector twice as large as in a solid solution

dislocation. Both dislocations consequently for a pair of *superpartial dislocations*, because the APB energy in the precipitate is relatively high (approximately 100 mJ/m²), then if the density of the precipitate is high, this strongly bound pair of superpartial dislocations stays blocked in the precipitate.

This whole process is called strengthening, which in this case can be considered dependent on the γ' phase characteristics, in other words, the strengthening increases depending on:

- a) content of the γ' phase
- b) size of the γ' phase
- c) amount of APB energy

and can be expressed by a change in shear stress:

$$\Delta \tau_{APB} = \frac{\gamma_{APB}}{2b}$$
(2.2)

where γ_{APB} ... antiphase boundary energy b ... Burgers vector

The contribution of strengthening of this kind can be approximately 300 MPa.

The effect of γ' phase intersected by dislocations

Due to the movement limitations of dislocations in γ' phase, there is an increase in the amount of stress necessary to overcome obstacles in form of γ' precipitate. If with increasing temperature the dislocation in its motion is able to intersect the γ' precipitate, then before that happens, the yield strength can increase sevenfold. The photo of transmission electron microscopy on Fig.2.12 represents (a) the results of the intersection process, where a yield of a part of the precipitate occurred and (b) a detail of the dislocation pairs in precipitates in motion.

Intersection or bypass of precipitates/particles by dislocations

Strengthening proceeded by precipitates or dispersion particles falls to strengthening mechanisms. If there are alloys of expelled second phase particles in the matrix (based on the decrease in solubility of additives in solid solution with decreasing temperature) or intentionally introduced oxidic (cabidic and other) particles, these shapes represent effective obstacles of the movement of dislocations through the matrix.



The contribution to the increase of yield strength depends on properties of these particles, i.e. on their strength, structure, distance between them, degree of coherence, orientation, shape and distribution within the matrix.

At certain applied pressure above the yield strength the dislocations move on yield planes of the matrix, meet particles and react with them. Depending on the aforementioned properties of particles and on their crystallographic orientation in terms relative to the matrix, various cases of interaction may occur:

- 1. Particles can permeable for the dislocations and during their intersection, yield of one part against the other occurs (Fig.3.12a). This special case, called *Friedel's intersection*, occurs only if the particle is coherent with the matrix (see *Animation-2-disloprot* i.).
- 2. Particles are impermeable for the dislocations; in motion, due to the effects of tension, they bend in proximity of particles, when they overcome them they leave loops around them (Orowan's loops). This case of overcoming obstacles is called *Orowan's bypass of particles by dislocations* (see *Animation-3-orowan*) and occurs if the particles are too big and/or non-coherent with the matrix.

Both these mechanisms can be represented using aforementioned schematic on which a dislocation reacts with a parallel series of particles with diameter d and distance L from one center of a particle to the next. Critical looping shear stress, which a dislocation needs to overcome this series of particles with the same distance on the shear plane can be expressed based on an idea that the dislocation line is affected by the stress applied, which forced it against the series of particles and bends it between the particles at an angle θ . The angle θ , which depends on the distance L between the particles, diameter of the particle d, contribution to the shear stress $\Delta \tau$ due to interaction with particles, Burgers vector b and force Γ on the dislocation line influencing the straightening of its bend, can be expressed by an equation:

 $\Delta \tau \cdot b \cdot (L - d) = 2\Gamma \cdot \sin \theta$

The right side of this equation describes an anchoring force, by every particle applies on the dislocation:

 $f_{kotv} = 2\Gamma \cdot \sin \theta$

Maximum force which a particle can exert depends on the distance of shear plane from the center of the particle. If the angle of bend achieves 90° before a maximum force f_{max} is applied, the dislocation bypasses the particle and forms a dislocation loop (Orowan's mechanism). On the other hand, if the maximum force f_{max} is applied before the angle of bend is 90°, the dislocation slips through the particle. Let us assume that a plastic deformation is beginning; then using the following equations, we can express the contribution to the critical shear stress $\Delta \tau_0$ at 0K:

a) in case of Friedel's intersection

$$\Delta \tau_0 = \frac{f_{\max}}{b \cdot (L - d)} \qquad pro \ f_{\max} < 2\Gamma$$

b) in case of Orowan's bypass

$$\Delta \tau_{0} = \frac{f_{\max}}{b \cdot (L - d)} \qquad pro \ f_{\max} \ge 2\Gamma$$

If there are two small and coherent precipitates, they influence the dislocation more strongly than dissolved atoms. Interaction of dislocation with obstacles is exhibited only along a small part of the entire dislocation length. Particles then act as point or local obstacles. We have not yet assumed that the particles are distributed regularly, but in real metals and alloys it is rather uncommon. A middle distance between particles can influence the stress and the previous equation is turned into:

$$f_{\max} = \tau_c \cdot b \cdot L$$

Statistical solution of the problem of dislocation-obstacle interaction is given using the Friedel relation:

$$L = \left(\frac{2\Gamma \cdot b}{\tau_c \cdot c}\right)^{1/3}$$

Where L is the middle distance between obstacles and c is the volume fraction of obstacles. By combining the two previous equations, we obtain:

$$\tau_{c} = \frac{f_{\max}^{3/2} \cdot c^{1/2}}{b^{2} \cdot (2\Gamma)^{1/2}}$$

This equation describes the contribution to the yield strength at 0K for random distribution of local obstacles. At certain temperatures, thermal activation has to be considered. In general it is assumed that the process of bypassing cannot be activated thermally, impermeable particles can be in this case overcome by climbing.



Fig.2.12 TEM image of Nimonic superalloy in tensile test a) the γ matrix and γ' precipitates after intersection and shear and b) pairs of edge dislocations

2.5.4 Difference in modulus of elasticity in γ matrix and γ' precipitate

Both matrices and strengthening phases have various moduli of elasticity and this difference is applied in:

- intersections of γ' precipitation phases by dislocations
- limiting mobility of dislocations by γ' phases

If the precipitates are of <u>greater dimensions</u>, then the process of intersection is replaced by process of bypassing by dislocations, which is related to formation of dislocation loops or climbing (**modification of Orowan's process**). Transition from one process to the other is shown using the dependence of critical shear stress τ_c on the precipitate size *h* on Fig.2.13.





Appropriate addition to the shear stress:

$$\Delta \tau = 0, 2 \cdot G \cdot b \cdot \Theta \cdot \frac{2}{\lambda} \cdot \ln \frac{h}{2b}$$
(2.3)

where λ median distance between precipitates

G elasticity modulus in shear

b Burgers vector

- *h* particle size of γ' phase
- θ angle between *b* and the dislocation line tangent



where f_V - volume fraction of γ' particles and $h - \gamma'$ particle size

The effect of increasing volume fraction f_V of γ' particles on the increasing creep strength is shown for given conditions on Fig.2.14.

Application of differences in elastic modulus on high-temperature use of alloys (creep resistance)

The governing process of strengthening is lowered mobility of the climbing dislocations.

Addition of shear stress:

$$\Delta \tau \approx \alpha \cdot \mathbf{G} \cdot \mathbf{b} \sqrt{\rho_m} \tag{2.4}$$

where ρ_{m} density of dislocations

 α coefficient for strength of dislocation lattice, usually ~ 1

From this equation can be deduced that increasing dislocation density ρ_m (caused before the creep itself) positively influences strength. If the governing process of creep in two-phase alloys is dislocation climbing around particles, then two cases can occur:

a) stress applied
$$\sigma > \frac{G\ell}{\lambda}$$

Dislocations will move around the precipitates whereas dislocation loops are formed, which indicate backwards tension. This prevents formation of new loops before repair occurs (which can occur by the dislocation loops climbing around the γ' particles). Kinetics of the reaction (creep rate):

$$\dot{\mathcal{E}} = \frac{2 \cdot \pi \cdot \sigma \cdot \lambda \cdot D}{h \cdot G^3 \cdot k \cdot T}$$

where D self-diffusion coefficient

k Boltzmann constant

 T_{\ldots} temperature

& creep rate

Factors that influence creep

These conditions allow slowing creep down:

- lowering the distance λ between precipitates, i.e. increase volume fraction f_V of γ' phase
- decreasing coefficient of self-diffusion D of the alloying matrix γ
- increasing particle size *h* by appropriate thermal processing (aging)



Fig.2.14 Effect of increasing volume fraction f_V of γ' phase on the creep rupture in columnar-grain, directionally solidified Ni based superalloy (PWA 1422)

(2.5)

b) stress applied $\sigma < \frac{Gb}{\lambda}$

Dislocation will climb around γ' precipitates, unless their aggregation occurs.

$$\dot{\mathcal{E}} = \frac{\pi \cdot \sigma \cdot b^3 \cdot D}{2 \cdot k \cdot T \cdot h^2}$$
(2.6)

Kinetics reaction :

Factors influencing creep

Decreasing creep rate can be achieved by

- lowering diffusion coefficient D in phase γ
- increase the size h of phase γ' particles

Example of when intersection and bypass will occur:

a) volume fraction f_V of phase γ' up to 20 % and precipitate size h > 28 nm \Rightarrow **bypassing** b) higher fraction f_V (e.g. up to 50 %), size of precipitate h 20-30 nm \Rightarrow **intersection**

2.5.5 Strengthening by coherent deformation

Properties of superalloys strongly depends on coherence of the γ/γ' interface, which is preserved in very small lattice misfit. This misfit δ is defined as:

$$\delta = 2 \left(\frac{a_{\gamma} - a_{\gamma}}{a_{\gamma} + a_{\gamma}} \right) \tag{2.7}$$

and its value is negative if $a_{\gamma'} < a_{\gamma}$

or positive if $a_{\gamma} > a_{\gamma}$

The changes is lattice parameters a_{γ} and $a_{\gamma'}$ are sensitive to molar fraction of the dissolved alloying element and its position in the periodic table, as can be seen on Fig.3.15. It also depends on the distribution of alloying elements between the γ and γ' phases. If the γ' precipitates grow thicker, value of δ will increase and decrease.

This mechanism occurs both in the conditions of *intersection* as well as *bypassing* of precipitates by dislocations. The size of coherent deformation ε depends on the size of δ ; the greater it is, the higher the strength (e.g.: at $\varepsilon = 0,6\%$, the strength increases by 200HV, which represents a yield strength increase of 200MPa)

The increase of shear stress:
$$\Delta \mathcal{T} = 3 \cdot \mathcal{G} \cdot \mathcal{E}^{3/2} \left(\frac{h \cdot f_V}{2 \cdot b} \right)^{1/2}$$
 (2.8)

where ε size of coherent deformation f_V ... volume fraction of γ' particles

The increase of shear stress $\Delta \tau$ can be exaggerated by increasing coherent deformation ε , by increasing volume fraction of particles f_V or by increasing particle size h. This can be accomplished by the following methods:

- 1) increase of ε with increasing $a_0^{\gamma'}$ alloying by Ti and Nb, which increase the lattice parameters of the γ' phase
- 2) increase of ε with increasing a_0^{γ} alloying by Cr, Mo and Fe, which increase lattice parameter of the γ matrix
- 3) increase of ε with decreasing a_0^{γ} adding Ni, which replaces Cr and Fe in γ and decreases lattice parameter of γ matrix



Fig.2.15 Dependence of lattice parameters of solid solution Ni and Ni₃Al phase depending on the amount of alloying elements at room temperature.

2.5.6 Stability of γ' phase

Ripening of γ' phase – at T > 0,6 T_M

During the increase in size of the precipitate, decrease of $\left(\frac{2}{\lambda} \cdot \ln \frac{h}{2b}\right)$ occurs, which eases the process of bypassing these precipitates by dislocations and decreases the degree of creep life. Thus, preventing the ripening of phase is necessary to maximize creep resistance during long-term exposure.

Ostwald theory of ripening:

$$h^{3} = \frac{64 \cdot \gamma_{C} \cdot D \cdot c_{0} \cdot V_{m}}{9 \cdot R \cdot T}$$
(2.9)

- where $h \dots$ mean size of precipitate
 - γ_C ... energy of γ/γ' phase interface
 - D ... diffusion coefficient of elements in the γ phase
 - $c_o \dots$ equilibrium molar concentration of elements
 - V_m ... molar volume of γ' phase

If the ripening process of γ' phase is to be modified, we can perform the following precautions:

- 1) increase the volume fraction of f_V in γ' phase
- 2) add elements primarily dissolving in γ' phase and low coefficient *D* in the γ matrix (Nb, Ta), with Nb slightly increasing $\gamma_{\rm C}$

The problem is, however, that at higher amounts of these elements, the matrix becomes less stable and precipitation of η (Ni₃X) phase can occur.

2.5.7 Topologically close packed phases

Phase η (Ni₃X)

These phases which form with high content of Ti, Ta or Nb, after long exposure to high temperatures can precipitate:

- a) in cells on the grain boundaries leading to a decrease in creep characteristics (time to fracture)
- b) inside the grains with Widmannstätten morphology, which decreases strength, but ductility is not influenced

 η phase nucleates on the γ' phase stacking faults. Mechanical characteristics are positively influenced by the addition of B, which equally segregates on the grain boundaries.

Precipitation of σ phase

 σ phase is a packed phase with tetragonal lattice and needle or block morphology. This brittle phase which can be chemically composed by FeCr, FeCrMo, CrFeMoNi, CrCo or CrNiMo, is formed through a destabilization of austenitic γ matrix after a long-term exposure to high temperatures in the <540; 980> °C range. Decreasing the amount of Ni in favor of elements such as Fe, Cr or Mo which promote formation of this phase leads to a decrease in creep strength and decrease of ductility at normal temperatures. The tendency of σ phase formation increases with increasing number of electron vacancies N_V (chapter 2.5.1).

Precipitation of Laves phases

Laves phases are electron compounds of elements in which the difference of atomic radii is 30 %. It is possible to describe them by a general formula (Fe,Cr,Mn,Si)₂(Mo,Ti,Nb) and they exhibit acicular morphology. They can precipitate in Ni superalloys containing Fe in a temperature range between <650;1100> °C either inside the grains or intercrystallically.

Their precipitation occurs if $\overline{N}_V \ge 2,3$ and the amount of Mo or W (or possibly their common volume) is >3 % or there is an increased amount of Ti, Nb, Mo and decreased amount of Ni. Due to the influence of these phases, decrease in ductility and yield strength occurs at normal temperature, the influence on creep characteristics is negligible.

2.5.8 Precipitation and stability of carbidic phases

Carbidic particles which precipitate on the grain boundaries influence their anchoring and thus increase their resistance to yield and migration at diffusion creep. However if the carbides are expelled in form on continuous coating at the grain boundaries, the fracture strength may be lowered as well as ductility and strength at break.

Carbides can contribute to certain strengthening of the superalloy matrix (especially in Co based superalloys) and are significant in directing the grain size in formed superalloys.

Carbides in superalloys have a general formula of MC, $M_{23}C_6$, Cr_7C_3 and M_6C , where M is a general metal. Their influence is related to the morphology and occurrence:

MC - relatively coarse, randomly distributed in the matrix volume (TaC, NbC, TiC)

 $M_{23}C_6$ - expelled intercrystallically ($Cr_{23}C_6$, $Cr_{21}(Mo,W)_2C_6$)

lower T (760-870) °C - continual platelet precipitate

higher T (950-980) °C – wider blocks, less continual

 $M_6C \longrightarrow$ blocks on the grain boundaries

Widmanstätten structure inside the grains

Cr₇C₃ - wide blocks on the grain boundaries

Carbides often occur together, but they are created by gradual reaction in solid state by dissolution of MC carbides (Fig.2.16), which are released from liquid phase. The most significant influence is that of intercrystallically released carbides which decrease plastic properties of

superalloys. The least advantageous combination of intercrystal precipitation is $M_{23}C_6$ and M_6C within the grains with Widmanstätten structure, because the plasticity and time to break at creep and at high temperature is decreased. During precipitation of carbides, the basic γ matrix is depleted and there is a change of its composition with all the other consequences.

At high temperatures, carbides are transformed:

$$MC \rightarrow M_6C$$
, $MC \ a \ Cr_7C_3 \rightarrow M_{23}C_6$



Fig.2.16 Microstructure of a superalloy with carbidic MC particle.

Carbide precipitation is highly influenced by the following elements:

*	Co, Mo, W, Nb	– decrease occurrence of $M_{23}C_6$
*	Mo, W	– promote formation of M_6C
*	Nb, Ta	 promote formation of MC

2.5.9 Modification of grain boundary properties

The properties of grain boundaries are an important parameter of every material, especially if these are materials meant for high-temperature applications. In case of superalloys which have to resist creep at high temperatures the grain boundaries can be influenced by small additions of B, Zr or Mg, which will increase their life and plasticity. These elements segregate due to their small atom size in comparison with nickel primarily on the grain boundaries and by their surface-active influence slow down diffusion.

Several theories have been established that explain the positive effect on the grain boundaries properties, one of which is an assumption that Boron prevents carbide precipitation on the boundaries and pushes carbon atoms into the grains. It is assumed that Mg and Zr act similarly. In any case, the way of breakage is changed from intercrystal into transcrystal. With higher concentrations of B or Zr (depending on their solubility in the given alloy) a danger emerges that borides or Zr precipitates will start forming. The amounts of these elements in superalloys rarely surpass their solubility and if this does happen, it is only slightly over the limit, therefore the detection of small precipitate particles of with any amount of these elements is rather difficult in these structures.

2.5.10 Optimization and development trends for Ni superalloys microstructure

From the analysis of Ni based (and Ni-Fe based) superalloys and their properties is evident that they are directed by three basic variables, which are:
- * amount of γ' (Ni₃Al) precipitates and their morphology
- size and shape of grains
- carbide distribution

From Fig.2.17 we can form a conclusion about the influence of the individual elements and their amount on the nature of superalloy microstructure, therefore on the amount, distribution and shape of the γ' phase, on the distribution and shape of carbidic particles, etc.

From the overall aforementioned analysis we can also conclude steps through which an increase of strength levels and plasticity characteristics of superalloys may be achieved:

- 1) strengthening of γ phase matrix (with increasing number N_V rises the yield strength increase $\Delta R_{p0,2}$)
- 2) increase of volume fraction f_V of γ' phase, in all types of Ni superalloys, causes increase in shear stress $\Delta \tau = f(f_V)$
- 3) increase of APB energy in γ phase, or stacking fault energies in γ' (important for creep)
- 4) strengthening of γ' phase by adding certain elements
- 5) increase of coherent deformation (at T < 0.6 T_m) $\left(\varepsilon = \frac{a^{\gamma} a^{\gamma'}}{a^{\gamma}}\right)$
- 6) decrease of the ripening rate of γ' phase (for T > 0.6 T_m)
- limiting formation of denuded areas, precipitation of M₆C within the grains with Widmanstätten structure and continual precipitation of M₂₃C₆ on the grain boundaries
- 8) limiting the formation of σ phase, Laves phases and the η phase
- 9) stabilization of grain boundaries properties



Fig.2.17 Schematic description of the evolution of microstructure and Cr content of Ni based superalloys (from spherical up to cuboidal γ' precipitates)

During the development of Ni based superalloys, the percentage of γ' precipitates has been increased, it currently is up to 80% in modern superalloys which due to this amount exhibit similarly interesting property characteristic for pure intermetallic γ' phase (Ni₃Al), i.e. positive thermal dependence of yield strength (Fig.2.18). We will examine this property closely in chapter 4.9.1.

High-temperature properties was optimized also by increasing the γ' particle sizes until it stopped at a value of approximately 1 μ m and also by change of the particle shape to cuboidal

(Fig.2.17). Next, secondary precipitation of fine γ' particles was achieved, so that the microstructure of some alloys is formed by large cuboidal precipitates as well as small spherical γ' phase

700

particles, i.e. a bimodal structure (Fig.2.2).

The morphology of carbidic particles was optimized in dependence on the amount of carbide-forming elements, such as Cr (concentration profile of Cr on Fig.2.17). The occurrence of carbidic particles prevents the yield of grain boundaries under creep; despite that is has been found that the optimal solution is discontinuous distribution of carbides along the grain boundaries instead of continuous carbide strings.

Fig.2.18 Influence of temperature and contents of γ' phase on the achieved yield strength of superalloys. Even at 40% of γ' , an anomalous thermal dependence of the yield strength is exhibited.

1300

1200

1100

1000

900

800

700

600

500

400 300

200

100

a)

0.2 % flow stress (MPa)



Fig.2.19 Thermal dependence of yield strength for strengthening in selected superalloys: a) wrought and b) cast.

Aforementioned images compare thermal dependencies of yield strength for selected superalloys as being related to the volume fraction of precipitates (Fig.2.18), as well as to the processing technology (Fig.2.19) for various compositions of alloys, i.e. for both wrought (a) and cast (b) alloys.

2.6 Superalloys of the new generation

2.6.1 Co-Al-W based alloys

Relatively new discovery (Sato et al., 2006) are Co based superalloys which also contain Al and W and possibly other alloying elements. They differ from the aforementioned common Co based superalloys by ternary γ' -Co₃(Al,W) phase precipitation which has an L1₂ structure and is stable in high-temperature systems. The lattice misfit between the matrix (solid solution γ -Co with an FCC structure) and γ' phases is small, which allows for formation of a coherent two-phase γ/γ' structure. The γ' phase has cubic morphology of submicron size and similarly to Ni based superalloys, has a regular continual matrix stacking (similarly to Fig.2.3a).

Traditional Co based superalloys, as we have stated earlier are strengthened only by dissolved alloying elements in solid solution and by precipitation of small amounts of carbidic particles. Their lower creep strength (Table 2.5) does not permit their application on rotating parts but the good oxidation, corrosion and abrasive resistance predetermines them for parts resisting the effects of the environment, such as turbine blades. Preparation of a new material with γ' precipitations combination expands the possibility of their use in terms of high-temperature strength as well as environment resistance, especially in energy industry (environment with increased concentration of sulfur during coal gasification, oils of lower quality, etc.).

Co-Al-W based alloy exhibits, similar to Ni based superalloys, an anomalous positive increase of yield strength at temperatures over 600°C (Fig.3.20) and maximum strength is achieved at 700%C



or even at 800°C, if it is alloyed by Ta. This phenomenon is also related to activation of various yield systems.

Fig.2.20 Thermal dependence of critical shear stress CRSS (111)[$\overline{1}$ 01] in compression for Ni and Co based superalloys in single crystal state in comparison with Ni₃Al and Ni superalloy (Mar-M200) also in single crystal state. Compression tests were performed with strain rate of 10^{-4} s⁻¹.

Despite the Co-Al-W alloy having the melting temperature 50°C higher than Ni based superalloys, it has not exhibited a higher phase stability of γ' precipitates; on the contrary, the solvus of this phase is 100°C lower. The key role in increasing thermal stability of γ' precipitates are played by alloying elements. It has been confirmed that this temperature is significantly increased by Nb, Ta and Ti, slightly by Sc, V, Cr, Fe, Ni, Hf, Zr and Mo, while Re does not influence it at all. Atoms of Nb, Ta and Ti contain positions of B in ordered phase A₃B, which promotes γ' phase formation and increases its content fraction. To preserve the strength even over the maximum temperature (peak anomalous thermal dependence of yield strength) the shear mechanism of γ' phase is a necessary factor. It is assumed that Ta decreases the stacking fault energies in γ' phases and thus promotes the strengthening even at high temperatures. Research of these perspective alloys are ongoing.

2.6.2 Platinum-group metal based alloys

Quaternary high-temperature materials of new generation are designed based on platinum group metals (Ir, Rh) and are meant to be used at extremely high temperatures. As we have stated earlier, high strength at high temperatures of Ni based superalloys is ensured by γ' phase presence (L1₂) with coherent interface. This phase is an effective obstacle for dislocation movement, which ensures sufficient resistance to creep at high temperatures.

New superalloys based on Ir-Nb-Ni-Al are prepared by mixing two binary alloys: Ir-20 at.% Nb

and Ni-16.8 at.% Al, which contains phase L1₂. Metals of the platinum group have higher melting temperature (Ir: 2447 °C) and better oxidation resistance. The aim is a combination of good heat resistance of Ir based alloys with good strength, low density (approximately 8.5 g/cm³ compared to the density of Ir 22.65 g/cm³), and relatively low prices of Ni superalloys. The schematic on Fig.2.21 represents a part of quaternary equilibrium diagram of the Ir-Nb-Ni-Al system. It can be expected, that areas of $L1_2$ exist in the whole volume of mixing fractions, from the purely Ni based alloy to the purely Ir based alloys. The coexistence of coherent phases L12-Ni₃Al and L1₂-Ir₃Nb is desirable in this type of allovs.



Fig.2.21 Schematic of a quaternary diagram of Ir-Nb-Ni-Al system



Fig.2.22 Yield strength in compression for selected Ir based alloys compared to MarM247alloys.



Fig.2.23 Temperature dependence of yield strength in compression of cast Ir- and Rh based alloys with 15 at.% of the second element and Ni and W based alloys

In Ir-Nb/Ni-Al based alloys, an equilibrium has been established between three phases of Ir₃Nb (L1₂), Ni₃Al (L1₂) and γ matrix. The yield strength under pressure of alloy Ir-3.1Nb-68.25Ni-6.75Al (at.%) at 1200°C moved from 130 to 350 MPa (Fig.2.22), which is more than in case of commercial Ni-superalloys MarM247 (50 MPa) and lower than binary alloys based on Ir (500 MPa). Fig.2.22 is given for comparison of yield strength under pressure for a quaternary alloy Ir-Ta-Ni-Al, prepared by

combining Ir-Ta and Ni-Al binary alloys. In comparison with Ir-alloys that the yield strength is much better in quaternary alloys.

The density of Rh based superalloys is higher (12.4 g/cm³) than in Ni based superalloys, they have lower melting temperature of 1960°C, lower density and better resistance to oxidation than Ir based. Although the strength in Rh based alloys is lower than Ir based alloys (Fig.2.32), specific strength of both types of alloys is almost identical.

Alloying elements in Ir based alloys and their contribution to high-temperature strengthening depending on the lattice misfit (Fig.2.24.) and how this misfit changed with increasing temperature (Fig.2.25) is being researched.



Temperature (°C)

Fig.2.25 Thermal dependence of lattice misfit for binary Ir based alloys

Fig.2.24 Dependence of yield strength on the size of lattice misfit during test under pressure of cast alloy based on Ir with 50 volume % of precipitates

Σ Important terms

Ni based superalloy, Co based superalloy, FeNi based superalloy, γ' cuboidal phase, strengthening mechanisms, effect of volume content of precipitates on creep properties, ripening of grains, optimization of properties.

Orowan's mechanism, phase precipitation, dislocation disociation, stacking faults, partial dislocations, coherency between matrix and γ' precipitate.



Questions

- 1. What is the basic classification of superalloys?
- 2. What properties are shown by Fe-Ni based superalloys and for which temperatures are designated?
- 3. What properties are shown by Co based superalloys and which structures is characteristic for them?
- 4. What properties and structure are shown by Ni based superalloys and for which application fields are they designated?
- 5. What are the origins of strengthening effect in Ni superalloys?

- 6. Whereby the creep resistence is ensured?
- 7. What phases are beneficial to creep resistence and what of them deteriorate it?
- 8. What types of superalloys are used in turbines if automotive or aircraft engines?
- 9. How the lattice of γ phase differs from that of γ' phase?
- 10. Which strengthening mechanisms play role in superalloys?
- 11. Explain the role of precipitation strengthening in superalloys.
- 12. When volumic percentage of γ' phase in superalloys shows positive temperature dependence of yield strength?
- 13. What element is added to superalloys to enhance the oxidation resistance?
- 14. What application advantages related to mechanical properties offer the directionally solidified or single crystal superalloys compared to cast polycristalline ones used in gas turbines?
- 15. What are the new generation superalloys?
- 16. What are the advantages of their applications compared to Ni superalloys?



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3. TITANIUM ALLOYS



Time needed to study: 4 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- Define basic properties of titanium and titanium alloys
- Describe basic classification of titanium alloys
- Explain differences of the microstructure of Ti alloys
- Explain microstructure effect on the properties of Ti alloys
- Estimate selected applications of Ti alloys in consideration of their properties
- Define basic characteristics of alfa, alfa+beta and beta alloys
- Specify phase transformation in Ti alloys
- Evaluate alloying and heat treatment effects on mechanical properties of Ti alloys

Ш	Lecture

3.1 General characteristics and basic properties of titanium

Titanium has become in the latter years a very important technical material whether in form of a technically pure metal or an alloy. Titanium has been discovered in 1791 (by an Englishman W.Gregor). In nature, it is the tenth most common element, but its use is limited primarily due to its high affinity to all non-metals (except noble gases). Despite being very chemically reactive, it exhibits great resistance to corrosion because - similar to aluminum - it covers itself with a oxide coating (TiO₂).

Titanium occurs in two crystallographic structures. Pure titanium (commercial purity-CP) has hexagonal closed packed lattice (HCP) at room temperature, which is called an α phase. At 882°C (according to some authors at 880 or 885°C) this structure is changed into a body centered cubic lattice (BCC) called a β phase.

3.1.1 Physical properties of titanium

Atomic weight	47.9 g/mol
Lattice	below 882°C HCP (α Ti)
	above 882°C BCC (β Ti)
Lattice parameter	HCP: $a = 0.29503 \text{ nm},$
	c = 0.48631 nm
	c/a = 1.5873
	BCC: $a = 0.33132 \text{ nm}$
Density	$4.505 \cdot 10^3 \text{ kg/m}^3$
Melting point	1670 °C
Young modulus (tensile)	112.5 GPa
Non magnetic	
Non toxic, biocompatible	
High resistance to corrosion in acidic and chlorides env	rironments

3.1.2 Advantages of titanium and titanium alloys against other metallic materials

Basic properties of Ti when compared to other pure metals are given in Table 3.1. Other advantages of Ti and its alloys can be summarized into the following points:

- high strength/density ratio (specific strength), far better than in other metals currently in use;
- outstanding corrosion resistance against the atmosphere, freshwater and seawater, most industrialgrade acids, bases, corrosion resistant in oxidizing or reducing environments and in environments with high amounts of chlorides.
- very good erosion resistance when compared to other commonly used metals.
- very good compatibility with animal tissue predetermines titanium for dental and surgical implants.
- processing similar to stainless steels or nickel alloys for high performance.

Properties	Ti	Mg	Al	Fe	Cu
Melting point (°C)	1665	650	660	1535	1083
Density (g/cm ³)	4.51	1.74	2.7	7.86	8.94
Heat conductivity	0.0407	0.35	0.57	0.17	0.92
Electrical resistivity ($\mu\Omega$ ·cm)	55.4	4.40	2.68	10.0	1.72
Heat capacity	0.126	0.245	0.211	0.109	0.093
Coefficient of thermal expansion $\cdot 10^{-6}$ (/°C)	8.9	25.7	24.0	11.9	16.4
Young's modulus (GPa)	112	45	72.5	200	122.5

Table 3.1 Comparison of titanium properties with other metals

Basic differences between steels, nickel and titanium alloys

Titanium compared to steels and nickel alloys exhibits the following properties, which influence its industrial applications:

- lower modulus of elasticity
- higher melting point
- lower coefficient of specific thermal conductivity
- tendency to gas absorption at higher temperatures

3.1.3 Mechanical and technological properties of titanium

Very good formability, weldability, but worse machinability. Formability depends on the type of lattice, which is related to the slip system (compare BCC and HCP lattice on Fig.3.1).

Strength of technical Ti depends on its purity and is in the following range: $R_{p0,2}$ 170-480 MPa, R_m 240-550 MPa, A_5 20-30 % (highly pure, up to 70 %).





3.1.4 Corrosion properties of titanium and its alloys

Unalloyed Ti is very resistant to corrosion in various environments: seawater, body fluids, vegetable and fruit juices, salt solutions of chlorides, sulfides, sulphates, HNO_3 solution, wet chlorine. Ti has a limited resistance to oxidation above 540°C in air.

Alloys depending on the composition and surrounding environments may be affected by galvanic corrosion (generated galvanic cells), crevice corrosion (hot solutions of chlorides, iodides, bromides and sulphates), erosion-corrosion and cavitation, stress-corrosion cracking.

3.1.5 Influence of elements on titanium properties

In relation to the existence of allotropic change (882°C) of α into β , the additives in Ti are divided based on whether they increase or decrease the temperature of this transformation, i.e. which of the two given phases stabilizes in larger temperature range (Fig.3.2. and Fig.3.3). This influence is closely related to their higher solubility in phases which they stabilize.

Harmfull additives

are especially interstitial elements, such as oxygen, nitrogen, carbon and hydrogen, which form interstitial solid solutions (O, N and C are α - stabilizers, H is a β - stabilizer) or brittle oxides, carbides, nitrides or hydrides. These additives lower the degree of plasticity properties (ductility is decreasing), worsen weldability and increase the corrosion susceptibility. On the other hand, they increase strength and hardness (Table 3.2 and 3.3).

Table 3.2 Amounts of impurities and alloying elements (wt.%) in commercial pure (CP) titanium and titanium alloys. The values give maximum allowed range, ELI (extra low interstitial) means extra low amount of interstitial elements

ASTM	Fe	0	N	С	н	AI	V	Pd	Ti
W.Nr.	max	max	max	max	max				
Grade 1	0.20	0.18	0.03	0.08	0.015	-	-	-	balance
3.7025	0.15	0.12	0.05	0.06	0.013	-	-	-	
Grade 2	0.30	0.25	0.03	0.08	0.015	-	-	-	balance
3.7035	0.20	0.18	0.05	0.06	0.013	-	-	-	
Grade 3	0.30	0.35	0.05	0.08	0.015	-	-	-	balance
3.7055	0.25	0.25	0.05	0.06	0.013	-	-	-	
Grade 4	0.50	0.40	0.05	0.08	0.015	-	-	-	balance
3.7065	0.30	0.35	0.05	0.06	0.013	-	-	-	
Grade 7	0.30	0.25	0.03	0.08	0.015	-	-	0.12-0.25	balance
3.7235	0.20	0.18	0.05	0.06	0.013	-	-	0.15-0.25	
Grade 11	0.20	0.18	0.03	0.08	0.015	-	-	0.12-0.25	balance
3.7225	0.15	0.12	0.05	0.06	0.013	-	-	0.15-0.25	
Grade 5 (6AI-4V)	0.40	0.20	0.05	0.08	0.015	5.5-6.75	3.5-4.5	-	balance
3.7165	0.30	0.20	0.05	0.08	0.015	5.5-6.75	3.5-4.5	-	
Grade 5 (6Al-4V ELI)	0.25	0.13	0.05	0.08	0.015	5.5-6.5	3.5-4.5	-	balance
ASTM F136									

Alloying additives

are substitution elements **Ta**, **V**, **Mo and Nb**, which play an important role in controlling the microstructure and properties of titanium alloys. They are β -isomorphic elements (BCC) with Ti, they do not form intermetallic compounds with Ti (thus they are also preferred in alloying), they stabilize the β -phase (Fig.3.2). Elements such as **Cr**, **Fe**, **Cu**, **Ni**, **Pd**, **Co**, **Mn** and some other transition metals form eutectoid system with Ti, they have lower solubility in α -Ti, they lower the transition temperature and stabilize β -phase. They are added in combination with β -isomorphic elements in order to stabilize β phases and prevent or lower the occurrence of intermetallic compounds (formed during thermomechanical treatment, thermal treatment or high-temperature use).

- ***** Fe, Cr are strong β -stabilizers ((α + β) and β alloys).
- *** Zr**, **Hf** excellent property: α and β isomorphic elements.

- **Solution** Sn, Al high solubility in α and β phase.
- Al, Zr, Sn are in almost all commercially available Ti alloys, because they are soluble in both phases and especially for their positive effect on increasing creep strength of the α phase (strengthening by solid solution).
- ✤ Ni, Mo, Pd, Ru increase corrosion resistance of CP Ti.



Fig.3.2 Influence of impurities and alloying elements on α to β transformation temperature (T_{β}) of titanium: a) and b) additives lower the T_{β} temperature; c) and d) additives increase the T_{β} temperature.

Material	Maximum content (%)		Minimum tensile strength (MPa)	Minimum yield strength (MPa)
	0	Fe		
CP Ti - grade 1	0.18	0.20	240	170
CP Ti - grade 2	0.25	0.30	345	275
CP Ti - grade 3	0.35	0.30	450	380
CP Ti - grade 4	0.40	0.50	655	485
Ti-6Al-4V	0.20	0.30	925	870
Ti-6AI-4V-ELI	0.13	0.25	900	830
Ti-5Al-2.5Sn	0.20	0.50	830	780
Ti-5Al-2.5Sn-ELI	0.12	0.25	690	655

Table 3.3 Tensile mechanical properties of Ti and its alloys (thin sheet) relating to O and Fe amounts



Fig.3.3 Equilibrium phase diagram of Ti-Al with highlighted structure modifications of α -Ti and β -Ti and area of both (α + β) phases occurrence (red arrows).

3.2 Phase transformations in titanium alloys

Basic types of phase diagrams are state on Fig.3.2, from which the influence of individual additives on the α to β transformation temperature can be deduced. All technical alloys of Ti contain in various degrees Al additive, therefore the binary system Ti-Al (Fig.3.3) has a similar significance to titanium alloys as the Fe-Fe₃C system for Fe. In Table 3.4 we have given temperatures for phase transition from β to α or $\alpha + \beta$ (i.e. β transus-T_{β}) with relation to the alloying elements.

Table 3.4 Transition temperature (T_{β}) of β phase for CP Ti and selection	lected Ti alloys
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Alloy	Beta transus T _β (°C)
CP Ti-grade 2	910
CP Ti-grade 4	945
Ti-5Al-2.5Sn	1050
Ti-0.3Mo-0.8Ni (Ti-code12)	880
Ti-6Al-4V (6-4)	1000
Ti-6Al-7Nb (IMI367)	1100
Ti-8Mn	800
Ti-13V-11Cr-3Al (13-11-3)	720
Beta C (38-6-44)	795
Ti-10V-2Fe-3Al (10-2-3)	805

3.2.1 Secondary phase precipitation

In the alloy systems of Ti, intermetallic compounds can form as well as other secondary phases. The most important ones are α_2 and ω .

Ti₃Al (α_2) was considered in some cases as a cause for stress corrosion cracking. Today this phase is the subject of intermetallic research for high-temperature use. This phase is ordered (HCP) and dispersion distributed in the basic matrix (range of 6-12% of Al content at 575°C), which is why Ti alloys don't have more than 8% of Al (Fig.3.3). The size and character of the precipitated phase depends on thermal treatment of the alloy. Phases α and α_2 both have similar crystallographic structures, precipitates preserve their coherence even if they achieve large dimensions.

By dispersive precipitation of α_2 , the yield strength is increasing as well as the modulus of elasticity, but plasticity properties are decreasing. Over 8% of Al makes the alloy brittle. This can be prevented by additional annealing, 50°C below phase limit (α + α_2). During this treatment, the mechanism of plastic deformation by precipitate intersecting with dislocations is changed into the mechanism of bypassing, because the free paths between the thickening precipitates are enlarged. Therefore, the plasticity properties are improved. Oxygen has great influence on the stability and kinetics of the α_2 phase. Its increased content decreases the α_2 formation rate. Additives such as Zr and Si also have influence, which causes non-coherence of the phases and deepen the crystallographic mismatch, Sn increases the melting temperature of α_2 .

Quenching from β phase region forms a in some cases metastable β_m , that can be decomposed depending on the alloying elements and annealing temperature. The decomposition of metastable β_m phase occurs as a complex process (Fig.3.5):

 $\begin{array}{l} \beta_m \rightarrow \beta {+} \omega \rightarrow \ \beta {+} \omega {+} \alpha \rightarrow \beta {+} \alpha \\ \beta_m \rightarrow \ \beta_1 {+} \beta_2 \rightarrow \ \beta_1 {+} \beta_2 {+} \alpha \rightarrow \ \beta {+} \alpha \end{array}$

The structure of ω -phase is HCP, it is released either in shape of cubics or ellipsoids. The volume of this phase is large, so in some cases, the volume fraction is as high as 0.5. With the increasing fraction of ω -phase, the yield strength and strength is progressively increased (R_m 1500 MPa), but the fracture toughness is significantly lowered (min.20 MPa·m^{1/2}!). At optimal size and with lower content of ω -phase, a sufficient ductility and fracture toughness levels can be preserved simultaneously with matrix



In case an eutectoid is formed, the equilibrium structure is composed of an α phase and the corresponding intermetallic phase:

$\begin{array}{l} \beta_m \rightarrow \ \beta + \omega \rightarrow \ \beta + \omega + \alpha \rightarrow \ \beta + \alpha \rightarrow \ \beta + \alpha + TiX \rightarrow \ \alpha + TiX \\ \beta_m \rightarrow \ \beta_1 + \beta_2 \rightarrow \beta_1 + \beta_2 + \alpha \rightarrow \ \beta + \alpha + TiX \rightarrow \alpha + TiX \end{array}$

The exact sequence of formed phases in different types of Ti alloys will depend on their composition and type of aging. Phases β_1 and β_2 are two solid solutions, one of which includes more of an additive than the other. The morphologies of α +TiX can change based on the type of the alloying element.

3.2.2 Martensitic transformation

The occurrence of martensitic transformation was detected in $(\alpha+\beta)$ titanium alloys, that were quenched from the β phase region (Fig.3.6). Through this transformation, acicular structure is formed in quenched and/or quenched and aged alloys. Hardening capacity of Ti alloys generally points to the ability of full transformation into a martensitic phase or preserving β structure up to room temperatures. Microstructures are however always dependent on the amounts of alloying elements; therefore generalizing the occurrence of types of structures and individual variants of martensite is relatively difficult.



Fig.3.6 Phase changes of α and β and martensitic transformation: a) with the presence of metastable β phase, martensite and ω -phase, b) occurrence of two variants of martensite α' and α'' .

The structure of martensite α' or α'' is a result of cooling and during the aging process, they disintegrate into α and β phases (Fig.3.7). According to crystallographic structure, we can distinguish

3 variants of martensitic phase:

- 1) **HCP** martensite α '
 - in alloys with high temperature M_S the morphology is massive;
 - in alloys with low temperature M_S (alloying elements stabilizing the β phase) morphology is acicular.
- 2) **Orthorhombic** martensite α " (Fig.3.6b)
 - area of its occurrence is identical to the minimal strength depending on its chemical composition;
 - unstable a reversible transformation into β phase may occur or it degenerates into an FCC or tetragonal lattice.
- 3) FCC martensite α "
 - was detected only in some alloys with Mo, V and Al.

Martensite α' is characterized by its blocky shape with uneven surface. This phase is formed by a block of parallel platelets with coincident orientation grouped into one so called packet (colony). Within individual grains of the initial β phase, several such colonies are formed but it under no circumstances passes the boundaries of the original β phase. This transformation is total, there is no untransformed β phase detected in the massive phase. In pure Ti, or in alloys with low content of additives, the α' phase is relatively soft and formable, but it significantly strengthens with higher content of impurities (O, N).

The temperature of α' phase formation depends on the amount of alloying elements. For instance, Zr, Sn and Al have low or negligible influence on the M_s temperature of the α' phase. On the other hand, additives that stabilize the β phase (Mo, V, Nb) have significant influence on the M_s temperature of the α' phase (they lower it, so that in cooling on air, the monophase structure of β phase is preserved).

The formation of martensite α " is schematically represented on Fig.3.6b. The concentrations of C' and C" on this image determine the composition of the alloy in which the orthorhombic variant of martensite α " is formed. The occurrence of this orthorhombic phase (o.p.) is determined by the spinodal (under which occurs a disintegration into two coherent phases), and solvus of the coherent orthorhombic phase (c.o.p.). The temperatures T₀ give the initial point of martensitic transformation from β into α ' or α ".

A number of elements that stabilize the β phase influence the formation of eutectoids:

- 1) they promote fast formation of an eutectoid reaction (Ni, Cu) the eutectoid reaction is difficult to suppress;
- 2) they slow down eutectoid reaction– the structure of the β phase is preserved metastable β titanium alloys are formed.

In many cases however, a creation of stressinduced martensite is possible (e.g. deformation at room temperature).

Fig.3.7 TTT diagram for hardenability of $\alpha + \beta$ alloys from the β phase: formation of martensite α' , martensite start M_S, martensite finish M_f.



3.3 Titanium alloys

The development of a wide range of titanium alloys is based on directed progress of crystallographic transformations using alloying and thermo-mechanical processing. Based on the occurrence of the aforementioned phases it also serves the classical division of titanium rolling products. Based on these phases, titanium alloys can be classified as α , β or $\alpha+\beta$ alloys (Fig. 3.8). The most common and used alloy is Ti-6Al-4V (45% of the overall Ti alloy production), next is technical Ti (representing 30% of production) and other alloys combined represent only 25% of the production. Selected properties of titanium alloys, pure titanium and steel are compared in Table 3.5.

Table 3.5 Comparison of density, strength and specific strength for Ti alloys and steel at 20°C.

Metal / alloy	Density (g/cm ³)	UTS (MPa)	Specific strength (MPa· cm ³ /g
CP titan	4.51	400	89
Ti-6Al-4V	4.43	895	202
Ti-4Al-3Mo-1V	4.51	1380	306
UHS steel (4340)	7.9	1980	251



Fig.3.8 Typical schematic examples of microstructures for Ti alloys (without a scale): a) α , b), c) $\alpha+\beta$ and d) β

3.3.1 Alpha alloys

Alpha alloys contain aluminum and tin. These elements stabilize the α area and either prevent the change of phase transformation temperature or cause its increase. These alloys have usually better resistance to creep than beta alloys and are used for high-temperature applications.

Alpha alloys are mostly very ductile and if the amount of interstitial elements is very low, the ductility and strength is preserved even in cryogenic temperatures. Contrary to the β alloys, which are characteristic for their ductile to brittle transition, alpha alloys are also useful for cryogenic applications (for example the Ti-5Al-2,5Sn for up to -255°C).

Alpha alloys exhibit sufficient firmness, strength and formability, but worse malleability than β alloys do. Bad malleability is caused by greater ability to form defects during forging, the occurrence of these defects can be decreased by lower removal rates and frequent heating.

Alpha alloys cannot be strengthened by thermal processing - unlike β alloys - because the alpha structure is very stable. They are most often used in annealed or recrystallized state, i.e. after removal of resitual tensions of processing. The basic variable element of the α alloy microstructure is grain size. For the given chemical composition, strength (short-term deformation) and creep (long-term deformation) can be influenced by grain size and the inserted deformation energy.

Alpha alloys, such as Ti-5Al-2,5Sn, are less resistant to corrosion, but they have higher firmness than pure titanium.

The main alloying element in α alloys is aluminum, but some α alloys and most pure commercial titanium contain low amounts of elements that stabilize the β area. Alpha alloys that contain small amounts of β stabilizers (such as Ti-8Al-1Mo-1V or Ti-6Al-2Nb-1Ta-0,8Mo) are sometimes labeled "super- α ". Even though they contain some residual β phase, these alloys are formed mostly by α phase and because they act more like α alloys in processing (strengthening by aging), they are evaluated more like classic α alloys than classic $\alpha+\beta$ alloys.

Since "super- α " alloys contain some β stabilizers, they can exhibit changes in their microstructure similar to $\alpha+\beta$ alloys. The microstructure can change from equiaxed α grains, if it is prepared in an $\alpha+\beta$ area, to the acicular structure of transformed β , if it is processed over β transformation.

Common temperature limit of use in titanium alloys is around 590°C for alloys IMI-834 and Ti-1100. The IMI-834 alloy has a "super- α " structure with an addition of carbon. It is processed deep inside an α + β area, so that ripening of grains is prevented and a mixed structure of α with acicular β is achieved. This transformed type of microstructure exhibits good creep resistance without sacrificing much fatigue strength. High creep strength in Ti-1100 alloy is achieved by controlling the amount of molybdenum and iron.

3.3.2 Alpha + beta alloys

The chemical composition of $\alpha+\beta$ alloys allows for creation of mixture of α and β phases, which can contain between 10-50% of β phase at room temperature. The most common $\alpha+\beta$ alloy is Ti-6Al-4V. Though this interesting alloy is relatively hard to form even in annealed state, $\alpha+\beta$ alloys have good formability in general. The properties of these alloys can be controlled by thermal processing which allows to change the amount and type of the β phase present. By solution annealing with subsequent aging at 480-650°C and precipitation of the α phase, a mono-grain mixture $\alpha+\beta$ is achieved in the matrix of residual or transformed β phase. The strength of these alloys can be improved by 30-50% by this method.



Fig.3.9 Microstructure of an alpha-beta alloy Ti-6Al-4V consequent of various metallurgical conditions: a) equiaxed α and small amounts of intercrystal β , b) equiaxed and acicular α and small amounts of intercrystallic β , c) equiaxed α in acicular α (transformed β) matrix, d) small amounts of equiaxed α in acicular α (transformed β) matrix, e) thicker needles of α (transformed β), α on original grain boundaries of phase β , f) platelet and acicular (transformed β), α on original grain boundaries of phase β .

If α outbalances β in an $\alpha+\beta$ alloy, this alloy is called "near- α ". Other denominations include "super- α " or " α with low amounts of β ".

Thermal or thermo-mechanical processing may strengthen $\alpha+\beta$ alloys if they contain one or more α stabilizers or one or more β stabilizers. For ensuring the strengthening, the alloys are quickly cooled from temperatures high in the $\alpha+\beta$ phase area or even over the β phase transformation temperature (T_{β}). After this solution annealing follows aging at medium temperatures and an appropriate α + transformed β mixture is created. The behavior of an alloy during thermal processing is a function of cooling rate from the temperature of solution annealing and therefore it can be influenced by the size of cross-section of the product. The content of stabilizers also influences the resulting strengthening - with the rising volumes, the ability to strengthen increases even for large sized particles.

Equiaxed structure is formed in alloy processing in $\alpha+\beta$ area and annealing at lower temperatures. the acicular structure is formed in thermal or thermo-mechanical processing above the β transformation and fast cooling. Fast cooling from temperatures within the $\alpha+\beta$ area leads to a structure formed by equiaxed primary α and acicular α formed by β transformation. Types of microstructure depending on thermal or thermo-mechanical processing are represented on Fig.3.9 and 3.10 (you can learn more about them in **a**). The image highlights original grain boundaries (GB). Every type of structure has its advantages and disadvantages, as shown in Table 3.6.



Fig.3.10 Diagram with composition and occurrence of phases for alloy Ti-6Al-4V annealed cooled on air or water quenched from various areas of phase occurrences: β (1065°C) or $\alpha+\beta$ (955°C).

Table 3.6 Rel	ative advantag	es of equiax	ed and acicu	lar structures
---------------	----------------	--------------	--------------	----------------

Equiaxed microstructure	Acicular microstructure
Higher ductility and formability	Superior creep properties
Higher critical stress for SCC in hot salts	Lower temperature of brittle-ductile transition
Higher strength (for equivalent heat treatment)	Higher resistance to fatigue crack propagation
Better tolerence to hydrogen	
Better properties at low- and hig-cycles fatigue	

A suitable choice of forging and thermal processing can help achieve a whole range of properties in $\alpha+\beta$ alloys. These alloys have higher ability of aging than "super- α " alloys. In "super- α " the ability to age is lower and if the composition is close to balanced, small or no change of these properties can be expected.

Considerable increase of firmness and yield strength can be achieved after hardening when unstable phases such as martensite α' or metastable β are formed within the $\alpha+\beta$ alloy. In water quenching from β phase area, suitable aging reaction may be performed, which then substantially decrease strength. The best combination of properties can be achieved by solution annealing and fast cooling from temperatures slightly above the β phase transformation with subsequent hardening. Fig.3.11

schematically shows formation and growth of Widmannstätten acicular structure in Ti-6Al-4V alloy depending on the temperature during thermal processing.



Fig.3.11 Schematic representation of formation and growth of Widmannstätten structure in Ti-6Al-4V alloy with a decrease of temperature in slow cooling from temperature over T_{B} .

3.3.3 Beta alloys

Beta alloys contain transition elements such as vanadium, niobium and molybdenum which lower the α to β transition temperature. This way they promote the formation of a BCC structure of the β phase. In comparison with α alloys they have outstanding malleability in wide interval of forging temperatures and thin sheets from β alloys are after solution annealing formable cold.

Beta alloys have outstanding turbidity, they easily react to thermal processing. Common thermal processing includes solution annealing with subsequent aging at temperatures from 450 to 650°C. During this thermal processing, fine dispersed α particles are formed in the residual β structure.

During thermal processing of Ti alloys over the T_{β} (β transition temperature), a coarse-grained β may be formed (0,5-1,0 mm), which must be taken into account in further forging and/or thermal processing. The β structure with grain size of ~ 0,1 mm can be prepared by processing "super – α " alloys at temperature high inside the α + β area (close to β transition). Rate of cooling also has a significant influence on the transformation products. By cooling slowly, ordered α are obtained, resulting in good creep resistance, but worse fatigue resistance compared to quickly cooled structures.

Beta alloys are sufficiently rich in β stabilizers (poor in α stabilizers), so a β structure can be completely preserved by an appropriate cooling rate into the room temperatures. However, beta alloys are metastable, α phase precipitations in metastable β are used to strengthen the alloy. Beta alloys contain small amounts of α stabilizers, which aid strengthening.

Compared to $\alpha+\beta$ alloys, β alloys and "super- β " alloys as a class have higher fracture strength at the given level of strength. To achieve optimal properties of these alloys it is necessary to perform a strict check of their production and processing, which cannot always be done.

In the past, beta alloys had limited use, for example as springs and fastening elements, where high strength was required. In latter years, beta alloys have received greater attention because their fracture strength is appropriate for the increased requirements of damage tolerance in space constructions. Some beta alloys containing molybdenum also have good resistance to corrosion. Beta alloys also exhibit better formability at room temperature and better malleability than $\alpha+\beta$ alloys; they also have higher strength than $\alpha+\beta$ alloys at temperatures where instead of creep strength, the decisive criterion is yield strength; another one of their advantages is better ability of thermal processing (solution annealing, turbidity and aging) in larget profiles than in case of $\alpha+\beta$ alloys.

Beta alloy Ti-10V-2Fe-3Al is an alloy typically suitable for forging (airplane construction parts); alloy Ti-15V-3Cr-3Al-3Sn is good for thin sheets and alloy Ti-3Al-8V-6Cr-4Mo-4Zr is good for springs and extrusions.

3.4 Processing of titanium alloys

During the preparation of titanium alloys, there is a possibility to use Ti sponge, which has to have controlled amounts of O, N, C, Si and Fe, and corresponding alloying elements in which purity have to be ensured. If Ti-scrap is used for Ti alloy production, it is necessary to include re-melting and purification into the technology of preparation. Among the most common pyrometallurgical technologies of titanium alloy preparation are vacuum induction melting, vacuum arc re-melting (double melting), vacuum induction melting with cold container and subsequent casting in vacuum or in a protective atmosphere.

	Thermal treatment	Cycle	Microstructure
1	Duplex annealing	Solution annealing 50-75°C below T_β , air cooling and afing for 2-8 h at 540 to 675°C	Primary α , plus areas with Widmannstätten's α - β structure
2	Solution annealing and aging	Solution annealing 40°C below T_{β} , water quenching (air cooling) and aging for 2 to 8 h at 535-675°C	Primary α , plus tempered α' or β - α mixture
3	Beta annealing	Solution annealing 15°C above T_{β} , air quenching and stabilisation for 2 h at 650 to 760°C	Widmannstätten's α-β colonies
4	Beta quenching	Solution annealing 15°C above T_{β} , water quenching and tempering 2 h at 650 to 760°C	Tempered α'
5	Recrystallization annealing	4h at 925°C, cooling 50°C/h to 760°C, air cooling	Equiaxed α with β at triple points of grain boundaries
6	Mill annealing	α - β hot working + annealing for 30 min to several hours at 705°C, air cooling	Partially recristallized α with small volume fraction of fine β particles

Table 3.7 Overview of thermal treatment of $\alpha+\beta$ titanium alloys

Primary processing includes rolling operations which result in profiles such as crowbars, belts, sheets, bars, pipes, wires and others. Secondary processing represents operations such as drop forging, extruding, hot and cold forming, chemical milling, working and adjoining. After secondary processing comes thermal processing, an overview of which is given in Tab.3.7. The schematic of thermal processing which is performed after drop forging for example in $\alpha+\beta$ alloys and which includes solution annealing and aging as shown on Fig.3.12.



Fig.3.12 Schematic representation of die forging and subsequent thermal treatment of an $\alpha+\beta$ structure.

Alloy	Composition	State	UTS (MPa)	Y.S. (MPa)	Elongation (%)
5-2-5	Ti-5Al-2.5Sn	SA (1/2-4h/700-870°C)	830-900	790-830	13-18
3-2-5	Ti-3Al-2.5Sn	SA (1-3h/650-760°C)	650	620	22
6-2-1-1	Ti-6Al-2Nb-1Ta-1Mo	SA (1/2-2h/700-930°C)	860	760	14
8-1-1	Ti-8Al-1Mo-1V	SA (8h/790°C)	1000	930	12
Ti-17	Ti-5Al-2Sn-2Zr-4Mo-4Cr	Treatment for α - β or β + aging	1140	1070	8
6-4	Ti-6Al-4V	SA (2h/700-870°C)	970	900	17
		А	1170	1100	12
6-6-2	Ti-6Al-6V-2Sn	SA (3h/700-820°C)	1070	1000	14
		А	1280	1210	10
10-2-3	Ti-10V-2Fe-3Al	SA (1h/760°C)	970	900	9
		А	1240-1340	1140-1240	7
β-III	Ti-4.5Sn-6Zr-11.5Mo	SA (1/2h/700-870°C)	690-760	650	23
		A	1240	1170	7

Table 3.8 Mechanical properties at room temperature for selected Ti alloys in relation with their thermal treatment

Note: SA -solution annealing, A- aging

Thermal treatment (TT) is included for various reasons:

- 1. lowering the residual stress from the production (removal of inner stress)
- 2. achieving more suitable combination of ductility, malleability and dimension and structural stability, especially for $\alpha+\beta$ alloys (annealing)
- 3. increasing strength by solution annealing and aging
- 4. optimization of special properties such as fracture strength, fatigue limit and creep strength limit

Alloy are therefore processed by the following methods based on the alloying element content and occurrence of phases:

- α alloys and super- α alloys do not change considerably in TT, therefore they are only processed according to points 1. and 2.
- β alloys are processed thermally according to point 1., 2. and 3..
- $\alpha+\beta$ alloys are thermally processed as seen in points 2. and 3. (Table 3.7).

The characteristics of thermal processing for selected Ti alloys are given wholly and with their mechanical properties in Table 3.8. The influence of thermal processing on the resulting microstructure based on cooling mechanism in $(\alpha+\beta)$ alloys are schematically given in O *Animation* \oiint{O} .

Relation between the structure, production and properties

The resulting microstructure of an alloy reflects the influence of various factors, such as:

- overall amount of impurities and alloying elements
- melting process for primary ingot preparation
- number of melting steps
- methods of mechanically processing the ingot into rolling products
- forging methods during forming
- casting processes and the volume of the casts, processes of increasing density in order to lower the casting porosity
- processes of powder metallurgy including the powder preparation
- adjoining processes in construction preparations
- final thermal processing
- working processes or surface treatments

During thermal and thermo-mechanical treatment optimization, various parameters have to be taken into consideration, as is shown on the following schematic on Fig.3.13.



Fig.3.13 Schematic thermo-mechanical processing and parameters for process optimization

The nature of the microstructure, which is a result of the aforementioned preparation and thermomechanical processing (Fig.3.14) influences the following mechanical characteristics of alloys and therefore also their further application:

- yield strength and breaking strength in tension
- ductility
- strength
- cyclical properties- low-cycle fatigue and high-cycle fatigue
- spread of fatigue breakage or of environmental pressure breakage

In conclusion, it is possible to summarize the basic knowledge on titanium alloy properties in terms of their basic division into α , $\alpha+\beta$ and β alloys into a schematic shown on Fig.3.14.



Fig.3.14 Basic material characteristics in relation to the structure for various groups of Ti alloys

3.5 Use of titanium alloys

From a detailed analysis of individual titanium properties is shown that these materials will find their application in two main fields:

- 1. corrosion-resistant equipment
- 2. high-strength structures

Overview of application fields

- 1) Aviation engines with gas turbine, aircraft constructions, space ships, helicopter rotors, ...
- 2) Energy industry gas turbines, jet turbine, pipeline systems, heat exchangers, devices for desulphurization of flue gas,...
- 3) Chemical industry pressure and reaction containers, heat exchangers, pipes, coats, protective pipes, pumps, coolers, valves, channels, filters, stirrer, ...
- 4) Automotive industry connection bars, valves, spring valves, swing arms, ...
- 5) **Maritime industry** surface ship hull, submarines, yachts and cruise ships, deck cooling systems, propeller, fire pumps, water jet propulsion system, ...
- 6) Fashion accessories- glasses, jewelry, watches, stationery, ...
- 7) **Petroleum industry** pipeline systems, coatings, springs, valves, ...

- 8) **Medicine** joint replacements, heart valves, pace-makers, dental implants, connecting wires, surgical equipment, wheelchairs, ...
- 9) Architecture- window frames, roofing, cornices and gables, fans, railings, ...
- 10) **Sport** golf clubs, frames and wheel bearings, horseshoes, tennis rackets, skis, ...
- 11) **Other** memory alloys, pollution control systems, hand equipment, military armored vehicles, hunting knives, ...

Nominal composition	General description and typical use
(trade marks)	General description and typical use
СР Ті	For anticorrosive protection in chemical and maritime industries.
Medium- and high-strength titanium alloys	
Ti-2.5Cu (Timetal® 230)	Binary age hardening alloy, ease of formability and weldability of commercially pure titanium with improved mechanical properties up to 350°C.
Ti-6Al-2Fe-0.1Si Timetal®62S	Properties and processing characteristics equivalent to or better than Timetal® 6-4, but with significantly higher Young's modulus. Due to the use of iron as the beta stabilizer, the alloy has lower formulation costs than Timetal® 6-4. The combination of reasonable cost and excellent mechanical properties makes it a practical substitute for many engineering materials.
Ti-6Al-7Nb (Timetal®367)	Medium strength titanium alloy dedicated for surgical implants.
Ti-3Al-2.5V (Timetal®3-2.5)	Cold formable and weldable, this alloy is used primarily for honeycomb-foil and hydraulic-tubing applications. Industrial applications such as pressure vessels and piping also use this alloy. Available with Pd stabilization to enhance corrosion resistance.
Ti-6Al-4V (UNS R56400, AECMA Ti-P63, Timetal®6-4, 6-4)	This titanium alloy is a versatile medium-strength titanium alloy that exhibits good tensile properties at room temperature, creep resistance up to 325°C, and an excellent fatigue strength. It is often used in less critical applications up to 400°C. It is the alloy most commonly used in wrought and cast forms. Turbines discs and blades, parts of airframe structures. Imlants, prosthesis.
Ti-6Al-6V-2Sn-0.5Fe-0.5Cu (UNS T56620, Timetal®6-6-2)	Improved strength properties up to do 315°C and greater depth hardenability compared with Timetal® 6-4. Airframe structures.
Ti-4Al-4Mo-2Sn-0.5Si Timetal®550	Readily forgeable and generally used in a heat-treated condition. It has superior room and elevated-temperature tensile strength and fatigue strength compared to Timetal [®] 6-4 and is creep resistant up to 400°C.
Ti-4Al-4Mo-4Sn-0.5Si Timetal®551	High strength and creep resistant up to 400°C. It has a composition similar to that of Timetal® 550, apart from an increase in tin content, which gives increased strength at room and elevated temperatures.
Ti-10V-2Fe-3Al (Timetal®10-2-3)	Readily forgeable alloy that offers excellent combinations of strength, ductility, fracture toughness and high cycle fatigue strength. Typically used for critical aircraft structures, such as landing gear, using only up to 315°C.
Ti-15V-3Al-3Cr-3Sn (15-3-3-3, Timetal®15-3)	Cold formable and weldable, this strip alloy is primarily used for aircraft ducting, pressure vessels, clips, brackets, nut-plates, springs, fire extinguisher bottles and other fabricated sheet metal structures up to 300°C.
Ti-15Mo-3Al-2.7Nb-0.2Si Timetal®21S	Good cold formability and weldability of a beta strip alloy, but withgreatly improved oxidation resistance up to 650°C and creep strength. Immune to attack by hydraulic fluids at elevated temperatures (commercial aircrafts),

Table 3.9 Selected Ti alloys and their use in aviation and other industries

	applications in commercial aircraft include engine exhaust plug and nozzle assemblies.	
Ti-8Al-1Mo-1V (UNS R54810, 8-1-1)	Designed for creep resistance up to 450°C, used primarily in engine applications such as forged compressor blades and disks. This alloy has a relatively high tensile-modulus-to-density ratio compared to most commercial titanium alloys. Low density, good weldability.	
High Temperature titanium alloys		
Ti-11Sn-5Zr-2.2Al-1Mo-0.2Si Timetal®679	Excellent tensile strength and creep resistance up to 450°C.	
Ti-6Al-5Zr-0.5Mo-0.25Si Timetal®685	Excellent tensile strength and creep resistance up to 520°C. Weldable and good forging characteristics.	
Ti-8Al-1Mo-1V Timetal®8-1-1	Designed for creep resistance up to 450°C, used primarily in engine applications such as forged compressor blades and disks. Relatively high tensile-modulus-to- density ratio compared to most commercial titanium alloys.	
Timetal®829	Combines creep resistance up to 540°C with good oxidation resistance. Weldable and, like Timetal® 685, good forgeable.	
Timetal®834	Near-alpha-titanium alloy offering increased tensile strength and creep resistance up to 600°C together with improved fatigue strength when compared with established creep-resistant alloys such as Timetal [®] 6-2-4-2, Timetal [®] 829, and Timetal [®] 685. Like these alloys, weldable and good forgeable.	
Timetal®1100	Near-alpha, high-temperature, creep-resistant alloy developed for elevated- temperature use in the range of 600°C that offers the highest combination of strength, creep resistance, fracture toughness, and fatigue-crack-growth resistance.	
Ti-5Al-2Sn-2Zr-4Mo-4Cr (Ti-17, Timetal®17)	High-strength, deep hardenable forging alloy primarily for jet engines. Allows heat treatment to a variety of strength levels in sections up to 15 cm. Offers good ductility and toughness, as well as good low-cycle and high-cycle fatigue properties.	
Ti-6Al-2Sn-4Zr-2Mo (Ti-6242,UNS 54620)	High-strength, ductility, excellent creep resistance up to 540°C. Used for gas turbines, aircraft structures.	
Ti-6Al-2Sn-4Zr-6Mo Timetal® 6-2-4-6	Stronger derivative of Timetal [®] 6-2-4-2 offering higher strength, depth hardenability, and elevated-temperature properties up to 450°C.	
Beta alloys		
Timetal [®] LCB	Metastable beta alloy produced in bar or rod form and targeted at titanium spring and other high-strength-requirement applications.low-cost automotive suspension spring applications.	
Ti-3Al-8V-6Cr-4Zr-4Mo (Beta C)	Equiaxed beta grain structure with fine alpha precipitates within matrix. Good ductility, high strength. Applications: Fasteners, springs, torsion bars, foil, tubulars and casings in oil, gas and geothermal wells.	
Ti-5Al-1Sn-1Zr-1V-0.8Mo Timetal®5111, ASTM Grade 32	Near alpha titanium alloy of intermediate strength, designed for high toughness, good weldability, stress-corrosion cracking resistance, and room temperature creep resistance; ideally suited for applications in marine environments where toughness and corrosion resistance are essential (it has been selected as the material of choice for a submarine application). Forging and machining characteristics of TIMETAL 5111 are very similar to TIMETAL®6-4.	



Ti as an aircraft material

High specific strength, good resistance to fatigue and creep and good fracture strength are characteristics that make titanium the preferred metal in preparing materials for *aviation*. Titanium was first produced and used in 1952 for engine gondolas and transport aircraft firewalls in Douglas DC-7. Today, many construction parts of many aircraft are made from titanium alloys. Titanium is the most important material for example in Boeing 757, supersonic SR-71 Blackbird, jet fighter aircraft F-22 and in space satellites and rockets. Titanium and its alloys are commonly used in turbine blades production for aviation engines, various casts and forged parts, shell airframe, firewalls, fan blades, forgings for high strength components of jet engines, gas turbines, rivets, screws, springs, high airframe parts, etc. When choosing titanium alloys, it should be considered for which applications they will be used, and therefore what mechanical properties it shall comply with (the performance requirements for the management structure also affects the price):

• rotating parts

Examples: jet engine blades, parts of gas turbines

Properties: high strength and metallurgic stability at high temperatures; low creep rate, possibility to predicts behavior with regards to creep strength and low-cycle fatigue

Microstructure: necessity of homogeneity and limiting of casting defects (segregation of α , inclusions, etc.).

• aviation pressure tanks

Properties: optimized high strength at lower temperatures; weldability, prediction of fracture strength at temperatures from cryogenic to slightly elevated.

Microstructure: directed microstructure and limiting casting defects. For cryogenic applications, the amounts of interstitial elements (O, N a C) has to be strictly controlled, as they decrease ductility and fracture strength (for example Ti-6Al-4V alloy ELI).

• aviation construction elements (or maritime and automotive applications)

Properties: high strength, higher resistance to thermal influences than aluminum alloys, higher corrosive resistance than brass and bronze, formability, easy preparation.



Important terms

Interstitial elements, polymorphic transition of titanium, alfa stabilizer, beta stabilizer, martensite transformation, thermal treatment of titanium alloys, cryogenic aplication.

To repete: brittle-ductile transition, polymorphic transition, principle of martensite transformation, stress induced martensite.



Questions

- 1. What is the basic classification of titanium alloys?
- 2. Can you define characteristic differences between α and β alloys?
- 3. What properties are typical for $\alpha+\beta$ alloys?
- 4. The well-known Ti alloy contains 6% Al and 4% V. Can you explain the role of these elements? What microstructure is typical for the alloy?
- 5. Explain the influence of thermal treatment on final properties of $\alpha+\beta$ alloys?
- 6. In what way the mechanical properties of TiAlV alloys can be modified?
- 7. What main differences in martensitic transformation can you define for steels and titanium alloys?
- 8. Is it possible to produce strengthening of α alloys by heat treatment?
- 9. Name the Ti alloys for aircraft applications.

- 10. What of them show the properties requiered for cryogenic applications?
- 11. What material parameter enables cryogenic using?
- 12. What mechanical properties are requested for β alloys?



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4. ALLOYS BASED ON INTERMETALLIC COMPOUNDS

Alloys that are formed by intermetallic compounds (IMC for short), exhibit very different properties, be it physical, mechanical, electromagnetic, optical or other. Therefore it is suitable to characterize this group in general i.e. in terms of their physico-metallurgical characteristics and then expand this analysis into application possibilities and only then focus on selected alloys. This long chapter is therefore divided into two parts to study, which are not equal in terms of difficulty to understand or time to study. For some terminology it is necessary to have good basics from physical metallurgy.



Time needed to study: 2 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- define intermetallic structures
- describe the differences in properties of IMC
- name the applications of use of IMC
- explain the reason of brittlenes of IMC
- explain the effect of hydrogen on the IMC properties

Lecture

4.1 Definition of IMC based alloys

IMC alloys form a separate group of metallic materials with outstanding properties used in various fields of technology, especially for high-temperature applications.

In accordance with their definition (Schulze,1967, Girgis,1983) IMC are metallic compounds which crystallographic structure is different from basic metals and their stacking is long-distance. These stacked compounds exist usually in a narrow range of concentrations around the stoichiometric ratio.

4.2 Structure of IMC

Bonds between different atoms are stronger than between atoms of the same kind, IMCs therefore form special crystallographic structures in which atoms of the same kind are organized in some preferential positions surrounded by atoms of another element.

Crystallographic structure is characterized by strength and character of the bond, which of course depends on electron configuration. The relation between type of structure and properties of atoms of basic elements however is not so simple. Phase types and structures are determined based on various criteria, which we will study in detail in the following paragraphs.

4.2.1 Zintl phases

Are formed between metals on left and right side of the periodic table and are characterized by total occupation of electron orbitals (electron octet), they are therefore studied as valence compounds with ionic bonds, typical for salts - NaTl (cubic B32), MgSi₂ (cubic C1). However, all kinds of bond types have been observed: ionic, metallic and covalent or mixed, which is related to specific electron distribution; Zintl phases can be considered electron compounds where the energy of the electronic

band structure makes up a big part of the overall energy and the type of structure is related to the specific concentration of valence electrons.

4.2.2 Hume-Rothery phase

These include the most well-known electron compounds: cubic B2 structure (type β -brass, FeAl, NiAl, CoAl), complex A13 (Zn₃Co, Cu₅Si), HTU A3 (type Mg) with electron concentration 3/2 (Cu₃Ga, Ag₃Al), or 7/4 (CuZn₃, Ag₅Al₃), complex cubic structure D82 (type γ brass) with electron concentration 21/13 (Cu₅Zn₈, Fe₅Zn₂).

The bonds in these intermetallics are not purely metallic, for example in NiAl, the covalent bond with slight metallic character has been observed without ionic part. Hume-Rothery rules describe only simple cases of bonds.

4.2.3 Frank-Kasper phase

They are characteristic for their size factor and arrangement of basic components, i.e. topologically close-packed arrangement:

- A15 structure
- Laves phases with AB₂ stoichiometrics the most populated group with these possible structure types: hexagonal C14 (MgZn₂), cubic C15 (MgCu₂), hexagonal C36 (MgNi₂)

They exhibit high symmetry, high coordination number and high density. Their formation is influenced by electron concentration. They have metallic bond.

4.2.4 Kurnakov phases

These are formed during phase transitions from solid solution of the constitution element at high temperature (but under melting point), their formation decreases crystal symmetry. In the simplest cases, the phase change is caused by the reaction of lattice stacking of the solid solution, where a superlattice is formed: Fe₃Al (D0₃), Ni₃Fe (L1₂), CuAu (L1₀) Cu₃Au (L1₂). The arrangement of atoms during superlattice formation is a result of a stronger bond between atoms of different elements in comparison with atoms of the same elements (interaction bonding energy, arrangement energy).

To predicts the stability of these phases, it is not sufficient to know this interaction energy or concentration of valence electrons depending on the constitution elements. Prediction of bond type and crystallographic structure has to be based on calculations of quantum mechanics (ab inition calculations) for specific phase while taking into account the electron configuration of the constitution elements.

Intermetallics do not form homogeneous group of materials, it includes various phases which differ in bonds, crystallographic structure and properties.

4.3 Structure defects of IMC

4.3.1 Point defects

In intermetallic phases, point defects are numerous, for example vacancies, interstitial, impurities, anti-positions and their combinations (Fig.4.1), their migration characteristics are not always easy to determine.

4.3.2 The structure of antiphase boundaries and domains

Antiphase boundaries and domains (APB and APD for short) are characteristic microstructure phenomena in compound arrangements, they cannot be observed within unarranged alloys. In arranged alloys, the motion of dislocations can contain APB (Fig.4.2). APBs are an effective barrier for dislocation movements.



Fig.4.1 Typical point defects in binary IMCs: a) vacancies, b) dual interstitials, c) bond of two antipositions, d) bond between three defects (two vacancies and one antiposition), e) bond between vacancies and impurities, f) free bond between wrong atoms.

If APBs close off certain area, APD is formed APD (Fig.4.3), its morphology influences mechanical properties as well. The formation of APD is to a certain point controllable by thermal processing and alloying.

Electromagnetic properties are also significantly influenced by APB and APD through the effect on the band structure.



Fig. 4.2 Dislocations in an arranged structure: a) formation of APB after the passing of one dislocation; b) formation of layer defect between two super-partial dislocations.

With IMCs, we can encounter these various situations in their structure:

- 1. formation of APB and APD during the solidification of the alloy
- 2. the transition from disarranged into arranged state (during cooling over some transition temperature)
- 3. dissociation of dislocations and formation of APBs in the shape of narrow bands connecting two or more super-partial dislocations (Fig.4.2)



Fig. 4.3 TEM images of APD in ordered structure

Terms superlattice and sublattice

The ordering of some superlattices (Fig. 4.4, 4.5 and 4.6) can be figured as if one was turning into the other by periodically introducing APB into certain crystallographic planes, as is schematically shown on Fig. 4.6 ($L1_2 \Rightarrow D0_{22} \Rightarrow D0_{23}$).



Fig.4.4 Crystallographic lattices of intermetallic phases (based on FCC and HCP): a) compound AB₃ with L1₂ structure, b) AB₃ with D0₂₂, c) AB₃ with D0₂₃, d) AB₃ with D0₁₉, e) AB with L1₀ and f) AB with L1₁.



Fig.4.5 Crystallographic lattices of intermetallic phases (based on BCC) a) compound AB with B2 structure, b) AB with B32, c) AB with B11, d) AB_2 with $C11_b$, e) AB_3 with $D0_3$ and f) A_2BC with $L2_1$.



Fig.4.6 Crystallographic lattices of intermetallic phases - transitions between various types caused by APB formation on planes {001}.

4.3.3 Superlattice dislocations

Anomalous growth of yield strength with temperature, which was mentioned in case of Ni based superalloys is related to the occurrence of phase Ni₃Al making up more than 40 vol.% (chapter 3), and this is related to the dislocation structure and yield systems activated at certain temperatures. In an arranged structure, superlattice dislocations (superdislocations) can be observed; movement of these dislocations is easier if their dissociation into superpartials occurs and stacking faults are created: SISF, CSF, SESF and APB (Fig.4.7).



Fig.4.7 A schematic of dissociation of superdislocations and formation of stacking faults (adjusted based on [3])

a) dissociation of superlattice dislocations [101] on plane{111} into four Shockley's partial dislocations and formation of APB and CSF:

$$a[\overline{1}01] \to \frac{a}{6}[\overline{1}\overline{1}2] + \frac{a}{6}[\overline{2}11] + \frac{a}{6}[\overline{2}11] + \frac{a}{6}[\overline{1}\overline{1}2]$$
(4.1)

b) dtto as a), with with other partial dislocations identical but with opposite signs 1/6 <112>, which change APB into SISF;

$$a[\overline{1}01] \to \frac{a}{6}[\overline{1}12] + \frac{a}{6}[\overline{2}11] + \frac{a}{6}[\overline{1}2\overline{1}] + \frac{a}{6}[\overline{1}\overline{2}1] + \frac{a}{6}[\overline{1}\overline{2}1] + \frac{a}{6}[\overline{1}12] + \frac{a}{6}[\overline{2}11] \quad (4.2)$$

c) dissociation of superlattice dislocations $[\overline{1}01]$ on plane $\{111\}$ into superpartial dislocations $1/2[\overline{1}01]$ and formation of APB;

$$a[\overline{101}] \rightarrow \frac{a}{2}[\overline{101}] + \frac{a}{2}[\overline{101}]$$

$$a[\overline{101}] \rightarrow \frac{a}{3}[\overline{211}] + \frac{a}{3}[\overline{112}]$$

$$(4.3)$$

$$(4.4)$$

d) dislocation $[\overline{1}01]$ dissociated on plane {111} into two superpartial dislocations 1/3 <112> and formation of SISF;

e) dislocation $[\overline{2}11]$ dissociated into 4 superpartial dislocations 1/3<112>, while forming SISF a SESF on two adjacent planes.

$$a[\overline{2}11] \to \frac{a}{3}[\overline{1}2\overline{1}] + \frac{a}{3}[\overline{1}12] + \frac{a}{3}[\overline{2}11] + \frac{a}{3}[\overline{2}11]$$
(4.5)

f) dislocation of superlattice $[\overline{1}01]$ on plane $\{010\}$ into superpartial dislocations $1/2[\overline{1}01]$ and formation of APB

$$a[\overline{1}01] \to \frac{a}{2}[\overline{1}01] + \frac{a}{2}[\overline{1}01]$$
 (4.6)

In intermetallic phases, other structural phenomena occur, which add to its plastic deformation and which will not be analyzed further here (for possible self-study):

- twinning
- dislocation pinning
- dislocation loops

4.4 Structure of grain boundaries and brittleness of IMC

The structure of grain boundaries plays a very important role in many properties of an IMC based polycrystal material. The purity of initial and final material is determined by chemical composition on the grain boundaries as well as close to them. On the grain boundaries, segregation of foreign elements and inclusions occurs (such as boron, sulfur, oxygen or hydrogen).

Normal bonds between various atoms do not have to be preserved on the grain boundaries, they may be deformed or bond between similar atoms may be formed. The long range order (LRO) differs from the order on the grain boundaries. Because of this, the grain boundaries represent the weakest link of an alloy and may significantly influence mechanical properties, processes of recrystallization, electrical conductivity or corrosion resistance.

The brittleness of intermetallic polycrystal compounds at room temperature is a critical problem, which limits their processing and use; a number of intermetallics is usually easily damaged at normal temperature by streak or by a light hit of the hammer. However the brittleness in IMC is still much lower than in ceramics because the bonds between atoms in IMC are (at least partly) metallic, whereas in ceramics they are primarily covalent or ionic.

Due to the existence of strong atomic bonds and therefore arranged states and complex crystallographic structures, plastic deformation in IMC is much more difficult than in metals or regular alloys. In general, the three main reason for damaging the material in decreasing order of importance: high deformation stress relative to fracture stress, inadequate active yield systems and "weakening" of grain boundaries.

Insufficient number and/or small mobility of dislocations and/or insufficient number of yield systems is a parameter dependent not only on crystallographic symmetry, but also on other specific parameters of concrete phases, therefore in choosing the phase and chemical changes by alloying, the aim is to achieve low energy and high mobility and at least five independent deformation modes (yield systems, twinning systems), which are in accordance with von Mises' criterion necessary for overall balanced plastic deformation. In some phases of IMC it has been observed that their single crystals are formable only in some orientations. In evaluating the brittleness crystal anisotropy is a necessary factor, which many elasticity modulus calculations depend on.

"Weakening" of grain boundaries and presence of microstructural non-homogeneities leads to local concentration deformations and tension, which can be another cause of brittleness of IMC. As an example we will state Ni_3Al , which has single crystals formable in all orientations at normal temperature, but in polycrystal Ni_3Al fractures form even at negligible plastic deformation.

A theory has been agreed on, that low ductility (almost zero) is the result of premature breach of grain boundaries; their strength is lower than the strength in the crystal volume, which makes them break sooner than the interior of the crystal begins to plastically deform.

Intermetallic compounds are also sensitive to segregation of impurities on the grain boundaries. Impurities such as sulfur and oxygen have higher electronegativity and weaken the metal-metal bonds on the grain boundary, which lowers the cohesive strength and supports intercrystal damage. Sulfur causes brittleness at normal temperatures, oxygen at higher temperatures. A very specific factor that influences grain boundaries is hydrogen, which is discussed in chapter 4.8.1. It has been proved however that polycrystal stoichiometric and unalloyed alloy Ni₃Al exhibits intercrystal damage even if it is prepared from metals of high purity. The phenomenon of "weakening" of grain boundaries is therefore related to the damage of lattice structure in the areas of grain boundaries. A role is also played by the grain boundary energies, i.e. if and how much ratio do low-angle and high-angle boundaries take.

It has to be noted that despite even significant progress in observing technology, the atomic streture of grain boundaries is in reality not well experimentally explored so as to offer a satisfying explanation of their role in IMC brittleness. Only a small number of boundaries has been observed this far using high resolution electron microscopy (HREM), which is thus far the only, if limited by its internal technology, tool to study such small objects.

4.5 Criteria in selecting specific IMC phases

The development of material based on certain intermetallic is performed with regards to its specific use, i.e. the intermetallic phase has to fulfill certain properties (mechanical, magnetic, functional, physical,...):

- sufficiently high melting temperature (the limiting temperature for construction applications is $0.75 T_M$ in traditional materials, in the most progressive high-temperature superalloys, the working temperature is approximately 1100° C)
- suitable density (suitable specific strength ratio of strength and density)
- resistance to corrosion alloying (Cr, Al, Si) and micro-alloying (Ti, Zr, Hf) compactness and resistance of the protective coatings formed
- unsuitable property brittleness

4.6 **Processing of IMC**

To prepare an alloy based on an intermetallic compound, the following preparation methods are available: net shape casting, ingot casting, vacuum melting and controlled solidification, directional solidification, single crystals growth, rapid solidification, thermal spraying, CVD, PVD, electro-depisition, epitax growth, interdiffusion, mechanical alloying, powder metallurgy methods (reaction sintering, HIP) and others.

4.7 Application fields of IMC alloys

The following overview of alloys based on IMC compounds is only brief, it should give an idea of the number and variability of IMCs in strucutral, magnetic, semiconductor and other alloys.

4.7.1 Structural applications

- Aluminides based on Ni₃Al, NiAl, Ti₃Al, TiAl, FeAl, Fe₃Al, Co₃Al
- Silicides based on MoSi₂, V₃Si, Fe₃Si, Ni₃Si
- Composites with matrix based on intermetallic alloys

4.7.2 Electromagnetic applications

Magnets

Soft magnets – high permeability

Based on transition elements Fe, Co, Ni in combination with Al, Si:

- 78-Permalloy with 78 wt.% Ni composition close to FeNi₃ (L1₂)
- Isoperm FeNi, its anisotropy is used in rolling
- Alfenol -Fe₃Al structure DO₃, 12-16 wt.% Al
- Sendust Fe₃(Al,Si)- 5 wt.% Al, 10 wt.% Si, 85 wt.% Fe ; Fe₃Al and Fe₃Si have identical structure
- Permendur FeCo structure B2, magnetic nuclei
- Borides based on $Co_{20}Al_3B_6$ structure D84, very high hardness >1000 HV

Hard magnets - high performance

Based on Fe, Co, Ni or Mn in combination with other elements:

- Cunife- 60 wt.% Cu, 20 wt.% Ni, 20 wt.% Fe
- Cunico 60 wt.% Cu, 20 wt.% Ni, 20 wt.% Co
- Alnico Fe, Al, Ni + Co, Cu, Ti, Nb
- Vicalloy 37 wt.% Fe, 53 wt.% Co, 9.4 wt.% V, 0.6 wt.% Si
- FePt
- Silmanal composition 86.6 wt.% Ag-8.8 wt.% Mn-4.4 wt.% Al
- MnAl
- MnAlGe
- Bismanol MnBi
- CoZrB- 76 at.% Co, 18 at.% Zr, 3 at.% B

Based on transition metal -lanthanide (rare earth element):

- Two-component Cu₇Tb, Co₅Sm
- Multi-component with metalloids Fe₁₄Nd₂B, Fe₁₄Nd₂C, Fe₁₇Sm₂N_x, Co₃GdB₂

Semiconductors

- alloys based on CdTe, GaAs for photovoltaic applications

Superconductors

- alloys based on Nb₃Sn, Ti₃Sb, V₃Si, ...

Optical applications

- GaAs, HgCdTe, LiTaO₃,...

Magneto-optical applications

- based on Fe-Ni, Fe-Co, GaMnN

Thermoelectric and electric applications

- based on Pb-Te, Si-Ge, Bi-Te,...

4.7.3 Applications in chemistry and metallurgy

Hydrides and their applications

- based on Mg₂Ni, Ti₂Ni, LaNi₅ and others for charging batteries and materials for hydrogen storage

High-temperature coatings for gas turbines

- alloys based on intermetallic compounds which are applied onto substrates by various technologies (plasma spraying, CVD methods, PVD methods and others)

Metallurgy processing of metals, pre-alloys and coatings

- in pyrometallurgy of metals or in metal refinement, such as in the case of Ag, Au, Pb, Bi, Pt
- in hydrometallurgy of metals
- metal plating (Pb, Sn, Al, Zn, Al-Zn, Ni-Cd, amalgams, Au, Ni-Zn, IMC, ...)

4.7.4 Other specific applications

- 1. Shape memory alloys Ti-Ni, Ti-Nb, Cu-Al-Zn, Cu-Al-Ni, and others
- 2. Goldsmithing Au-Cu, Au-Ag, Ag-Cu, Au-Al, Au-Ni,...
- 3. Dental alloys based on Ag-Hg-Cu-Sn, Ni-Co-Cr-Mo, and others.
- 4. Diffusion barriers based on Al-Ni, Ta-Si-N
- 5. Heat accumulation Cu-Mg-Zn, Al-Cu-Si, Cu-P-Si, Ni-Si



Important terms

Brittleness, superlattice, aluminides, phase stability, structure ordering.

Questions

- 1. What is the basic classification of intermetallic phases?
- 2. Can you define the characteristic differences between the various type of intermetallic phases?
- 3. What type of superlattices do you know?
- 4. What is the cause of embrittlement of intermetallic phases?
- 5. Can you explain the term of antiphase boundary and with what it is related its formation?
- 6. What intermetallic alloys fall into the materials designated for structural applications?
- 7. What intermetallic phases serve as electro-magnetic materials?
- 8. Can you name the selection criteria for particular applications of intermetallic phases?
4.8 Selected alloys



Learning objectives:

After careful study of this chapter you should be able to do the following:

- · define basic properties of particular intermetallic phases or alloys
- describe the causes of brittleness of intermetallics
- explain the principle of anomalous temperature dependence of yield strength of L1₂ structure
- name intermetallic compounds based alloys for particular application



4.8.1 Aluminides for structural applications

Aluminides of transition metals contain sufficiently high amounts of Al (10-30 wt.%), to allow for a continuous oxide layer of Al_2O_3 to form on the surface if the alloy is exposed to air or oxygen. This amount of Al is much higher than in traditional alloys and superalloys. A layer of Al_2O_3 is the cause of its outstanding resistance to oxidation and carburizing in higher temperatures (1000°C or higher) and therefore, contrary to classic steels and Ni-superalloys, presence of Cr is not necessary for protection against oxidation and corrosion. Moreover, Al_2O_3 is more stable at high temperatures than Cr_2O_3 . Aluminides have much simples chemical composition than superalloys, they form crystallic structures with long-range ordering (superlattices), they have lower density, higher melting temperature than superalloys and interesting properties, such as in some IMCs, the yield strength increases with temperature, which makes these alloys an ideal material for high-temperature use, other have outstanding specific strength and resistance against sulfurization, high electrical resistance.

Ni₃Al

Ordered phase Ni_3Al is the basic component of superalloys. Superalloys have been, through the last forty years the basic high-temperature construction material, but continual development of parts and engines in aviation and space industry moved the working temperatures of modern turbo engines up to temperatures very close to melting temperature of these alloys. Further development in aviation industry now requires materials, that can be used in temperatures higher than superalloys can manage.

Basic physical properties

of the binary stoichiometric Ni ₃ Al :	
Density:	$7.5 \cdot 10^3 \text{ kg} \cdot \text{m}^{-3}$
Melting temperature:	cca 1362°C (in peritectic transformation on Fig. 4.8)
Type of crystal structure:	L1 ₂ (ordered FCC)

For certain stoichiometric conditions, these alloys are resistant to oxidation because a cohesive protective oxide coating forms on their surface, the Ni₃Al remained arranged in long-range composition and exhibits considerable solubility of additives, the strength of Ni₃Al is comparable to classic superalloys, but their density is 10% lower.

Mechanical properties

Yield strength is low for polycrystalline and stoichiometric Ni₃Al and moves from 50 MPa (at -204°C) up to 70-80 MPa (at 25°C). A very attractive characteristic of the material is anomalous increase of yield strength with temperature up to a critical level T_P (600 to 800°C for polycrystal and single crystal Ni₃Al) (Fig.4.9). The micromechanism of this anomaly was and still is a subject of many studies. The most successful explanation so far of the anomalous temperature dependence of yield strength in Ni₃Al is given by theory based on a combination of primary octahedral, cubic cross and primary cubic slip with increasing temperature (Fig.4.10). The deviation from stoichiometry as well as all substitution elements - with the exception of Cr - raise the yield strength (Fig.4.11). But in some cases, the influence of additives lowers the critical temperature T_P .

The influence of grain size on the yield strength maximum temperature has also been studied. Some authors state that for range of 4-275 μ m, or possibly 12-70 μ m the maximum temperature is not influenced by grain size. Weihs found out that for grain size of 2.9 μ m the anomalous dependence of yield strength can be completely suppressed in relation to the sliding at grain boundaries and preffered occurrence of the slip on the {010} cubic plane.

Polycrystalline unalloyed and stoichiometric Ni₃Al alloys do not achieve very high *ultimate tensile stress* at room temperature, which is related to later discussed brittleness; on the contrary, as Stoloff states, they only achieve values of 200 MPa, higher values are achieved only through alloying by ternary elements or suitable preparation method (directional solidification). Polycrystalline unalloyed and stoichiometric alloy exhibits brittle intercrystalline cracking at approx. 2 % elongation.



Fig.4.8 Binary diagram of Ni-Al system according to Okamoto, 1993.



Fig.4.9 Anomalous temperature dependence of yield strength for various deviations from the stoichiometric composition for polycrystalline Ni₃Al: a) binary and b) alloyed.



The following factors have great influence on mechanical properties and mode of deformation damage in Ni₃Al based alloys:

- 1) changes in chemical composition: the deviation from stoichiometric towards higher or lower amount of aluminum,
- 2) state of microstructure:
 - polycrystal or single crystal state, orientation of grain growth and grain size,
 - single phase state or presence of another phase (β or γ),
 - presence of microporosity or casting defects,

- possibly other characteristics (subgrains, low-angle boundaries, APD)
- 3) presence of alloying elements (B, Cr, Ti, Zr, Mo, Be, Fe, Hf ...), which improve ductility or machinability of the alloy,
- 4) type of mechanical loading: alloy exhibits at elevated temperatures different strength in tension and compression,
- 5) strain rate (Table 4.1),
- 6) temperature and environment during the mechanical loading (Table 4.1).

An increase in strength of Ni_3Al based alloys has been proven with the change of aluminum content at room temperature, i.e. a steeper increase of hardness with rising amount of aluminum. However, at 800°C the non-stoichiometric alloys exhibited lower hardness than stoichiometric Ni_3Al . A similar influence has been observed on yield strength values, where strengthening was much more prominent at room temperature with the increasing content of aluminum than for lower content of aluminum (Fig.4.11). A suitable explanation is strengthening by substitution atoms.

An obstacle for a wide application of this intermetallic phase, however, is its <u>brittleness</u> in polycrystalline single phase state. A notable progress has been achieved when Aoki and Izumi found through experimentation that addition of a very small amount of boron to Ni₃Al (in orders of ppm) dramatically influences its ductility at room temperature in polycrystal state, from 2% up to 50%. Further research focused on ductility of Ni₃Al alloyed by boron has led to a knowledge that the content of aluminum has to be slightly below 25 at.%, which means it is a hypostoichiometric composition $Ni_{3+x}Al_{1-x}$.

Subsequently, two theories have been put forward, explaining the brittleness of Ni₃Al:

- one sees brittleness of an intermetallic as an intrinsic property of grain boundaries, where high ordering inside the crystal volume and low ordering of the grain boundaries are exhibiting;
- the other, based on empirical data, attributes this unwanted property to negative effect of environment, i.e. embrittleness due to effects of hydrogen orginated from the environmental humidity.

Both these theories also explain the positive effect of boron on ductility of this intermetallic phase. According to latest findings, it is highly likely that these two factors co-operate.

The second theory is supported by experimental results, because it has been found that polycrystal stoichiometric Ni₃Al reaches relatively high ductility values in oxygen (48-51%), which significantly decreases to 11-13% in air and 6-9% in water. Decrease in ductility was also found in boron-alloyed Ni₃Al alloys, that were submitted to gaseous hydrogen or cathodically charged by hydrogen, as show results in Table 4.1 and on Fig.4.12.

Table 4.1 Effect of boron on Ni₃Al becoming brittle (with 24 at.%) due to the environment, experimented on air at room temperature

Alloys	Strain rate (x 10 ⁻³ s ⁻¹)	Testing environment	Elongation (%)	Yield strength (MPa)	UTS (MPa)
IC-2: Ni-24 a	it.% Al				
	3.3	oxygen	7.2	279	439
	3.3	air	2.6	280	333
IC-19: Ni-24	at.% Al +100 wt. % B				
	3.3	oxygen	39.5	216	1310
	3.3	air	18.2	215	699
	3.3	water	12.6	208	518
IC-15: Ni-24	at.% Al +500 wt. % B				
	3.3	oxygen	39.4	289	1320
	3.3	air	41.2	290	1260
	0.033	air	39.4	270	1220
	0.033	water	38.7	288	1200



Fig. 4.12 Effect of hydrogen pressure on ductility at room temperature for Ni₃Al with and without boron

Liu was the first to point out that reactions between the humidity of common environment and aluminum component of Ni_3Al releases atomic hydrogen according to this equation:

$$2Al + 3H_2O_{(ads)} = Al_2O_3 + 6H_{(ads)}$$
(4.7)

The result of a reaction between steam and the reacting element on the edge of the rupture is formation of atomic hydrogen, which subsequently diffuses on the surface inside the alloy and is the cause of brittleness. Despite the fact that the plasticizing effect was also observed for additions of Zr, Hf and Re, alloying by boron remains the most effective.

High strength of the alloy, as was mentioned above, is ensured by alloying with boron up to 500wght.ppm (with hypostoichiometric composition, i.e. up to 24 at.% of Al

The development in construction shapes and production technologies has lead to preparation of Ni_3Al based alloys that are formable, have high strength are can be well cast and welded. These briefly enumerated characteristics however have to entail the comprise:

- resistance to oxidation and carburizing by the environment at temperatures up to 1100°C; high strength and at the same time an outstanding resistance to oxidation at medium working temperatures (from 700 to 900°C), where many alloys suffer a decrease in ductility, is ensured by substituting part of the aluminum content by chromium, which supports the formation of a protective oxide coating that forms at sufficient rate in these high temperatures.
- high yield strength from 650 to 1100°C in tension and pressure in comparison with superalloys
- higher resistance to material fatigue than in superalloys resulting from the absence of secondary phases (carbides)
- high strength in creep which depends on grain size (requirement of coarse-grain structure)
- outstanding attrition resistance at high temperatures (over 600°C) increases with temperature
- outstanding resistance to corrosion, ensure by protective oxide coating, which forms on the alloy surface.

Some selected characteristics of Ni_3Al based alloys of composition given in Table 4.2 are presented in Table 4.3 and a comparison with superalloys in Table 4.3 is given on Fig.4.13 through 4.16.

In terms of technical applications of Ni_3Al based alloy products, the Oak Ridge National Laboratory (ORNL), (Tennessee, USA) has procured a right to issue license. In Table 4.2, composition of IC-50 alloy is given, which was developed in these laboratories and is used commercially, as well as other alloys, which have modified composition based on partial substitution

of aluminum by chrome in order to increase strength at medium temperatures (600°C to 800°C). From these alloys that also contain some amount of zirconium, the most formable alloy in heat is IC-218LZr, despite exhibiting slightly lower strength than IC-218 and IC-221. Another alloy, IC-357, which is also formable at temperature and contains 11 wt.% of Fe apart from Cr and Al doesn't exhibit lower high-temperature strength, because the addition of Fe leads to an increase in β -phase fraction in the alloy. Due to the presence of this phase, the alloy is poor cold formable that the alloys without Fe are. Alloy IC-396 is a high-temperature alloy for castings containing 3 wt.% of Mo in addition to Al and Cr.

	Content of elements (wt.%)							
alloy	Al	Cr	Fe	Zr	Мо	В	Ni	
IC-50	11.30	-	-	0.60	-	0.02	Bal.	
IC-218	8.50	7.80	-	0.80	-	0.02	Bal.	
IC-218LZr	8.70	8.10	-	0.20	-	0.02	Bal.	
IC-221	8.50	7.80	-	1.70	-	0.02	Bal.	
IC-357	9.54	6.95	11.20	0.35	1.28	0.02	Bal.	
IC- 369LZr	7.98	7.72	-	0.20	3.02	0.005	Bal.	
IC-396	7.98	7.72	-	0.85	3.02	0.005	Bal.	
IC-221M	8.00	7.70	-	1.70	1.43	0.008	Bal.	
IC-221W	8.00	7.70	-	1.50	3.0	0.003	Bal.	
IC-438	8.10	5.23	-	0.13	7.02	0.005	Bal.	

Table 4.2 Chemical composition of Ni₃Al based alloys suitable for commercial use

Table 4.3	General	properties	and	characteristics	of s	elected	Ni ₃ Al	based	alloys
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	Alloy							
Characteristics	IC-50	IC-396LZr	IC-396	IC-221M	IC-438			
Density (g/cm ³)	7.60	7.88	7.87	7.86	7.87			
Melting temperature (°C)	1395	-	-	1171* to 1353	1350			
Phases	o lot	a la l	or lost	γ/γ′ Ni₃Zr₅	o los			
	Ϋ́́ΥΫ́	γ <i>γγ</i>	Ύ/Ύ	eutectic	ŶŹŶ			
Air melting	yes	yes	yes	yes	yes			
Hot working of cast ingots	no	yes	no	no	no			
Cold working of cast bars and sheets	yes	yes	yes	yes	yes			
Casting	yes	yes	yes	yes	yes			
Powder consolidation by extrusion	yes	yes	yes	yes	yes			
Welding	no	no	no	yes	no			
Operating experience	low	none	some	most	new			
Property data	low	medium	low	most	low			
Availability	low	none	low	most	low			
Machinability								
Electric discharge machining	yes	yes	yes	yes	yes			
Grinding	yes	yes	yes	yes	yes			
Surface machining	poor	poor	poor	poor	poor			
Corrosion data	limited	none	limited	limited	limited			
Carburizing data	some	none	some	some	some			

Note.:*eutectic temperature

Ni₃Al based alloys can be prepared by various technological processes, such as classic ingot metallurgy, arc melting or drop casting, centrifugal casting, classic powder metallurgy, explosive compaction, reactive slintering, spray atomization and deposition, directed crystallization. The best production method is according to ORNL experience vacuum induction melting with subsequent

electro-slag remelting (similar to superalloys), where better fatigue properties and hot formability are ensured in these alloys. An EXO-Melt process has been patented, Fig.4.17 offers a schematic.

	Content of elements (wt.%)								
alloy	Al	Cr	Fe	Ti	С	Si; Y	Ni		
HU	-	18.0	42.45	-	0.55	-	39.0		
Haynes 214	4.5	16.0	3.0	-	0.03	0.1; 0.02	76.35		
Alloy 800	0.4	21.0	45.5	0.4	0.05	-	32.5		

Table 4.4 Composition of selected Ni based alloys given in Fig.4.13 through 4.15



Fig.4.13 Comparison of tensile mechanical properties of alloys (from Table 4.2 and 4.4):a) yield strength, b) ultimate tensile stress (UTS)c) total elongation



Fig.4.14 Comparison of tensile mechanical properties of alloys (from Table 4.2 and 4.4) a) yield strength, b) UTS, c) total elongation



Fig.4.15 Comparison of creep behavior for selected IMC based alloys and superalloys (Composition in Table 4.2 and 4.4).



Fig.4.16 Comparison of resistance against a) oxidation and b) carbonization in selected alloys (composition in Table 4.2 and 4.4).

The best hot working by forging is achieved at 1100 to 1200°C with lowered amounts of Zr. Hot forming by extrusion is performed on alloys enclosed in a 3mm depth capsule of carbonized steel at temperatures from 1100 to 1200°C. With finer microstructure (grains less than 10 μ m), superplasticity appears in alloys, that enables turbine disks production by hot working (1100°C, strain rate of 8.3x10⁻³ s⁻¹).

Cold forming is performed including annealing at 1050-1100°C. However for example IC-50 alloy can be cold rolled even without annealing up to 60%. From the IC-396M alloy castings, wires of 2 mm in diameters can be produced with intermediate annealing at 1100°C.

Use

Ni₃Al - based alloys are currently used primarily as:

- heaters (exothermic reaction during Ni₃Al creation)
- components of furnaces for thermal processing of automotive parts (resistance to carburizing atmosphere)
- rollers in annealing furnaces for steel sheets
- forms for die casting and ingot molds (preparation of metallic glass)
- parts of diesel engines (cylinders and valves, turbo compressors)
- special parts for aviation industry (turbine blades for jet engines)
- matrices for hot pressing of permanent magnetic alloys
- Ni₃Al as a matrix for composites with boride, carbide, oxide or carbon particles or fibers (cutting tools)

Currently, five companies have license to produce Ni₃Al based alloys:

- 1) Armco, Inc., Middletown, Ohio
- 2) Hoskins Manufacturing Company, Hamburg, Michigan
- 3) Metallamics, Inc., Traverse City, Michigan
- 4) Cummins Engine Company, Columbus, Indiana
- 5) Valley-Todeco, Inc., Sylmar, California

In comparison with many superalloys, Ni₃Al based alloys exhibit much better mechanical properties such as yield strength and formability, especially at high temperatures. Resistance to material fatigue is also higher at temperatures up to 500°C than in Ni-superalloys as well as creep resistance, which is comparable to most superalloys, but is lower than single crystal Ni-superalloy which is used for turbine blades of jet engines. With its properties, the Ni₃Al based alloys are close to superalloys and expand their spectrum. They can not compete (yet) with superalloys developed for aircraft and space applications. Here, the Ni₃Al based alloys are used only in some application. However this progressive type of material offers promising future with less demanding applications, such as gas, water or jet turbines, switches in aircraft, automotive parts, permanent moulds, i.e. where a combination of strength and good fatigue, wear (erosion and cavitation) and oxidation resistance is required.





💥 NiAl

This compounds represent the most well known example of intermetallic compounds with B2 structure, which is shown on Fig.4.18.

Physical properties

Melting temperature	1638°C (congruent for 50:50 stoichiometric composition)					
Type of crystal structure	B2 (modification of BCC lattice)					
Density	$5.85 \cdot 10^3$ kg·m ⁻³ (stoichiometric)					
	from $5.35 \cdot 10^3$ kg·m ⁻³ (with excess of Al)					
	to $6.5 \cdot 10^3$ kg·m ⁻³ (with excess of Ni)					
Thermal conductivity	76 W/m.K (at standard temperature)					
Type of bond	mixed-metallic b. with contribution of covalent and ionic b.					
Modulus of elasticity	235 GPa (room temperature, stoichiometry)					
	max. value achieved for 48 at.% Al (related to the character of lattice					
	defects at this deviation from stoichiometry)					

High oxidation resistance Relatively wide range of homogeneous existence of β-NiAl phase (Fig.4.7)

- The melting temperature is much higher than of its constitution components, which confirms the strong bond between Ni and Al and thus also its phase stability.
- The existence of string Ni *d* Al *p* hydridation along the <111> direction between neighboring pairs of Ni-Al gives rise to a strong covalent bond along this direction and weak ionic repelling between two closest neighbors atoms along the <100> direction. These directional bonds are superimposed by metallic bond. This type of bond is considered the reason for anisotropy of mechanical properties.



Fig.4.18 Crystal structure B2 of NiAl with observed slip vectors a<100>, a<110> and a<111> on the (011) plane.

Martensitic transformation

After cooling NiAl with surplus Ni, martensitic transformation occurs with a structure of either $L1_0$ or rhombohedral cell with 7R layering based on Ramsdell labeling (Fig.4.19).

Temperature M_s increases steeply with the content of Ni and ranges from -200°C for 61.5 at.% Ni up to 900°C for 69 at.% Ni. Tension-induced martensite with acicular morphology forms in NiAl, which can contribute to an improvement of strength in cast polycrystal NiAl at and under martensite formation temperature. This phenomenon is based on the fact that the casting structure has non-homogeneous distribution of composition which leads to local formation of thermoelastic martensite in areas with higher amounts of Ni at that temperature. The alloy acts as a duplex structure formed by grains with B2 structure and martensite. The influence of tension adds to the formation of more martensite and this not only on the forefront of the break, but as was already mentioned in single crystal alloys (Fig.4.20) also in areas of tension concentration on the B2/martensite interface. Of



course this higher amount of tension-induced martensite along the already existing thermoelastic martensite is sufficient to cause slight increase of alloy strength.

Fig. 4.19 Atomic arrangement of austenite and martensite for Ni-Al: a) lattice with two possible elementary cells; b) 2D projection of close packed ordering ABC (or ACB) and rectangular symmetry of martensite lattice. Arrows indicate the corresponding shift directions vis-a-vis the basal plane (110). (According to Boulay P.et al.: *Acta Materialia*, 51, 2003, p. 1421–1436)



Fig. 4.20 Compression stress-strain curves (strain rate 10^{-4} s⁻¹) for single crystal alloy Ni61.5-Al38.5 without martensite and alloy Ni64-Al36 with transformed martensite at 0°C (floating zone melted, M_s = 160°C). (According to Sauthoff G.: Intermetallics, 8, 2000, p. 1101–1109)

It is necessary to point out, that NiAl martensite exhibits special strengthening behavior. In contrast with B2 NiAl, NiAl martensite can be strained up to 5% with low deformation tension during the process or rearranging various variants of martensite with subsequent shallow growth of strengthening, as can be observed on Fig.4.20 in Ni-Al alloy with 36%Al. However this behavior of martensite in polycrystal NiAl does not suffice to increase strength to the same level as in single

crystal NiAl alloy at temperatures under M_s . The most significant strength increase occurs in polycrystal alloy only by a formation of tension-induced martensite in sufficient amount.

Phase NiAl also fulfills the requirements for a reversible phenomenon of shape memory (as will be seen in chapter 6):

- 1. martensitic transformation is thermoelastic
- 2. initial and final phase is arranged
- 3. martensite is intrinsically twinned

Mechanical properties

Yield strength of polycrystal NiAl depending on temperature and composition is given on Fig.4.21. From its development, the *temperature* dependence is evident with high limits at low temperatures and with steep decrease at intermediate temperatures (680°C), at higher temperatures, a softening occurs, which is related to thermally activated of creep processes. Alloying of NiAl with a ternary element leads to solid solution strengthening.



Fig.4.21 Temperature dependence of yield strength in NiAl based polycrystalline alloys with grain size of 50 μ m

Fig.4.22 Temperature dependence of yield strength for various orientations of NiAl single crystal alloys with near stoichiometric composition

Depending on the availability of slip systems, *strength* and *ductility* are higly anisotropic (Fig.4.22 and 4.23): NiAl with orientation in "hard" direction <100> does not exhibit practically any ductility below brittle-to-ductile transition temperature (BDTT) (350°C) (despite that, local plastic deformations are detected); whereas NiAl with "soft" orientations <110> and <111> exhibits ductility up to 2.5% below the BDTT (200°C). This phenomenon occurs probably due to low dislocation mobilities because of extended dislocation cores. Above the BDTT, the ductility increases steeply with temperature due to the thermal activation of the process.

Fracture toughness also depends on the orientation and the temperature. Details of the fracture process are not yet accurately researched. Fracture of binary and polycrystalline NiAl is intercrystalline at room temperature, at 400-500°C it changes into transcrystalline cleavage fracture and above 600°C the fracture has a ductile character. Brittle fracture at room temperatures can be suppressed by an addition of \geq 300 mass ppm of boron. Plastic behavior strongly depends on stoichiometry and amounts of impurities and alloying elements, especially interstitial elements. Low-cycle and high-cycle fatigue behavior is similar to Ni based superalloys.



Fig.4.23 Flow stress (0.2% proof stress in compression at strain rate 10^{-4} s⁻¹) dependence on temperature for binary and ternary NiAl phases; circles – stoichiometric NiAl, squares - stoichiometric (Ni_{0.8}Fe_{0.2})Al, triangles - off-stoichiometric (Ni_{1.0}Fe_{0.2})Al_{0.8}

Alloying

Limited tensile strength was achieved by adding Co (2% ductility) and Fe (22% ductility in hot extruded state and 10% ductility in rapid solidified state).

Creep strength can be improved by precipitation strengthening with Ta, Nb and Hf (but it decreases tensile strength) or substituting nickel by 15 at.% Fe. It is also possible to positively influence it by solid solution strengthening or strengthening by dispersion phase (AlN, α -Mo fibers).

Corrosion properties

Binary NiAl forms a continuous protective layer of Al_2O_3 in wide range of temperature and concentrations in single-phase area of existence. The material was long used for coating parts that work in corrosive environments. Resistance to oxidation can be increased by alloying with Y or some other elements (Hf, Zr).

Preparation

High ductility and low yield strength of binary alloys based on NiAl at temperatures over 600°C allows for their preparation by traditional thermo-mechanical processes:

- o HIP
- Hot pressing
- o Extruding
- Hot rolling, hot forging and hot pressing
- Directional solidification and single crystals growth (for turbine blades) modification of Bridgman method, FZ-UDS and Czochralski method.

Example of an alloy composition:

Ni - (49.0 ± 0.6) Al - (1.0 ± 0.8) Mo - (0.7 ± 0.5) Nb/Ta/Zr/Hf - (0-0.5)Fe - (0.01-0.03)B/C

Melting, casting, hot extrusion (900-1050°C) – resulting strength R_m 700 MPa at room temperature and 350 MPa at 1000°C. However, the creep rate at 816°C in air is lower than for binary NiAl.

For NiAl typical contents are: 40-80 wt.ppm O and C, 1-5 wt.ppm S, P and N, 1000 wt.ppm Si, \geq 300 wt.ppm B, C.

Use

Use of NiAl based alloys as free-standing structural material is limited for two reasons:

- low resistance to damage at regular temperature
- low strength and creep resistance at higher temperatures

<mark>∭</mark> Ti₃Al

Ti₃Al compound is basically an α_2 phase in Ti-Al system, as shown on the binary diagram on Fig.4.2. **Physical properties**

Phase stability temperature	up to 1090°C (for stoichiometric composition 25 at.% Al)
Type of crystal structure	hexagonal D0 ₁₉
Density	$4.2 \cdot 10^3$ kg·m ⁻³ (stoichiometry)
	4.1 až 4.7 $\cdot 10^3$ kg·m ⁻³ (for alloys based on Ti ₃ Al)
Thermal conductivity	7 W/m·K
Modulus of elasticity	149 GPa (for 26 at.% Al)

Relatively wide area of phase existence (22-39 at.% Al) (Fig.4.2 in chapter 4). Similarly to Ni-Al system, it is still in the process of approximating reactions in terms of existence of some phases.

Mechanical properties

Specific strength and fracture behavior is more favorable than for Ni superalloys and common Ti alloys even at temperatures of 500-700°C.

Ductility at T_{room} - can be improved by adding Nb (over 10 at.%) or other β stabilizers (Mo, Ta, V), as seen in Table 4.5. In ternary system Ti-Al-Nb, its cross-section for Ti₃Al-Nb is shown on Fig. 4.24, various structure types can be formed in function of temperature and Nb content:

- two-phase $-\alpha_2 + \beta$ phases
- three-phase $-\alpha_2 + \beta + O$ phases (O beeing the distortion form of α_2 Ti₂AlNb)
- two-phase $-O + \beta$ phases



Fig.4.24 Vertical section of the Ti-Al-Nb ternary diagram with occurrence of α_2 , β and O phases in Ti₃Al-Nb microstructure depending on the amount of Nb and temperature

Use

Even though ductility at room temperature can be influenced by alloying, the fracture toughness and tolerance to impact is disadvantageous, the fracture mechanism for the α_2 structure is cleavage.

Another limitation is a strong influence of environment where the surface oxidation (even in Ti-Al-Nb based alloys) causes stress-induced cracking.

Alloy	UTS (MPa)	Y.S. (MPa)	Elongation (%)	К_{IC} (MPa.m ^{1/2})	Creep fracture ^a (h)
Ti-25Al	538	538	0.3		
Ti-24Al-11Nb	824	787	0.7		
Ti-25Al-10Nb-3V-1Mo	1042	825	2.2	13.5	44.7
Ti-24Al-14Nb-3V-0.5Mo			26.0 ^b		360

Table 4.5 Typical properties of Ti₃Al based aluminides

^a at 650°C, 38MPa; ^b special production method

🐹 🛛 TiAl

 γ phase in Ti-Al system (Fig.4.2)

Physical properties

Melting temperature	1440 °C
Type of crystal structure	$L1_0$ (fig.4.4e)
Density	$3.7-4.0 \cdot 10^3$ kg·m ⁻³ (stoichiometry)
Thermal conductivity	22 W/m·K
Modulus of elasticity	160-180 GPa (depends on temperature)

Mechanical properties

Ductility, creep strength, fracture strength strongly depends on structure type (Fig.4.25) and microstructure (Fig.4.26), i.e. on the amounts of Al and on the thermal processing (See Fig.4.27-4.29):

- structure formed by a γ phase (L1₀ structure)
- duplex structure
- lamellar structure $(\gamma + \alpha_2)$ (more resistant to creep)
- other two-phase structures supersolvus (small particles of α in γ-phase), subtransus (transformed grains with small islands of undissolved γ-phase), dual structure (γ grains and α₂ grains), Widmanstätten structure (α₂ needles in γ grains)

Creep resistance can be increased by adding Nb, Ta, W and Si.



Fig.4.25 Comparison of atomic arrangement of Ti and Al in three types of structure lattices: (a) B2 in phase β_2 -TiAl; (b) L1₀ in γ -TiAl and (c) D0₁₉ in α_2 -Ti₃Al.



Fig.4.26 Microstructures in TiAl based alloys: a) γ phase; b) duplex ; c) fully lamellar





Fig.4.27 Room-temperature tensile ductility of wrought binary TiAl depending on microstructure





Table 4.6 Values of mechanica	l properties for different	two-phase structures	of alloys based	l on TiAl	at room
temperature (v	with strain rate 2.5×10^{-5} s	s ⁻¹ , crossbeam movem	nent rate 0.01 m	m/min)	

Composition (at.%)	Microstructure	σ _{0.5} (MPa)	σ _f (MPa)	<mark>ɛ</mark> f (%)	K _Q (MPa⋅m ^{1/2})
Ti-47Al-3 7(Nb Cr Mn Si)-0 5B	dunley	408	426	1.0	13.3(n).17(n)
Ti_47Al_2 7(Nb,Cr,Mn,Si)_0.5B	near lamellar	546	640	2.1	13.5(p), 17(0) 22.7(n) 22.2 (n)
T: 47AL 2Cr 0 2C:		121	040 F1F	2.1	22.7(p), 55.5 (0)
11-47AI-2Cr-0.2SI	gama	421	515	3.0	12.8
Ti-48.5Al-2Cr-0.2C	duplex	575	664	2.4	1.4
Ti-45Al-(5-10)Nb	duplex	1090	1100	1.0	17.6(p), 25.2 (o)

 $\sigma_{0.5}$ -yield strength at 0.5% strain, σ_f - fracture strength, ϵ_f - fracture elongation,

 K_Q - fracture toughness (crack propagation in parallel(p) and orthogonally (o) to the direction of extrusion)

Corrosion resistance

Resistance to oxidation can be significantly increased by adding high temperature melting metals such as Nb, W, Mo, and Ta. Below, the maximum amounts of interstitial elements in γ phase are given; if there is α_2 phase in the structure, it can increase absorption of these elements (more Ti):

Oxygen: 500- 1000 ppm (addition of Er lowers the amount of oxygen to 300 ppm) Nitrogen: 20-50 ppm Carbon: 5-20 ppm

Example of commercial alloys composition:

Ti-48 at.% Al-1 at.%V-0.1 at.% C (V increases ductility, C improves creep resistance) Ti-48 at.% Al-2 at.% Cr-2 at.% Nb 45-52 at.% Ti- 1-3 at.% (Cr,Mn,V)-2-4 at.% (Nb,Ta,Mo,W)

Preparation:

Casting, forming, thermal processing (depending on the composition), P/M.

Use

For especially suitable material rigidity, its aircraft applications are advantageous - stators of high-pressure compressors, blades of low-pressure turbines, rotating parts of turbochargers, combustion valves. Other applications can be found in biomedicine.

Table 4.7 Comparison of selected properties for alloys Ti, Ti₃Al, TiAl and Ni-superalloys

Property	Ti-alloy	Ti₃Al	TiAl	Ni-superalloy
Structure	A3/A2	D0 ₁₉	L1 ₀	A1/L1 ₂
Density (x10 ³ kg·m ⁻³)	4.5	4.1-4.7	3.7-4.0	7.9-9.1
Young's modulus (T _{room}) (GPa)	95-115	100-149	160-180	195-220
Yield strength (T _{room}) (MPa)	380-1150	700-990	400-650	250-1310
Tensile stress (T _{room}) (MPa)	480-1200	800-1140	450-800	620-1620
Creep temperature limit (°C)	600	760	1000	1090
Oxidation temperature limit (°C)	600	650	900	1090
Elongation to fracture (T _{room}) (%)	10-25	2-10	1-4	3-5
Elongation to fracture (high T) (%)	12-50	10-20	10-60	8-12.5
Fracture toughness K _{Ic} (T _{room}) (MPa·m ^{1/2})	High	13-42	10-20	25

FeAl and Fe₃Al

In the binary diagram on Fig.4.30, the occurrence of intermetallic Fe- and Al- based phases is highlighted. We will discuss in detail only the FeAl and Fe₃Al compounds.

Physical properties

Melting temperature	continual decrease with content of Al to 1250°C for 52 at.% Al
Type of crystal structure	FeA1 - B2 (ranging from 35 to 50 at.% Al)
	Fe ₃ Al - D0 ₃ (near to Fe-25 at.% Al) up to 540° C,
	B2 at 540-760°C, over 760°C disordered structure
Density	$5.4-6.7 ext{ x10}^3 ext{ kg·m}^{-3}$

Advantages:

- high corrosion resistance (formation of Al₂O₃ layer) in oxidizing and sulfation environments
- low density relative to other structural IMC based materials
- low price thanks to saving of strategic metals



Fig.4.30 Binary Fe-Al diagram with intermetallic phases FeAl and Fe₃Al

Mechanical properties

Aluminides based on Fe in unalloyed state have unfavourable mechanical properties including:

- low ductility and fracture strength at room temperature
- low strength at temperatures over 600°C
- sensitivity to environmental embrittlement

Some unsuitable characteristics can be influenced by alloying with different additives.

Alloying:

Fe₃Al

- addition of TiB₂:
 - lowers the grain size
 - increases ductility of recrystallized material from 2% up to 5-7% as well as temperature of recrystallization from 650° up to 1100°C which allows to preserve ductility of the formed material at room temperatures even after subjecting it to temperatures of 1000°C; ductility of these materials is high over 600°C, that simplifies the hot working.
 - increases yield strength at room and elevated temperatures
- addition of Cr (2-6 at.%) modifies composition of the surface layers and lowers the possibility of reaction of Al atoms with water vapor
- addition of Mo and Nb can increase ductility at room temperature up to 15% and yield strength to 500 MPa at 600°C

The composition of Fe₃Al based alloys designed for commercial use and composition of some other commercial alloys is compared in Table 4.8. Their mechanical properties are compared on Fig.4.29 with dispersion strengthened (ODS) superalloy MA-956.



Fig.4.31 Properties of Fe₃Al based alloys and FeNi based superalloy (MA-956): a) yield strength, b) UTS and c) total elongation

Element (wt.%) Alloy	AI	Cr	В	Zr	Nb	С	Мо	Si	Y	Y ₂ O ₃	Ti	Ni	Fe
FAS	15.9	2.20	0.01										bal.
FAL	15.9	5.5	0.01	0.15									bal.
FA-129	15.9	5.5			1.0	0.05							bal.
FAH	15.9	5.5	0.04	0.15	1.04	-	1.0						bal.
Fecralloy	4.5	16.0				0.02			0.3				bal.
MA-956	-	20.0								0.5	0.5		bal.
Type310	-	25.0				0.15		0.5				20.0	bal.

Table 4.8 Composition of IMC alloys based on Fe₃Al

FeAl

- addition of B (0.05-0.2 at.%) can suppress intercrystalline cracking and slightly increase ductility (3%) only in Fe-40Al, together with addition of Nb, Mo and Zr it is possible to increase high temperature strength.

Corrosion properties

Fe-Al based alloys have better corrosion resistance at 800°C in sulfation environments than common Fe-Cr-Ni alloys (including coated ones) and Ni based ones. Aluminides with more than 30% of Al are well resistant to corrosion in an environment with melted nitrates even at 650°C.

Use

Depending on the stated properties, these alloys are used in systems for chemical separation of air, combustion systems and piston valves in cars, immersion heaters, heat exchangers, catalyst tanks and other systems for chemical and petrochemical production or coal conversion process. Thermal expansion coefficients are close to that ones of steels and allow to use them for thermal spraying of different chemical and petrochemical reaction containers assuring effective protection against high temperature oxidation, carburizing and sulfurization.

Preparation:

Similarly to Ni₃Al, it is produced by ORNL (see – The Exo-MeltTM process).

Alloy	Crystal structure	Critical ordering temperature (°C)	Melting temperature T _m (°C)	Density (g∙cm³)	Young modulus (GPa)
Ni₃Al	L1 ₂	1362	1362	7.5	179
NiAl	B2	1638	1638	5.85	239
Fe₃Al	D0 ₃	540	1540	6.72	141
	B2	760	1540		
FeAl	B2	1250	1250	5.56	261
Ti₃Al	D0 ₁₉	1090	1600	4.2	145
TiAl	L1 ₀	1440	1440	3.91	176
TiAl ₃	D0 ₂₂	1350	1350	3.4	

Table 4.9 Comparison of selected properties for stoichiometric Ni, Ti and Fe based aluminides.

4.8.2 Silicides

No other group of intermetallic compounds are as popular in variable areas as the group of silicides. This type of compounds and alloys are used as high temperature structural materials, even in hi-tech space applications, such as heaters in high temperature furnace equipment as well as protective high temperature coatings especially for high temperature melting metals. They are also formed during metal plating of contacts and connections in microelectronic devices by thin metal layers (they have lower electric resistance than polycrystalline Si and are compatible with Si substrate), such as diodes for Schottky's barriers, resistance contacts, metal plating of control electrode and connections, $CoSi_2$ and NiSi₂ prepared by epitaxial growth for transistors, Pt, Pd and Ir silicides for infrared detectors. In thermoelectric generators that change solar energy into electricity, high melting point and good oxidation resistance are exploited for semiconductor disilicides of Cr, Mn and Fe. Silicides of transition metals whereas silicides of heavier transition metals are diamagnetic, especially Zr based silicide exhibits especially high diamagnetism. Fe₃Si and Fe₅Si₃ are ferromagnetic (in Fe₃Si the Curie temperature is ~805 K). Some silicides are superconductors (V₃Si, CoSi₂, Mo₃Si, PtSi, PdSi and Th₂Si₃).

If technological application of silicides is mentioned, a metallurgist first thinks of the name "Kanthal Super", that is $MoSi_2$ based material (80% of $MoSi_2$ and 20% glass phase) for furnace heating elements. This material is so interesting because its two main characteristics:

- 1. Its resistivity increases with temperature (i.e. with increasing current in order to increase the temperature the output power as well as heating rise rapidly). Unlike SiC heating elements, its resistivity does not change with time.
- 2. It has an ability to form a highly protective cohesive layer of SiO_2 during its operation, that does not peel off and is auto-regenerative. Life of heaters based on $MoSi_2$ is therefore very long.

In the following paragraphs, you find other investigated silicides and their classification based on the strucure type including basic properties and possible applications (Table 4.10).

Silicides based on VIII. group transition metals

Ni₃Si, Fe₃Si, CoSi₂ and NiSi₂

- Ni₃Si has an L1₂ structure, therefore it exhibits, same as Ni₃Al, anomalous growth of yield strength with temperature; however is has low ductility at room temperature, bad workability, good oxidation resistance and outstanding corrosion resistance in environment of concentrated acids (this phase form a base for Hastelloy D alloys); ductility can be increased by alloying with B, but not as significantly as in Ni₃Al; the addition of Ti however (up to 11 at.%) significantly increases ductility and suppresses polymorphic change in the interval from T_m up to the temperature of change from ordered into disordered state.
- $NiSi_2$ phases with cubic C1 structure was studied only for microelectronics engineering, not from the viewpoint of mechanical properties.
- $Fe_3Si has D0_3$ structure, at T_{room} it exists in a wider range (8-27 at.% Si), due to outstanding resistance to corrosion it forms a commercial alloy Duriron (25.2 at.% Si), that resists boiling H_2SO_4

Fe₃(Si,Al) – or also alloys Fe-Al-Si – these exhibit outstanding magnetic properties (high magnetic permeability), they are used as cores of magnetic heads. Sendust, well-known alloy with composition of Fe-16.6 at.% Si-9.7 at.% Al. Alloys also have good corrosion and wear resistance, but are extremely brittle, cores are therefore prepared by cutting into plates and grinding.

Silicides based on refractory metals

These can be divided into

- disilicides, which crystallize in four types of crystal structures (Fig.4.32):

- tetragonal C11_b (MoSi₂, WSi₂) application for construction use are limited by small tolerance to low-temperature damage, but a combination of both is a promising material for high-temperature strength, or possibly as a matrix for composition materials.
- 2. hexagonal C40 (CrSi₂, VSi₂, NbSi₂, TaSi₂)
- 3. orthorhombic C54 (TiSi₂) modules E and G at room temperatures and high temperature and thermal conductivity are much higher than in MoSi₂, at temperatures of ~1300K it exhibits higher bond strength than MoSi₂.
- 4. orthorhombic C49 (ZrSi₂, HfSi₂)
- silicides with A15 structure some are superconducting with high critical temperature T_c of transition into superconducting state and find use for thermonuclear reactors, generators, energy exchange, physics of particles with high energy. For example, the V₃Si compound is brittle at all temperatures, but suitable production technologies allow for a preparation of formed composite superconductors for small coils
- silicides of type $5:3 M_5Si_3 (M = Nb, Ta, Mo, Ti, Zr)$ with either hexagonal D8₈ or tetragonal D8_m structures exhibit the higher melting temperature out of all IMCs
- multicomponent silicides, which form the following systems:
 - ✤ Fe-Cr-Si high temperature use
 - ✤ Zr-Mo-Si
 - ✤ Mo-Ni-Si
 - ♦ Mo-Si-C MoSi₂ composite material with SiC whiskers



Fig.4.32 Models of crystal structures of common silicides.

Silicide	Structure	Density (·10 ³ kg/m ³)	T _m (K)	Modul of elasticity E (GPa)	Shear modulus G (GPa)	Poisson number
Cr₃Si	A15	6.54	2043	351	137	0.286
V₃Si	A15	5.62	2198	213	81.9	0.298
MoSi ₂	C11 _b	6.2	2353	440	191	0.15
WSi ₂	C11 _b	9.86	2438	468	204	0.14
CrSi ₂	C40	5.00	1823	347	147	0.18
VSi ₂	C40	4.63	2023	331	142	0.167
V_5Si_3	D8 _m	5.27	2283	257	101	0.271
TiSi ₂	C54	4.39	1773	265	115	-
CoSi ₂	C1	4.95	1600	116	-	-
Ti₅Si ₃	D8 ₈	4.32	2403	~150	-	-

Table 4.10 Physical and mechanical properties of selected silicides

Applications

High temperature coatings based on silicides

- oxidation resistance, less for carburizing
- MoSi₂, WSi₂, ReSi₂, PtSi₂ where the metal is more noble than Si or when the metal oxide is fugitive, therefore only SiO₂ remains on the condensed phase.
- NbSi₂, TaSi₂, TiSi₂, ZrSi₂, CrSi₂ weaker resistance to high-temperature oxidation is improved by addition of another element
- for Nb alloys, the following systems are used: Cr-Ti-Si,V-Cr-Ti-Si, Cr-Si-Al.
- for superalloys are used these systems Mo-Si-Al-Cr-B
- methods of coating: stamping, suspension, chemical application from gaseous phase (CVD), electrolytic application, fluid layer, immersing into molten metal, plating, pplasma spraying or flame, vacuum application from gaseous phase, detonation processes.

Silicides in electronics

- superconductors and magnets – ternary silicides based on Ce or U: CeCu_2Si_2, URu_2Si_2, CeRh_2Si_2, LaCu_2Si_2

e.g.: URu₂Si₂- is the first compound that exhibits both superconductivity and magnetic properties

- microelectronics- Schottky's barrier and resistance contacts for deposition of thin layer of metal onto Si substrate, thermal processing is included- silicides are formed on the metal-Si interface: TiSi₂, CrSi₂, ZrSi₂, NiSi₂, ErSi₂, HoSi₂, WSi₂, GdSi₂, YSi₂, DySi₂, CoSi₂, TaSi₂, HfSi, MnSi, NiSi, Pd₂Si, IrSi, IrSi₃ and others...
- for metal plating in integrated circuits low resistance and high-temperature stability in connectors and control electrodes lowest resistance in $TiSi_{2,}(13-16 \mu\Omega.cm)$
- silicides for epitaxial growth on Si substrates single crystal films are formed with low resistance and higher stability and reliability than in polycrystal silicides in connections and contacts
- infrared detectors and sensors for military and civil applications based on silicide Schottky's diodes- PtSi and Pd₂Si.

4.8.3 IMC alloys for electromagnetic applications

Soft magnets

Alloys with high initial and maximum permeability

The group of these materials includes alloys based on transition metals such as Fe, Co, Ni combined with Al, Si:

*	78-Permalloy	- with 78 wt.% Ni - composition close to FeNi ₃ (L1 ₂)
*	Isoperm	- FeNi - its anisotropy is used for rolling
*	Alfenol	- Fe ₃ Al - DO ₃ structure, 12-16 wght.% Al
*	Sendust	- Fe ₃ (Al,Si)- 5 wt.%Al, 10 wt.%Si, 85 wt.% Fe; Fe ₃ Al and Fe ₃ Si have
		the same structure (see silicides)
*	Permendur	- FeCo - B2 structure

• Borides based on $Co_{20}Al_3B_6$ - D84 structure, very high hardness >1000 HV

In these types of materials we distinguish alloys that achieve high initial permeability μ_i , or maximum permeability μ_{max} in general, then alloys with constant permeability and alloys with permeability changing with temperature. The required magnetic properties in these alloys are not achieved only by the alloy's composition but also by thermal processing or mechanical alteration of nuclei and often also by complex forming of the alloy.

If we add silicon and aluminum to iron, we obtain an alloy with very good magnetic properties. An alloy with content of 10% of Si and 5% of Al is called **sendust**, and has extremely high permeability μ_{max} up to 160 000 and low coercive intensity 1.99 A/m. Magnetic anisotropy and magnetostriction is almost absent in this alloy.

Another improvement is achieved by adding Cobalt. A material with content of 2% of Si and 6% of Co is called **hyperm** and sheets produced from this alloy have magnetic saturation of up to 2.2 T. It is used where there is an effort to save space and lower weight, for example in engines of cranes or trams. Thin sheets from silicon steels with thickness of approximately 0.02 - 0.2 mm are used for higher frequencies, so that loses due to turbulent currents are as low as possible. Since at high frequencies the loses due to turbulent currents (Z_0) increase with the square of frequency and square of sheet thickness and decrease linearly with electrical resistivity, which the hysteresis loses increase only linearly, low sheets with high electrical resistivity have been prepared from these alloys. Examples include sheets EHW with $\mu_i=700$; $\mu_{max}=11000$; $Z_0=1.0$ W/kg.

Alloys with constant initial permeability in weak magnetic fields

In light-current and high-frequency technology it is sometimes required that the alloy has a constant initial permeability μ_i in certain magnetic fields. Hysteresis loop in this case is thin and skewed. These properties are exhibited by for example nucli from powder iron or powder Permalloy, which are mixed with for example glass powder, shellac or some ceramic matter.

A more effective influence on the properties is observed in alloys with an addition of cobalt, this group includes for example **perminvar** with its content being 45 % Ni, 30 % Fe and 25 % Co. Perminvar has a significant electrical resistivity and after correct annealing achieves values of $\mu_i = 450$, which is constant in magnetic fields up to coercive intensity of 159 A/m.

However, constant permeability is often required for a wider range of magnetic fields. This can be achieved either by weak forming of annealed material or incomplete annealing of a strongly formed material. Such material, in which crystals deform and recrystallize in certain direction of crystal axes, then behaves similarly to products stamped from powder, but exhibits higher characteristics. Constant permeability can also be ensured by strengthening using an alloying element. An example of such material is an alloy based on Ni-Fe-Ag, which is technically permalloy where 2-3% of Ag content causes strengthening.

Isoperms have very low remanence and very constant permeability; their composition usually is 40-50% Ni, 3-4% of Al, 10-15% of Cu and Fe the rest. Its magnetic properties can be influenced by strengthening (strengtheable isoperms). Forming and annealing prepares an alloy which permeability (30-80) is constant up to 7950 A/m intensity. Isoperms are used where high constant permeability is required as well as low loses due to turbulent currents, such as in case of high-frequency coils.

Materials for high saturation are alloys of iron with cobalt with a possible addition of vanadium. These are so called **permendures** with 50-70% of Co, which achieve induction of saturation up to 2.4 T and are used in magnetic nuclei. A big disadvantage for common applications is their high cost due to high content of Co.

Alloys with temperature-dependent permeability

These alloys contain elements that lower their point of magnetic change (T_c) of the prevalent ferromagnetic metal up to the area of room temperature, therefore even a small change of temperature causes change of the alloy's magnetic induction. This way a compensation can be performed for example in devices with constant magnets and their properties decrease due to temperature. These alloys include for example **termoperm** (Fe+30% Ni) and **calmalloy** (Ni+30-35% Cu, 1-2% Fe).

Nanocrystal magnetically soft alloys

These are the latest alloys which are still subject of research, but are already available even for normal use. Nanocrystal magnetically soft materials are prepared from amorphous metal bands based on Fe-B. This new class of materials is characteristic by their grain size of 10-25 nm.

Based on research, two groups with the best characteristics have been selected:

- Fe-Cu-Nb-B-Si called the *Finemet* group
- Fe-Zr-(Cu)-B-(Si) called the *Nanoperm* group

The *Finemet* group is characteristic for an optimal grain size of approximately 15nm, offers induction saturation of around 1,2 T and exhibits very good properties at high frequencies comparable with the best amorphous materials based on Co alloys.

Finemet-type alloys are supplied to the market by e.g. the Hitachi Special Metals (Japan), Vacuumschmelze GmbH (Germany) or Imphy (France) in form of small nuclei for special use at high frequencies.

The*Nanoperm* group differs by its grain size. If the optimal preparation conditions are met, the grain size is up to 25 nm. A common feature of Nanoperm alloys is very low energy loses at low frequencies (60 Hz), which allows their application is transformers for energy distribution.

For their outstanding soft magnetic properties (extremely low coerciveness, high permeability, low energy loses, etc.) these materials are still subject of research. Nanoperm alloys are supplied by Alps Electric Co. (Japan).

Hard magnets

Very thin metallic magnets

They are **cunife** and **cunico** based on Fe, Co and/or Ni combined with other elements:

- Cunife- 60 wght.% Cu, 20 wght.% Ni, 20 wght.% Fe
- Cunico 35 60% wght.% Cu, 20 wght.% Ni, 20 to 41% wght.% Co

It is technologically very difficult to manufacture thin (flat) magnets, because they are prepared either by sintering of powder materials or casting alloys. Formable alloys based on Cu-Ni-Fe, Cu-Ni-Co, Pt-Co, Fe-Co-V a Fe-Cr-Co, are an exception, they exhibit properties of permanent magnets. Whereas the first three types of materials are now obsolete, the latter two types are manufactured and used relatively often. Thanks to formability in cold, it is possible to produce even very thin belts (even 0.25 mm) and even wires out of these alloys. Moreover, by forming, some types achieve anisotropic properties, i.e. they exhibit a marked improvement of magnetic properties in the direction of forming.

Properties:

Cunife alloys are anisotropic and have these magnetic properties: remanence 0.5 to 0.58 T, coercive intensity 35 000 to 47 760 A/m; energy product of BH between 4370 and 7560 J/m³. Cunico alloys have these magnetic properties: coercive intensity 55 700 A/m, energy product of BH around 3980 J/m^3 .

Formable magnetically hard materials are relatively soft (hardness HV approx. 220) in raw state (before thermal processing), therefore they are workable and formable using all usual methods. After thermal processing, their hardness and brittleness increases significantly. Casts with face width of under 0.25mm can be cast out of cunico alloy.

Use:

These alloys are delived in shapes of belts, tubes, wires and they can be made into wide range of shapes of permanent magnets for production of small devices. This belts from formable magnetically hard alloys are used to produce miniature magnets for various uses: information displays, magnets for on-board units, indicator elements, compasses, etc. From these semi-products other, mode complicated magnetic elements of more complex shapes can be made (pressing, stamping, cutting out, bending).

Magnetic alloys

Out of magnetically hard materials, **Fe-Ni-Al based alloys** exhibit unusually suitable magnetic properties; these alloys can be thermally strengthened. **Alni** alloys have a very small amount of carbon and are not malleable. **Alnico** alloys are characteristic for larger amounts of cobalt.

The composition of alnico alloys (Alnico 1; 2; 3; 4; 5; 6; 12) is characterized by 60 to 63% of Fe, 14 to 28% of Ni, 8 to 12% of Al, up to 24% of Co and possible also 6% of Cu; they can also contain Ti or Nb. Magnetic alloys AlNi and AlNiCo take an important position on the market, despite the field of progressive magnet types based on rare earth metals (REM) developing rapidly.

Properties:

Magnetic alloys have - after PEM magnets - the highest magnetic energy, coerciveness and remanence. High Curie temperature (T_c) predetermines them for applications at increased temperatures.

A marked improvement of magnetic properties is achieved by thermal processing in strongly magnetic field (alnico). Thermal processing of alloys consists of heating them up to a temperature of 1200 °C and subsequent quenching. After quenching comes hardening (tempering) in order to precipitate the fine phase and obtaining optimal coercive intensity without observable decrease of remanence.

Hardened alloys do not show a tendency towards aging. Up to 250°C they are insensitive to temperature changes, at 500°C, their magnetic properties are only slightly decreased, but at 650°C the influence of the temperature on the magnetic properties is observable. Usefulness of these alloys is expanded due to a possibility of welding.

Alni- and alnico- type alloys allowed for significant changes in construction of many electrical engineering devices with their magnetic properties as well as their shock resistance, influence of temperature and alternating electrical field. Density of these alloys is around 7500 kg/m³.

Use:

In traditional areas, such as electric motors of medium size, generators, speakers, acoustic transducers, electricity meter, electricity measurement devices, retaining industrial systems, and others.

Co-Fe-V based alloys composed of 52% Co, 9.5 to 14 % V and the rest of Fe are called **vicalloy I**, **II** etc. Vicalloy I, which can be formed cold after quenching, rolled into pipes, belts, forged, stamped and worked is an *isotropic* alloy whereas vicalloy II (with the vanadium content of 13.5%), which is also well formable, workable after quenching is more suited for production of belts and wired, and is *anisotropic*.

Properties:

Magnetic properties of vicalloy I: remanence 0.8 to 1T; coercive intensity 6370 to 23 280 A/m; BH 3980 J/m³; for vicalloy II: remanence 0.65 to 1.4T; coercive intensity 22 280 to 35 820 A/m; BH 7160 to 13 930 J/m³.

Use:

Application of Co-Fe-V alloys is limited by its large Co content, which is among the more expensive metals. Therefore they are used for small magnets in watchmaking industry, compasses, wires or tapes for sound recording etc.

Formable materials without iron based on Ag-Mn-Al containing 86% Ag, 9 % Mn and 5% Al represent alloys of the **silmanal** type.

Properties:

Magnetic properties of this type of alloys are increase by forming, quenching and hardening. They are well formable and are produced in shapes of pipes and wires. They have the following magnetic properties: remanence 0.056 T, coerciveness 43 000 to 45 800 A/m, BH 320 J/m³.

Use:

Applications are aimed at some special equipment due to high price of these alloys.

Outstanding magnetic materials, but not well applicable due to their price, alloys based on **Pt-Co** or **Pt-Fe** or **Pt-Ni**., are anisotropic and obtain their magnetic properties by quenching from temperatures of between 1000 and 1300°C and hardening. **Pt-Co** alloys achieve remanence of 0.65 T, coercive intensity 215 000 A/m, BH 36 610 J/m³. They are used in production of complex magnets (such as electric clocks).

Another group of materials for permanent magnets are magnets prepared from metal powders which allow achievement of high dimensional accuracy and almost completely remove laborious processing. They are the sintered metallic magnets. The production thought sintering is suitable for magnets of small dimensions. The powder metallic magnets include alloys such as **bismanol** (MnBi). MnBi alloy is a compound of two metals in stoichiometric ratio of atomic mass. Preparation of the alloy is difficult, the melt is ground into powder after solidification, which is then stamped in electrically heated die (300°C) in pulse magnetic field. Magnetic properties of this alloy are dependent on temperature.

This group also includes magnets from very fine metallic powder based on **FeCo**, which are pressed with addition of metallic or organic binders at cold with pressure of 2000 to 1000 atm and magnets from single-domain metallic powders, that are produced electrolytically and then pressed after being wrapped in protective binder (lead, cadmium, etc.).

Magnets based on rare earth metals (RE magnets)

- ✤ Transition metal -lanthanide : Cu₇Tb, Co₅Sm,
- Transition metal -lanthanide-metalloid : $Fe_{14}Nd_2B$, $Fe_{14}Nd_2C$, $Fe_{17}Sm_2N_x$, Co_3GdB_2 ,

In relatively recent past, a new generation of permanent magnets has been developed that contain rare earth elements, most commonly Sm or Nd. These magnets have the highest magnetic energy stored in their volume unit out of the known materials. RE magnets are produce by sintering of very finely ground substances, because their direct casting is not possible. Basic types have stoichiometric chemical composition: SmCo₅, Sm₂Co₁₇ and Fe-Nd-B. These magnets allow significant miniaturization of dimensions, because they achieve retaining force at much lower dimensions than for example ferrite magnets (Fig.4.33).

Properties:

Nd-Fe-B magnets are the strongest permanent magnets with high residual induction, high coercive intensity. Another one of their assets is much lower production cost compared to Sm-Co magnets. Nd-Fe-B magnets are currently widely used in pulse motors, spindle motors, brushless motors, magnetrons, speakers, sensors, relays, tools, etc. Nd-Fe-B have a tendency to corrode, therefore nickel, zinc or epoxy resin is applied on their surface. Depending on the production process, Nd-Fe-B magnets are divided into sintered and bonded type.

Re magnets are hard and relatively brittle, which is necessary to take into account especially in manipulating magnetized products in proximity of other magnets or ferromagnetic materials (iron), where they can be damaged due to violent contact with another part. They are produced in finished forms, they can be slightly adjusted by grinding. It is necessary to take care not to heat up the ground areas (temperature T_c for SmCo₅ = 720°C, Sm₂Co₁₇ = 825°C, Fe-Nd-B = 310°C !)

Use:

Permanent magnets based on RE metals have a range of applications where it is required to create a strong magnetic interaction (retaining force) or where small dimensions are a priority. Applications include rotors and stators of engines, linear engines, magnetic clutches and brakes, magnetic polarizers of liquids, magnetic separators, anti-theft systems in shops. Another applications for magnets is in wrist watches, IT etc.

Top development results in an area of small DC motors, in which the magnetic field of the stator is created by permanent magnets, was used for example in cosmic automatic vehicle Sejourner in a NASA mission to the surface of Mars. The vehicle was propelled and driven by 11 Maxon RE16 engines, 16 mm in diameter with transmissions and motion sensors. Technologies developed for cosmic application are now transformed into a new range of industrial engines offered under the name RE-max with 5 basic diameters: 13, 17, 21, 24 and 29 mm. The benefits in propelling technology are here especially for high performance permanent magnets from Nd placed inside the self-supporting winding rotor. Performance of magnets and overall construction arrangement are a foundation of miniaturization of motors. In the area of brushless DC motors, (EC motors) in which the mechanical commutator with brushes is replaced by electronic control of commutation, i.e. alternating the current into sections of winding according to the angle of rotor, miniaturization occurred as well; a motor with 6mm in diameter was developed (MAXON, 1999), its dimensions allow applications is medical technology (endoscopy, infusion pumps), assembly automatons for electric technology with surface assembly, in aviation and other top technological fields.

Fig. 4.33 Development of size and magnetic properties of permanent magnets in 20th century

4.8.4 IMC alloys for superconductors

Materials for superconductors are generally divided into groups based on the critical temperature T_c of transition into superconducting state:

- 1. low-temperature superconductors (LTS) they can be cooled by He
- 2. high-temperature superconductors (HTS) they can be cooled by liquid nitrogen

The first group, i.e. LTS can be classified according to the type of material into two other subgroups:

- ✤ LTS type 1 elemental (Pb,
- LTS type 2 Nb and its compounds (Nb₃Al, Nb₃Ga, Nb₃Sn), compounds of other elements

and it is this LTS type 2 group where intermetallic compounds and alloys based on IMC belong; they are stoichiometric in terms of composition and have a structure with high degree of arrangement. These properties are necessary to preserve superconductivity. These lattices occur within the structures:

- ✤ A₃B (BCC) B atoms can be transitional and non-traditional metals, A atoms are transitional metals, they form close arrangement into orthogonal chains across the crystal structure, which is probable and suitable for superconductivity
- ✤ A15 from more than 70 intermetallics with this structure, more than 50 superconductive, some are prepared by PVD, CVD high pressure technologies or by fast cooling.

Examples of composition:

 $Ti_{3}Sb, Zr_{80}Sn_{20}, V_{3}Ga, V_{3}Si, V_{\sim 3}Ge, V_{77}As_{23}, Nb_{3}Al, Nb_{3}Ga, Nb_{3}Sn, Nb-Si, Nb-Sb, Ta_{85}Pt_{15}, Ta_{\sim 80}Au_{20}, Mo_{40}Tc_{60}, Mo_{3}Al, Mo_{3}Ga, Mo_{77}Si_{23}, and others.$

4.8.5 Hydrides and their applications

Many metals, solid solutions, intermetallic compounds and amorphous alloys dissolve certain amount of hydrogen in interstitial positions and forms interstitial solid solutions that may be concentrated, but not necessarily stoichiometric. Hydrides of elemental metals are called binary hydrides, hydrides of IMCs or binary alloys are called ternary hydrides. While in common metallurgy



processing the metals must be protected against hydrogen embrittlement, in this specific case metal hydrides are used as a moderators of nuclear reactions, reversible hydrogen storage materials for energy power and cathodes in charging accumulators.

Group	Prototype	Crystal structure	Hydride/Deuteride
AB ₅	LaNi₅	CaCu ₅ , D2 _d	LaNi₅H _{6,5}
AB ₂	ZrMn ₂ ,TiMn ₂ ZrCr ₂ ,ZrV ₂	MgZn ₂ , C14 MgCu ₂ , C15 (Laves phases)	$ZrMn_2D_3$, $TiMn_2D_3$ $ZrCr_2H_{3.8}$, $ZrV_2H_{4.9}$
AB	TiFe	CsCl, B2	TiFeH, TiFeH _{1.9}
A ₂ B	Mg₂Ni Ti₂Ni	Mg ₂ NiC _a Ti ₂ Ni	Mg ₂ NiH ₄ Ti ₂ NiH
A ₂ B-AB	Ti₂Ni-TiNi	Multiphase alloy	Ti₂NiH, TiNiH

Table 4.11 Examples of intermetallic compounds forming hydrides



Fig.4.34 Hydrogen atoms (blue) at interstitial positions in tetragonal lattice of MgH₂ hydride.

Even though most physical and chemical properties of IMC hydrides are comparable with properties of binary hydrides (Fig.4.34), some differences have been observed:

- 1) intermetallics are much more reactive with hydrogen and less sensitive to impurities in gas
- 2) brittle intermetallics easily disintegrate into powder after adsoption of hydrogen and subsequent expansion of its lattice
- bond with hydrogen (enthalpy of hydride formation) occurs through substitution or offstoichiometric mixtures
- 4) geometric and chemical diversity of interstitial positions is much greater

Phase diagrams, thermodynamics and enthalpy of hydride formation

The behavior at hydrogen absorption can be described by PCT curves (pressure-composition isotherms) as is shown on Fig.4.35. Intermetallics are able to dissolve hydrogen in α phase (solid solution) up to certain amount (at.%); however, if concentration of H increases, a significant H-H interaction occurs in some places and hydrides are formed (β phase in the image). Coexistence of both phases at equilibrium pressure $p_{eq}(T)$ corresponds to the plateau of the isotherm in the diagram. Length of this plateau shows how much hydrogen can be reversibly stored with small changed in pressure. In pure β phase the pressure of gaseous hydrogen steeply increases with its concentration. At much higher concentrations and pressured of hydrogen, other plateaus may form as well as other hydrides phases, which reflects the state when filling up of other interstitial positions of other types occurs. Equilibrium pressure increases with temperature and the plateau is shorter. Two-phase area is limiter by critical point T_c, over this point the transition from α to β phase continues.

(4.8)

Dissolution of hydrogen and formation of hydrides in metal can be a exothermic or endothermic reversible reaction:



Fig.4.35 Pressure-composition isotherms, also called PCT curves.

Thermodynamic properties are described by van't Hoff equation:

 $M + \frac{x}{2}H_2 \Leftrightarrow MH_x + \Delta H$

$$\ln\left(\frac{p_{eq}}{p_{eq}^{0}}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$
(4.9)

which shows the relation between the equilibrium pressure, absolute temperature T, change in enthalpy ΔH , change of entropy ΔS and gas constant R.



Fig.4.36 Van't Hoff diagram of various metallic systems (compound)-H (Note: 1 atm = $1.013 \cdot 10^6$ Pa)

The progress of van't Hoff dependence $\ln (p_{eq}/p_{eq}^{0})$ on 1/T is shown on Fig.4.35, from which is then evaluated ΔH and ΔS . The progress of van't Hoff's dependence for various binary and ternary hydrides are given on the next Fig.4.36. Calculations of cohesive properties and especially enthalpies

of hydride formation are however very complex and time consuming and they often don't coincide with experimentally obtained data.

Instead of gas saturation by hydrogen, cathode hydrogenation can be used, in which the pressure of gaseous hydrogen (in atm.) corresponds to the electrochemical potential E:

$$E = -\frac{RT}{2F} \ln[p(H_2)] = -0.0296 \log[p(H_2)]$$
(4.10)

where F is the Faraday constant.

In the considered applications of real hydrides, these properties are observed:

- 1. Equilibrium pressure of absorption is higher than equilibrium pressure of desorption, i.e. there is a static hysteresis, which has its origin in hysteresis of elastic properties and plays a role in expansion and contraction of lattice. Another (dynamic) hysteresis is possible, where PCT curves are measured faster than the metal-H system achieves equilibrium thermal state.
- 2. Plateau of α - β phase transition is not flat but exhibits some slope. This slope reflects state of hydrogen atoms not containing interstitial positions of only same size, but their random distribution occurs.
- 3. Some IMC hydrides can be thermodynamically unstable and have a tendency to form disproportionate phases, very stable hydrides and other compounds or hydrides, such as:

$$LaNi_5H_{6.5} => LaH_2 + other hydrides$$
 (4.11)

This reaction however requires diffusion of atoms of metal, therefore its significance at room temperatures is limited. During the cyclic saturation at higher temperatures, this phenomenon may be a cause of PCT curve degradation, so it is necessary to choose a suitable IMC and saturation cycle. Fig. 4.36 states stabilities for selected hydrides of metals and alloys. Table 4.12 shows maximum possible amount of hydrogen in selected alloys.

With regards to the required properties, the application of intermetallic hydrides can be divided into three groups:

- 1) Open gaseous system:
 - a) stationary storage of hydrogen as a fuel

for example containers from 10 tons of IMC type AB_2 ($Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$) with volume of 2000 m³, which can be saturated and de-hydrogenized in 1 hour (manufactured by Mannesmann)

b) mobile storage of hydrogen used as a fuel in automotive industry

for example in the early 90s, Daimler Benz experimented with hydrogen-fuelled cars - 8 thousand refuelings corresponded to a distance of more than 600 thousand km (75km/refuel), refueling was performed from 20 to 95 % in 10 minutes through a reaction exchange of heat. DB patented special hexagonal AB₂ IMC: $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$, which absorbs only up to 2 wght.% H at 300K. Currently, there are Daimler-Chrysler Mercedes buses running in Germany that have combustion cells for hydrogen from bottles places on the roof and can travel 250 km without refueling (daily service). Steam is the only flue gas.

c) isotope separation

Deuterium and tritium, isotopes of hydrogen, react with metal or intermetallic able to form hydrides and deuterides and tritides are formed that have some common properties with the hydrides of the corresponding basic metal of IMC, but also many different physical and chemical properties (isotope effect, mass-influenced diffusion), which is used in isotope separation.

d) cleaning of H_2 (and D_2 , T_2) for laboratory purposes

- level of impurity in hydrogen of the order of 10 or 100 ppb can be achieved

Alloy (metal)	Phase	Hydride	Structure	Hydrogen amount (wt.%)	p _{eq} (MPa)/ T (K)
LaNi₅	AB ₅	LaNi₅H ₆	Hexagonal	1.4	0.2/298
CaNi₃	AB ₃	$CaNi_3H_{4.4}$	Hexagonal	1.8	0.05/298
ZrV_2	AB ₂	$ZrV_2H_{5.5}$	Hexagonal	3.0	10 ⁻⁹ /323
TiFe	AB	TiFeH _{1.8}	Cubic	1.9	0.5/303
Mg ₂ Ni	A ₂ B	Mg_2NiH_4	Cubic	3.6	0.1/555
Ti-V based	Solid solution	Ti-V-H ₄	Cubic	2.6	0.1/298
Mg	element	MgH ₂	Hexagonal	7.6	0.1/573

Table 4.12 Structures and absorption capabilities of selected metal hydrides

2) Closed gaseous system

Closed loop of IMC-H system which works at compression, heat exchange or as thermal sensor is filled by hydrogen only once. Continuous damage by impurities from gas does not occur. It required good heat exchange and good phase stability against formation of disproportionalities.

- a) thermal machines
- b) thermal pumps, heat accumulators
- c) coolers
- d) actuators

3) Electrochemical cells

Electrodes of type NiMeH in secondary cells, schematically represented on Fig.4.37.



Fig.4.37 Schematic of rechargeable battery with electrodes NiMeH (e.g. hydride LaNi₅) and NiOOH in KOH electrolyte

Important terms

Ni aluminides, Ni₃Al, property of stacking faults in Ni₃Al, hydrogen embrittlement, anomalous temperature dependence of yield strength, structural aluminides, lamelar microstructure of TiAl, silicides for electronics, magnetic alloys based on IMC, alloys for hydrogene storage.



Σ

Questions

- 1. What particular properties of Ni₃Al has been determined?
- 2. Due to what phenomena is the Ni₃Al alloy creep resistant ?
- 3. What type of microstructure of γ -TiAl based alloys is more favorable for creep resistant alloys?
- 4. What property of γ -TiAl based alloys is influenced by Ti₃Al phase?
- 5. What IMC based alloys can be used in aircraft industry and why?
- 6. What aluminides are used for petrochemical industry and to what properties it is due?
- 7. What alloys show the anomalous positive temperature dependence of yield strength?
- 8. What IMC based alloys fall into the permanent magnets?
- 9. What advantageous properties show FeNdB based magnets?
- 10. What do you can define on the base of PCT curves?
- 11. What materials are designated for hydrogen storage?
- 12. What properties of IMC based hydrides are investigated and controlled?
- 13. Can you name the applications of IMC based hydrides?



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5. SHAPE MEMORY ALLOYS



Time needed to study: 2 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- define the differences between a thermoelastic and deformation martensite
- describe the principles of the shape memory effect
- explain the mechanisms of one-way and two-way shape memory
- name the applications according to the types of shape memory effect

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Lecture

5.1 Basic characteristics of materials with a shape memory effect

Shape memory alloys (SMA) are a group of metallic materials, which are able to return to a given, pre-defined shape or size after they were submitted to thermal treatment. In general, these materials are plastically deformed at low temperature and then exposed to elevated temperature that allow them to return to the shape before the deformation.

If the materials show the shape memory effect only at heating, they are described as materials with *one-way shape memory* (Fig.5.1a). Some materials also change with following cooling, these are described as materials with *two-way shape memory* (Fig.5.1b).



Fig.5.1 Schematic illustration of a) one-way and b) two-way shape memory

The first transformation associated with shape memory was observed already in 1932 by Chang and Read, who recorded the reversibility of the transformation in AuCd alloy using metallographic observation and changes in electrical resistance. In 1938 the transformation was also observed in CuZn brass and in 1951 the shape memory effect was also detected in a bended rod made of AuCd. However, until 1962, when the shape memory effect was detected in a equiatomic NiTi, nobody thought about a practical usage of the effect.

Today, there is a large known group of alloys (Table 5.1 and 5.2) that show the shape memory effect, but only those which show a significant amount of strain or generate considerable force when changing shape are commercially used. Currently, they are the materials based on Ni-Ti (Ni-Ti-Cu, Ni-Ti-Cu-Zr, Ni-Ti-Fe, Ni-Ti-Cu-Hf) and based on Cu (Cu-Zn-Al, Cu-Al-Ni, Cu-Al-Ag, Cu-Zn-Al-Mn). New perspective systems of shape memory alloys are being researched: alloys based on Co (Co-Mn, Co-Ge, Co-Cu, Co-Ni), based on Fe (Fe-Mn, Fe-Mn-Si, Fe-Cr-Ni-Mn-Si), based on Ti (Ti-Nb,

(5.1)

(5.2)

Ti-Nb-Sn, Ti-(8-10)Mo-4Nb-2V-3Al, Ti-Nb-Al, Ti-Mo-Ga, Ti-Nb-Zr, Ti-4Mo-4,4Zr-4,9Al-2Sn-2Cr-1Fe, Ti-Nb-O and Ti-Nb-Ta and others. Other types of shape memory alloys exhibit the shape memory effect in combination with magnetic features: Ni₂MnGa, Ni₂MnAl, Co-Ni-Ga(Al), Co₂MnGa, FePt, CoNi, FeNiCoTi a Ni-Fe-Ga, so-called Heusler systems or FSMA.

Table 5.1 Overview of the alloys with observed shape memory effect

Ti-Pd-Ni	Fe-Mn-Si
Ni-Ti-Cu	Ni-Ti
Au-Cd	Ni-Fe-Zn-Al
Fe-Zn-Cu-Al	Cu-Al-Fe
Ti-Nb-Al	Ti-Nb
U-Nb	Zr-Cu-Zn
Hf-Ti-Ni	Ni-Zr-Ti

Table 5.2 Composition of the selected shape memory alloys and the transformation temperatures

Alloy	Composition	Temperature interval of transformation (°C)	Hysteresis of transformation (°C)
Ag-Cd	44-49 at.% Cd	-190 to –50	15
Au-Cd	46.5-50 at.% Cd	30 to 100	15
Cu-Al-Ni	14-14.5 wt.% Al,	-140 to 100	35
	3-4.5 wt.% Ni		
Cu-Sn	cca 15 at.% Sn	-120 to 30	
Cu-Zn	38.5-41.5 wt .% Zn	-180 to -10	10
Cu-Zn-X (X=Si,Sn,Al)	Little amounts wt.% X	-180 to 200	10
In-Ti	18-23 at.% Ti	60 to 100	4
Ni-Al	36-38 at.% Al	-180 to 100	10
Ni-Ti	49-51 at.% Ni	-50 to 110	30
Fe-Pt	cca 25 at.% Pt	Approx –130	4
Mn-Cu	5-35 at.% Cu	-250 to 180	25
Fe-Mn-Si	32 wt.% Mn, 6 wt.% Si	-200 to 150	100

5.2 Thermoelastic martensite

Shape memory alloys can be defined as alloys in which a thermoelastic martensite is created Martensitic transformation **austenite** \rightarrow **martensite** takes place, if the free energy G of the martensite is lower than in the austenite (Fig.5.3). For a self-transformation to occur, the following must apply:

$$\Delta G < 0$$

it is possible to write the following about the change of free energy ΔG :

$$\Delta G = \Delta E - p\Delta V - T\Delta S$$

where ΔE is the change of total energy, p is the pressure, ΔV is the change of volume, T is the temperature and ΔS is the change of entropy.

For the majority of solid and liquid substances, the $p\Delta V$ term is negligible at the atmospheric pressure, therefore the equation (5.2) can be transferred into the following form:

$$\Delta G = \Delta E - T \Delta S \tag{5.3}$$

In a reversible process and at constant pressure, the thermal energy exchanged between the system and the surroundings corresponds to the change of enthalpy (ΔH) of the system and the equation (5.3) can be expressed as:

$$\Delta G = \Delta H - T \Delta S \tag{5.4}$$

The change in Gibbs free energy is zero at the T_E temperature, therefore:

$$\Delta G^{T_E} = 0 = \Delta H^{T_E} - T_E \Delta S^{T_E}$$
(5.5)

and therefore at the T_E temperature:

$$\Delta H^{T_E} = T_E \Delta S^{T_E} \tag{5.6}$$

Assuming the terms ΔH and ΔS are independent on temperature, we can write a relation that expresses the amount of disposable free energy for the transformation as the function of supercooling ΔT :

$$\Delta G = \Delta H \frac{\Delta T}{T_E} = \Delta S \Delta T \tag{5.7}$$

The size of ΔG is basically the sum of the various energies of the transformation:

$$\Delta G = \Delta G_{ch} + \Delta G_s + \Delta G_e = \Delta G_{ch} + \Delta G_{nch}$$
(5.8)

where

 ΔG_{ch} ... chemical energy, which is available for the structural change from austenite to martensite ΔG_s ... surface energy needed for the formation of a austenite/martensite phase boundary

 $\Delta G_e \dots$ elastic energy of the system

 $\Delta G_{nch\cdots}$ non-chemical component of the energy consisting of surface and elastic energy

The ΔG_{nch} counteracts the transformation and its existence explains why the temperatures of the ends of phase transformations are not consistent with the temperatures at their beginnings.



Fig.5.2 The development of the Gibbs energy for the austenite→martensite transformation

The transformation begins to take place below the critical temperature T_E , at which the free enthalpies of both phases are the same, meaning the temperature M_s (martensite start). With decreasing temperature the conversion continues until the

temperature M_f (martensite finish). The M_s - M_f temperature interval is an important parameter in defining the memory behavior.

The martensite transformation enables the alloy under the M_f temperature to deform using the twinning mechanism. The deformation (the record of loading on Fig.5.3a) is then cancelled, when the twinning structure returns to the original phase of the matrix (austenite). When heating the martensite phase without the application of stress, the **martensite** \rightarrow **austenite** return begins at the temperature A_s (austenite start) and at the temperature A_f (austenite finish), the alloy is completely in the austenite phase. The equilibrium temperature T_E is close to the value of $(M_s + A_f)/2$. The range of the A_s - A_f cycle depends on stored elastic energy, while the A_s - M_f hysteresis is associated with the energy dispersed during the transformation.

Martensite transformation in the shape memory alloys exhibits the following basic characteristics:

- The transformation is joined by a non-elastic deformation of crystalline lattice and a non-diffusive process. The phase transition is a result of a cooperative and collective movement at atomic distances smaller than the lattice parameters (shear mechanism). In the absence of diffusion, the process is almost instantaneous.
- Martensite transformation is a transformation of the 1st order, in which the phase with the KSC lattice changes to a martensite, which is an arranged and twinning structure. The initial and resulting phase coexist together during the transformation. The result of this coexistence is an
invariant plane that separates the two phases. The lattice vector of both phases characterized by a clearly defined common orientation relationship (Baines's match), which depends on the nature of the alloy.

- The transformation of the elementary cell causes a volume and shear deformation along the defined planes. The shear deformation can be several times larger than the elastic distortion of the elementary cell. This transformation is crystallographically reversible.
- Many different variations of martensite can be created from one crystal of the parental phase, because the martensite phase has a lower symmetry of the crystalline lattice than the parental phase.
- Stress and temperature have a great influence on the martensite transformation. The transformation takes place if the difference of the free energies of both phases reaches a critical point.

Although martensite transition is a reinforcing mechanism, for example in steels and other alloys, the shape memory effect is not exhibited in them, because when heated, the martensite is tempered and changes its crystalline structure sooner than it returns to the parental phase (see the comparation in Table 5.3). The development of the parental phase can be observed using the measurement of resistivity depending on the temperature (Fig.5.4) or using the thermal analysis of differential scanning calorimetry (DSC).

Table 5.3 Comparation of the martensite transformation in the alloys based on Fe and SMA

 NON-THERMOELASTIC MARTENSITIC TRANSFORMATIONS (e.g. Fe-Ni System) Large shape strain associated with the transformation can only be accomodated by plastic deformation of the matrix. Special interface arrangement between parent and martensite which allows fast growth is destroyed and P/M interface immobilize. Additional growth will be extremely difficult and it is esier for the system to nucleate new platesthan allow growth of the old ones. This requires higher driving force and larger undercooling which results in higher hysterysis. When such martensite undergo reverse transformation, they do not shrink and revert to the parent phase but it nucleate and grow in the martensite phase. 	 THERMOELASTIC MARTENSITIC TRANSFORMATIONS (e.g. Au-Cd System) When transformation occurs by small shape strain, matrix can accomodate this without exceeding its elastic limit. Irreversible plastic deformation does not occur so glissile interface persists. Upon cooling and stressing amount of martensite increases by the motion of existing interfaces. This requires lower drivig force and results in smaller hysterysis
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The nonferrous metal shape memory alloys have a BCC structure of the following types as their parental phase: B2(CsCl), D0₃(Fe₃Al) or L2₁(Cu₂AlMn), that are presented on the Fig.5.5. Although this parental phase has a different type of crystalline lattice than steels, it is referred to as austenite according to the iron alloys nomenclature. When cooled down, this parental phase reorganizes to a martensite: B2 \rightarrow B19' or B19. The sequence of atomic shifts is displayed on the Fig.5.6. In the first stage, the given face centered tetragonal part of the original B2 lattice is transformed into a orthorhombic B19 with parameters different from the original.

Upon further cooling, a martensite formation starts with layering sequences according the Ramsdell marking: 2H, 3H, 9R or 18R (Fig.5.7). In NiTi, a monoclinic or rhombohedral martensite is create from the B2 structure, and both these structures are arranged and twinned with layering errors resulting from the shear and shift displacement of the atomic planes during transformation. Habit plane of the transformation is (011), which is an atomic plane in the parental phase, by the shearing of which the martensite is created. As it is diagonal of the cube face, and the cube has 6 faces with 2 diagonals and further, the martensite is twinned in two directions, then the transformation may result in as much as 24 different variants of the martensite.



Fig.5.3 Deformation of a shape memory alloy material in a martensite state upon loading (one-way shape memory) a) the stress-strain curve, b) microscopic processes of SME during cooling, deformation and heating



Fig.5.4. The change of resistivity of a shape memory material depending on the temperature and deformation



Fig.5.5 Crystalline lattices B2, (CsCl), D0₃(Fe₃Al) or L2₁(Cu₂AlMn)

A large number of martensite varieties allows the so-called self-adaptive nature of the thermoelastic martensitic structures. The creation and growth of varieties takes place in such a way that no internal tension occurs, therefore after the transformation is finished, the sample is in a state

without tension. If enough stress is applied, all the varieties within the grain combine into one variety (Fig.5.8). The morphology of an athermal martensite is known as the "fish bone" and is a result of the creation of twinned self-adaptive varieties (Fig.5.9). The shape changes as varieties try to eliminate one another, resulting in the creation of a small macroscopic deformation.



Fig.5.6 Sequence transformations: $B2 \rightarrow B19^{\circ}$



Fig.5.7 The sequence of the periodic layering according the Zhdanov-Ramsdell notation.

When heated above the A_s temperature, the deformed martensite starts to invariantly change back to the parental BCC structure and orientation. When heated above the A_f temperature, the return to the pre-deformation state is finished (Fig.5.3). The hysteresis may vary from 1,5°C for the R-phase in the NiTi up to 35°C in some Cu alloys. A hysteresis of more than 100°C (for coupling and connecting elements) can be achieved by a suitable thermal and mechanical treatment or by alloying. By adding Cu to NiTi the hysteresis of 5°C is achieved.



Fig.5.8 The scheme of changes in a microstructure: a crystal of the β phase (a) is changing after cooling and transformation to a martensite with self-adapting twinned varieties A, B, C, and D (b); upon application of the stress, the A variety becomes dominant (c). Upon heating, the material returns back to the β phase and recovers its original shape.



Fig.5.9 A typical martensite NbRu microstructure, with coarse and fine twinning.



Fig.5.10 Three types of closely spaced layers in a martensite resulting from the B2 parental phase of the CsCl type

5.3 Stress induced martensite

A martensite can be created in these alloys not only upon cooling, but also isothermally as a result of the application of sufficient stress, in other words, a stress induced martensite (SIM) is created. If the stress is removed, the deformation disappears and the martensite returns to its original parental phase. This *mechanical shape memory* may result in great deformations. This behavior is often referred to as *superelasticity* or *pseudoelasticity*.

Pseudoelasticity (*superelasticity*) occurs in the shape memory alloys only if the matrix is in a totally austensite state, and only up to a certain critical temperature \mathbf{M}_d . Martensite transformation does not depend on the change of temperature (heating-cooling) in this case, but only on the amount of loading. Above the M_d temperature, the martensite will not be created, no matter how high the stress is.



Fig.5.11 Stress-strain in a Cu-Zn based alloy: stress induced martensite (SIM) formation.

The stress-strain dependence in a Cu-Zn based shape memory alloy, which was deformed at the M_d temperature is depicted on the Fig.5.11. The maximum stress, at which the martensite variants merge can be completed is equal to 104 MPa, while the yield strength is only 35 MPa. The paternal phase (austenite) of this alloy exhibits the yield strength of 350 MPa. This typical effect, when the ratio between the yield strength of the parental phase and the martensite is 10:1, has been observed in all shape memory alloys.

When the stress reaches a critical value necessary for the creation of a stress induced martensite, there is a long delay, during which the transformation of austenite to martensite takes place. When the material is transformed, more stress would induce a real plastic deformation or a transformation to a secondary martensite structure in some alloys. Therefore, if we unload the stress in the moment when the transformation is finished, the martensite *spontaneously* transforms back to its parental phase, because the martensite is not a stable phase at the temperature of creation of the stress induced martensite. The mechanical hysteresis is included in the reversible transformation. Superelasticity is not linear, that is why it is difficult to establish a Young's module in this temperature interval, because it is dependent on the temperature and deformation.

The mechanical features of the shape memory alloys are changing with the temperature during their austenite \leftrightarrow martensite transformation. Fig.5.12 shows the collective dependence stress-deformation (σ - ϵ) for a shape memory alloy under, in the middle and over its transformation temperature interval. The course of the σ - ϵ dependence for the parental phase (curve A) is totally different and it corresponds with the conventional course of deformation of classic materials. In the austenite phase (at temperatures above M_d) the restoration of shape after stressing and heating does not take place and there is no phase change.

In the middle part (curve B) of the Fig.5.12 the superelastic behavior is depicted: when mechanically stressed at the temperature slightly above A_f , but under M_d , the stress induced martensite can be induced. It is further deformed and when the stress is constant, the deformation rises. After unloading, with the stress decreasing the material returns to the austenite phase and restores its original shape.

Martensite phase (below the M_f temperature) is easily deformed with several percent deformation already at low stress levels (curve C on the Fig.5.12). Line $4A_sA_f$ on the hysteresis curve represents the return of the material to the shape before deformation after unloading and during the following heating and the simultaneous martensite \leftrightarrow austenite transformation.

These different manifestations are visually shown in the animation (@ *Animation-5-SME*) and a video sequence (@ *video2-SMA*). For a more detailed description of the audiovisual aids, see chapter 13.



Fig.5.12 Stress – strain curves at various temperatures for three different structure phases with respect to martensite \leftrightarrow austenite transformation: A- in the austenite phase above M_d, B- in the austenite state below M_d but above A_f(SIM) and C- in the martensite phase below M_f(SME).

5.4 Manifestation of shape memory effect

5.4.1 One-way shape memory

The phenomenon of one-way shape memory can be described easily on the example of dragging a wire made of NiTi in the martensite phase. One end of the wire is fixed, then it is stretched over the yield strength at the room temperature and after unloading the wire remains prolonged (Fig.5.3).

After that, the wire is heated over the transformation temperature A_s of the alloy and its length immediately returns to the original state (Fig.5.12, curve C). Subsequent cooling under the transformation temperature M_s does not cause any macroscopic change of shape.

5.4.2 Two-way shape memory

The shape memory alloys may, under certain conditions, exhibit a real two-way shape memory, which enables them to get into two different shapes (low temperature shape and high temperature shape) even without outer force (the course of hysteresis curve is on the Fig.5.13). A suitable "training" can cause the two-way shape memory effect so that the part will have a certain shape in the martensite phase and the it will change spontaneously upon heating above. The change begins, as with the one-way phenomenon, at the A_s and is finished at A_f . This process can be theoretically infinite, if the applied stress and working temperature are not too high. These limit values are different for every system.

Two-way shape memory implies the suppression of certain variants of the martensite. These variants are originally created upon cooling. The alloy is therefore under a certain external stress during the reverse transformation (heating after deformation) (Fig.5.14b). When heated above A_s the applied stress is the cause of micro stretches created in the parental phase. This programs the parental phase during the subsequent cooling, so that it behaves as during the stress induced transformation. In the formation of the martensite, there is only a limited number of martensite varieties that are favored due to the micro stretch. This then causes a spontaneous deformation. Upon further heating, there is a normal one-way shape memory effect process and a return to the original shape. By repeating this cycle of transformation we can obtain a perfect two-way memory. The differences between the one-way and two-way shape memories can be visually observed on Fig.5.14.



Fig.5.13 The course of shape memory alloy deformation during a two-way shape memory effect (ΔT is the temperature hysteresis, ΔL is the change of length of the shape).



Fig.5.14 The comparison of shape memory alloy material behavior at a) one-way and b) two-way shape memory.

5.4.3 Damping capacity

The third characteristic feature of the shape memory alloys is the damping capacity, which is the result of the thermoelastic martensite behavior. The high mobility of the inter-variant borders eases the shrinking under stress and the growth of martensite varieties. The stress inducing movement of the

varieties and borders of the twins is much lower that the stress causing the grain boundary slip in conventional alloys. Under the influence of a cyclic stress above a certain threshold, this mobility of

boundaries leads to their forward-backward movement and their resulting friction force helps the energy dispersion (the damping effect). The maximum temperature, at which the damping effect takes place in the given alloy in the martensite state, is the A_s temperature. For application of the damping effect, the composition of the alloy has to be chosen so that the structure is martensite at working temperatures.



Fig.5.15 The comparison of the damping capacity of NiTi based bar with Al bar of similar shape.

5.5 Selected properties of the shape memory alloys

5.5.1 Mechanical properties

Mechanical properties are determined, as with other materials, from the record of a tensile test. In the Fig.5.16 below, there is a schematic tensile diagram of the NiTi alloy in the martensite state at 20°C, where ε_0 is the deformation after unloading.



Fig.5.16 Diagram of tensile test for a NiTi alloy up to the fracture

The diagram on the Fig.5.16 can be divided into four areas:

- Area I corresponds to an elastic deformation of the martensitic state, it is an initial deformation with the elastic module E_i previous to the part with seemingly non-linear deformation (II).
- ✤ Area II is characterized by a non-elastic deformation associated with the reorientation of the martensite varieties while creating a certain delay on the record (,,plateau").
- Area III is similar to a classic material. Further reorientation takes place as well as the plastic deformation (with the E_s module) of the oriented martensite M up until the yield strength σ_y . The mechanism of this deformation has not been exactly explained yet.
- Area IV is characteristic for the plastic deformation of the oriented martensitic structure, which leads to a fracture (fracture strength σ_f).

5.5.2 Degradation and fatigue

Reliability of the equipment made of shape memory alloys depends on the overall durability. Time, stress temperature, deformation, the method of deformation and the number of cycles are all important external parameters. Internal parameters that influence the durability of an alloy are: composition, production and thermal processing. From the general point of view, it is possible to determine the biggest influence on the number of desired cycles based on the deformation-stress parameters, as the Table 5.4. shows. The higher values of deformation and stress can be obtained for special processing and ternary alloys (e.g. NiTiCu).

Number of cycles	Maximum strain (%)	Maximum stress (MPa)
1	8	500
100	4	275
1000	2	140
100 000 +	1	70

Table 5.4 Fatigue characteristics of a NiTi alloy

5.6 Preparing and processing of SMA

NiTi

The basis for the preparation and thermal processing is the equilibrium phase diagram of Ni-Ti with the binary equiatomic intermetallic NiTi compound (binary diagram in the Fig.5.17) that has a specific range of solubility for an excess of Ni or Ti and also for other metals. It also exhibits ductility comparable with other common alloys. This solubility allows the alloying and changing of the mechanical features as well as the transformation characteristics of the system.



Fig.5.17 A binary diagram of the Ni-Ti with intermetallic phase NiTi (in the middle) and other neighboring phases NiTi₂ and Ni₄Ti₃.

The alloying using the excess of Ni is commonly performed. This excess rapidly reduces the transformation temperature and increases the yield strength of the austenite. Other elements are Fe and Cr (they decrease the transformation temperature), Cu (decreases the hysteresis and decreases the transformation stress of the martensite). Ordinary impurities such as oxygen and carbon may also move the transformation temperature and decrease the mechanical properties, that's why it is necessary to reduce and control the presence of these impurities in the alloy. This is the reason why it is necessary to ensure the production in a vacuum or an inert atmosphere, for example by plasma arc melting, electron beam melting or vacuum induction melting.

Welding and brazing of these alloys is difficult. Heat processing to introduce the desired memory shape usually takes place at 500-800°C, but it can also take place at 300-350°C with sufficient time.

CuAlNi, CuZnAl

Melting of shape memory alloys is similar to aluminum bronze (induction melting with protective atmosphere). The alloys can be also prepared by powder metallurgy and rapid solidification. Thermoforming can be performed on air. Alloys with low content of Al (up to 6 wght.%) may be processed in cold with inter-annealing. The CuAlNi alloys on the other hand are very fragile at low temperatures and can be processed only at high temperatures.



Fig.6.18 Cross section of a ternary diagram of Cu-Zn-Al with marked temperatures M_S and the composition of SMA based on CuZnAl.

Fig.6.19 Ternary diagram Cu-Al-Ni: vertical section with 3wt.% Ni

The addition of Mn decreases the transformation temperatures in both alloys and move the eutectoid reaction towards higher contents of Al (ternary diagram cross sections are on Fig.5.18 and

5.19), while also improving ductility. Other alloying elements include B, Ce, Co, Fe, Ti, V and Zr, which act on the grain refinement.

Typical composition of alloys CuZnAl: 10-30% Zn, 5-10% Al; CuAlNi: 11-14.5% Al, 3-5% Ni

These alloys are metastable in nature that is why it is necessary to perform heat treatment: solution annealing in the beta phase matrix area followed by controlled cooling, so that the beta phase was maintained for the shape memory effect. It is also necessary to prevent the evaporation of zinc and growth of grains during prolonged heat processing. Cooling is performed by quenching in water, but for some alloys of CuZnAl and CuNiAl, the cooling on air is sufficient. In hardened state, the transformation temperature is mostly unstable, that is why the aging after quenching is performed at temperatures above A_f, which ensures the stability of transformation temperatures. Alloy that were quickly hardened into martensitic state are sensitive to the effect of martensite stabilization. This effect causes the inverted transformation to be shifted towards higher temperatures, which delays or completely restricts the recovery of the shape. For alloys with yield strength above the room temperature, a slow cooling or gradual hardening is used with inter-annealing to aging in the area of beta phase matrix. The thermal stability of Cu alloys is limited by the kinetics of decomposition, that is why it is necessary to avoid longer exposures to temperatures over 150°C (CuZnAl) and over 200°C (CuAlNi).

5.7 Applications

The great advantage of the shape memory alloys is the possibility of their use in various fields, ranging from the aviation and cosmic industry, through medicine and even decorative items. Their use, however, varies according to the characteristics and requirements of their function. Adverse factor that restrict their further spreading is the economic demands of their preparation on one hand (compared to materials based on Cu, Al or steel) and the low fatigue features of most of the shape memory alloys on the other hand. A component made of a shape memory alloy is capable of enduring up to 100 times less cycles at some conditions (under pressure, torsion or bending) compared to a steel one.

Cu based alloys are more fragile than NiTi based alloys, especially if there is no control of the grain size during the manufacturing, that is why they can only be processed in heat. To maintain the austenite structure in Cu based alloys at room temperature, it is necessary to perform quenching, this will, however, make the alloy less stable than the NiTi alloys. One of the advantages of the Cu-Al-Ni alloys is the significantly higher transformation temperature compared to NiTi. Other favorable feature is their lower price.

Using NiTi alloys in various fields has other advantages, such as more favorable achieved size of memory deformation (8 % versus 4-5% in Cu based alloys), their thermal stability and other features (Table 5.5), but especially their biocompatibility. The following list includes some of the applications of the shape memory alloys, is divided according to the nature of the shape memory effect:

One-way shape memory alloys

- junctions in the connections of the high pressure hydraulic control pipelines in military aircraft
- junctions in the pipelines of naval vessels, and in the pipelines in the chemical and petrochemical industries (NiTi)
- retaining rings and strips in electro technical industry (Cu-Zn-Al-Mn, Ni-Ti-Nb)
- control elements of the connectors in electro technical industry
- devices that use strong forces during transformation demolitions, disconnection of rockets of space shuttles, in underwater devices

Two-way shape memory alloys

- pre-stressed interconnection elements
- electric circuit breakers
- security systems in liquid and gas distribution devices
- hot water caps in thermostatic controllers
- connection systems in aviation and space structures

• decorative objects

Stress induced martensites

Medical applications (NiTi)

- orthopedics fixation of bone fractures, spinal surgeries vertebrae separation
- orthodontics braces, root canal instruments the alloy increases the flexibility of the root tool, which enables the fine monitoring of the root tool in the canal during all the phases of the procedure. The tools do not require prior forming before the start of the procedure
- cardiovascular tools catheters, angioplasties, needles, probes, etc.

Common usage applications

- rims of glasses
- tips of fountain pens
- cell phone antennas
- reinforcements of fashion accessories and bras
- decorative objects

Damping capabilities

Shape memory alloys exhibit a specific damping capability in more than 40 % compared to the conventional steels, Cu based alloys or Al based alloys, that have a 0.5-1.5 % specific damping capability and cast-irons with 10-12 % specific damping capability. The possible applications are based on these features, for example specific parts in the construction of buildings and bridges that resist earthquakes, components of sporting equipment that damp vibrations (rackets, skis), the components that damp the vibrations after missile impact in the military industry, etc. High economic costs of preparation of these materials are still the main obstacle of expanding their applications, as these costs are reflected in the high prices of the applications.

Table 5.5 The features of commercially used alloys

Property	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni
Melting temperature (°C)	1300	950-1020	1000-1050
Density (g/cm ³)	6.5	7.64	7.12
Rezistivity (μΩ.cm)		8.5-9.7	11-13
Austenite	100		
Martensite	70		
Thermal conductivity (W/m.°C)		120	30-43
Austenite	18		
Martensite	8.5		
Young modulus (GPa)			
Austenite / β phase	83	72	85
Martensite	28-41	70	80
YS (MPa)			
Austenite /β phase	195-690	350	400
Martensite	70-140	80	130
UTS (MPa)	900-1500	400-700	500-800
Total elongation (%)	30-50	10-15	4-6
Maximum As (°C)	120	120	170
Hysteresis ∆(°C)	30	15-25	15-20
Reversible strain (%)	Max.8.5	4	5
Corrosion resistance	excellent	acceptable	good
Biocompatibility	excellent	bad	bad

	Aids for disabled		Micro-actuators
	Aircraft flog/alat adjustars		Mahila nhana antannaa
•	Aircrait hap/slat adjusters	•	Mobile phone antennas
•	Anti-scald devices	•	Orthodontic archwires
•	Arterial clips		Penile implant
•	Automotive thermostats	•	Pipe couplings
•	Braille print punch		Robot actuators
	Catheter guide wires		Rock splitting
	Cold start vehicle actuators		Root canal drills
•	Contraceptive devices	•	Satellite antenna deployment
•	Electrical circuit breakers		Scoliosis correction
•	Fibre-optic coupling	•	Solar actuators
	Filter struts		Spectacle frames
•	Fire dampers		Steam valves
•	Fire sprinklers	•	Stents
•	Gas discharge		Switch vibration damper
•	Graft stents		Thermostats
•	Intraocular lens mount		Underwired bras
	Kettle switches		Vibration dampers
	Keyhole instruments		ZIF connectors
•	Key-hole surgery instruments		

Important terms

Martenisite transformation, transformation austenite \leftrightarrow martensite, temperature hysteresis, damping capacity, one-way shape memory, superelasticity, two-way shape memory, stress-induced martensite (SIM), transformation temperatures A_f, A_s, M_f, M_s, M_d.



Questions

- 1. Define the principle of shape memory effect .
- 2. What is the basic of two-way shape memory effect?
- 3. Explain the superelasticity phenomena.
- 4. Can you explain damping properties of NiTi alloy?
- 5. Explain the differences of martensitic transformation in steels or $(\alpha+\beta)$ Ti alloys and shape memory alloys.
- 6. Can you cite the application of shape memory materials in medicine?
- 7. What is the limitation of application of NiTi based shape memory materials?
- 8. Can you name the applications of materials with superelastic properties (SIM)?
- 9. How do the alloying elements influence the shape memory effect?
- 10. Name the methods of transformation temperatures setting for SMA?

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6. **BIOCOMPATIBLE MATERIALS**



Time needed to study: 2 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- Define conditions of biocompatibility
- Describe differences between biocompatibility and bioactivity
- Name groups of materials used for biocompatible applications
- Name biocompatible metallic alloys and define their properties



Lecture

6.1 Basic characteristics of biocompatible materials

Biocompatible materials are any materials of natural of synthetic origin that are in contact with live tissue and/or biological liquids. Certain physical, chemical and mechanical features are required for the biological applications, based on the intended use in the living organism, for example, there will be different requirements for the bone substitutes and different for the substitutes of tendons and ligaments. In all the cases, the materials do have to be compatible with the body. In other words, the biocompatibility and in some case also the bioactivity are the key features in the successful implementation of the implants into the body.

When determining the biocompatibility, it is easier to determine which features do not satisfy it than to determine which ones represent it: biocompatible material must not damage the "in vivo" normal body functions, meaning that it must not cause any inflammatory, allergic, toxic or immunologic reactions, it must not influence the blood clotting or stimulate changes in plasmatic proteins and enzymes. Furthermore, it must not cause carcinogenic, mutagenic or teratogenic (total changes) effects on the surrounding tissue.

Bioactive material is much more aggressive in the body and produces the desirable specific reactions between the material and surrounding tissue, for example, it may support the connection of tissue when fixating an implant in the body. The example of this is the hydroxyapatite in the case of bone implants.

Most of the materials react with the surrounding environment and exhibit corrosion or dissolution (chemical effects), abrasion or wearing down (friction), mechanical damage (deformations, fractures, fatigue). Among the typical reactions of host environment there is the tissue adaptation, be it positive (osseointegration) or negative (shielding the load, inflammations, allergic reactions, or cancer).

Materials for internal use (in vivo) have to meet the demanding requirements. Among the most important ones there are:

- 1. biocompatibility: non-toxic, non-carcinogenic, causing no or very little side reactions with human body, chemically stable, resistant to corrosion
- 2. ability to withstand large and variable stress in the highly corrosive environment of the human body
- 3. possibility of preparation of complex shapes and sizes

6.2 **Properties requirements**

6.2.1 Mechanical properties

Biocompatible materials have to meet the requirements for high values of mechanical properties during the static and cyclic tests, in which the yield strength, tensile strength, elastic modulus, fatigue resistance, creep resistance compressive strength and resistance to abrasion are all monitored. The requirements for properties are different depending on the nature of application (compare the application in orthopedic and orthodontics) or the type of used material (ceramics, gel, metal alloy).

6.2.2 Corrosive properties

Materials have to be resist to various types of corrosion: total surface corrosion, pitting and crevice corrosion, corrosive cracking under stress, corrosion fatigue, and intercrystalline corrosion. None of these forms of corrosion, except for the surface corrosion, cannot be tolerated in materials used for surgery implants. The speed of surface corrosion in metallic materials must be less than 0.25 μ m/year. For oxide ceramic materials for bio implants, the corrosion is very little, but even ceramics is a subject to degradation in vivo. Polycrystalline spinel exhibits a decrease in static strength in the environment of body fluids. The higher the purity and density and lower the porosity of the ceramic materials, the higher the resistance to strength decrease in the body. However, the bioactive ceramics are another case, as they gradually release their cations and anions and incorporate into the bone structure or tissue. In these types of materials, the corrosion is not monitored.

We cannot talk about corrosion in polymers, but even these material are subject to degradation in the body. This is associated with the interaction of the tissue and the residual monomers remaining after the polymerization, with the chemical degradation of the molecular structure of the polymers and with the dissolution of the additives such as plasticizers, fillers and pigments. Sometimes the unfavorable crosslinking and the degradation of liner polymers may occur. Some manifest an occasional hydrolysis when absorbing lipids and interacting with proteins. The degradation of polymers is far more complex than in metals and ceramics.

6.3 Types of biocompatible materials

Among the materials which are used in the medical field, there are artificially prepared metallic, ceramic, composite and polymeric materials. In the following sections we will take a closer look at some of them.

6.3.1 Metals and metallic alloys

They have been used for a long time as biocompatible materials, often in orthopedics as replacement of hard tissue (bones), implants, intramedullary fixation, and coating of implants or in the orthodontics for dental fixation. We must not forget as well about some tools and parts of appliances.

The metallic materials are more suitable for the constructional biocompatible applications than polymeric or ceramic materials from the point of view mechanical properties such as the resistance to fatigue, fracture toughness, high strength and hardness. However, from the point of view of biocompatibility, there are only a few materials used in the industry, which are also suitable for a long-term use in the human body. The corrosive environment in the human body with low tolerance of living tissue and even of very low concentrations of most of the products of metallic corrosion removes most of the metallic materials from the game. The possible candidates, such as noble metals, are removed due to their unsuitable mechanical properties for the construction materials in orthopedics. Traditional materials used for replacements are stainless steel, Co-Cr alloys and Ti alloys. Recently also the Zr or Ta based alloys are being used, they are, however, very expensive. Despite the above mentioned positive properties of the metallic materials, it is possible to monitor certain negative reactions of the tissues in the orthopedic applications. The reactions are local, but sometimes they may be extended to greater distances. The stiffness of these materials, especially in steels and Co-Cr alloys, is high, their Young modulus is within the limits of 189-230 GPa, while in a human cortical bone it is only 10 to 20 GPa. These differences in elastic modulus that we may compare in the Table 6.1, as well as the unbalanced distribution of stress between the implant and the bone leads to a so-called stress shielding followed by resorption of the bone or even loosening of the implant. Another effect of the metallic materials behavior is the creation of degradation products followed by the reaction of surrounding tissues. This reduces the long-term functionality and durability of the joint prostheses.

If we were to design an ideal alloy for implants in orthopedics, then it should have the Young modulus of magnesium, strength of Co-Cr alloys, corrosion resistance and biocompatibility of titanium and the process ability of steel. Therefore, there is currently a search for suitable materials even among metallic foams or metallic glasses that may meet the specific demands for lower elastic modulus.

A little from history

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The first metallic alloy used for an implant to the human body, which was prepared already in the beginning of the 20th century was vanadium steel. The first implant were the bone fixation plates to stabilize bone fractures and speed up the recovery. But already these first implant brought the problems such as their crackling, low biocompatibility and corrosion in the human body, with the following loss of functionality. The selection of materials was also very limited at that time. In the 1920s Zierald published a study about the reaction of tissues to different metals. Iron and steels, the most widely used materials dissolved quickly and caused the erosion of surrounding bones. A significant change of tissue color has been observed around the samples from copper and nickel that were implanted into bones. Materials that did not cause coloring, Au, Ag or pure Al, were, on the other hand, too soft and weak for most of the applications.

In 1926 the stainless steel was introduced into surgery application with 18% Cr and 8% Ni. It was evaluated as the material most resistant to corrosion in the body fluids and also stronger than vanadium steel, initially introduced by Sherman.

Later in 1926 the 18-8Smo steel was used. It contained a small percentage of Mo to improve the resistance to corrosion in salt water and it is known until today as stainless steel 316. Since 1947 there were consideration about the possible applications of Ti and its alloys for implants. Pure Ti and its alloys manifested an excellent resistant to corrosion in body fluids. In the 1950s the content of C in the stainless steel 316 was lower from 0.08% to 0.03% to improve its resistance to corrosion. This steel was named 316L and is used in the field of biomedicine even today (Table 6.2).

Properties Material	Young modulus (GPa)	Y.S. in compression (MPa)	Fracture toughness (MPa√m)	Density (g/cm³)
Cortical bone	10-20	130 - 180	3 - 6	1.8 – 2.1
Magnesium	41 - 45	65 - 100	15 - 40	1.74 – 2.0
Ti alloys	106 - 117	758 - 1117	55 - 115	4.4 - 4.5
Co-Cr alloys	230	450 - 1000	-	8.3 – 9.2
Steels 189 - 205		170 - 310	50 - 200	7.9 - 8.1
Syntetic HA	73 - 117	600	0.7	3.1

Table 6.1 The comparison of mechanical properties of materials used for implants with the cortical bone

Note: HA - hydroxyapatite

Nickel containing stainless steels

All the stainless steels contain at least 10.5% Cr, which ensures the formation of a protective layer on its surface and allows the alloy to withstand in corrosive environment. The most widespread steel materials for implantations were the austenitic stainless steels 316 and 316L (AISI 316L (according to the ASTM: F55, F138)), which are alloyed with molybdenum compared to steels 304 (Table 6.2) and their resistance to corrosion (pitting and crevice) in chloride environment is higher. These steels are less economically demanding, can be prepared using standard methods (forming, welding) and their mechanical properties can be controlled (Table 6.2 a 6.3). Forged steel have a higher yield strength than cast steels, but their fatigue strength, biocompatibility and resistance to corrosion is lower than in other alloys used for implants. Steels, however are tougher and more processable.

The 316L steel is a modification of the 316 steel with a lower content of carbon. Another used steel is the 904L type, which is a low-carbon, highly alloyed steel with the addition of copper, therefore it achieves better corrosive properties in a reducing environment (in sulfuric acid). It has a higher resistance to pitting and crevice corrosion and also to stress corrosion cracking in chloride environments. The advantage is that it stays non-magnetic under all conditions and can be welded and shaped very well. Due to the higher contents of Ni and Mo its price is also higher.

In general, however, these steels are less resistant to corrosion than metallic materials, which we will describe below. Therefore their use in vivo is usually short-term, such as screws and plates for the bones, intramedullary fixations, temporary fixations, etc. Before sterilization, packaging and delivery for operational purposes, a passivation using the HNO_3 is carried out.

Element	Cr	Ni	Mn	Мо	V	Nb	Cu	Si	С	Ν	S	Р	Со	Oth.	Fe
Steel		wt.%													
304	19	<mark>10</mark>	1	-	-	-	-	0.5	0.015	-	0.015	0.023	-	-	Bal.
316L	16	<mark>12</mark>	<2	2.5	0.06	0.005	0.09	0.39	0.015	0.06	0.001	0.01	0.3	-	Bal.
904L	20	<mark>25</mark>	<1.5	4.5			1.5		0.02	0.1					Bal.
Rex734	21	<mark>9.4</mark>	3.5	2.4	<0.02	0.3	0.04	0.3	0.04	0.4	0.001	0.008	-	-	Bal.
P558	17.4	<mark><0.08</mark>	12	3.2	< 0.02	0.05	0.04	0.4	0.2	0.9	0.001	0.012	-	-	Bal.

Table 6.2 The comparison of chemical composition of steels used as biocompatible materials

Martensitic steels 410, 416, 420 and 440 are used for surgical instruments. These steels are hardened with higher content of carbon (up to 1.2%) and lower content of chrome (up to 12-18%). They do not contain nickel nor nitrogen. Due to their hardening, the cannot be shaped in cold, the have low weldability, lower resistance to corrosion and they are magnetic.

Nickel free stainless steels

These relatively new material were introduced for the reason of solving the problem of oversensibility of some people to nickel. The lower content of nickel that supports the resistance to corrosion in stainless steels is compensated by the higher addition of nitrogen, as you can see in the Table 6.2. Their preparation may seem problematic, since if the conditions during cooling (quenching) are not met, they may excrete nitrides, as stated in the diagrams on Fig. 6.1 and 6.2

Steel	UTS	Y.S.	Y.S.	Y.S.	A (%)	Z (%)	Hardness
	(MPa) SA	(MPa) SA	(MPa) (15%)	(MPa) (34%)	SA	SA	SA
304	515	205			40	50	(Rock) 80
316L	588	314	585	922	49	84	(HV30)155
904L	490	220			35		(RockB) 70-90
Rex734	898	584	912	1325	39	52	(HV30)289
P558	923	600	965	1419	54	74	(HV30)367

Legend: R_m = ultimate tensile strength, $R_{p0.2}$ = yield strength, A= elongation at break, Z= contraction in cross section, SA= homogenization, 15%=15% cold deformation by removal, 34%=34% cold deformation removal.

However, these types of steels exhibit a high mechanical values (Fig.6.3 and Table 6.3) and better resistance to corrosion than the 316 steel mentioned above. For the time being, they appear as an excellent material for future application from the point of view of properties combination (mechanical and corrosion properties, price, and production). These steels also found further applications (energetics, elastic elements in springs, railways, supporting elements, cutting tools, molds, dies and punches, nuclear reactors components, heavily loaded structural sections (thickness up to 200 mm) thanks to their excellent properties, such as in the Cr18Mn12 steel with 1% N:

- Super-high strength and good toughness: Y.S. > 760 MPa, Z > 50%, KCU > 0.7 MJ/m² (in small cross-section the UTS ≤ 2950 MPa)
- Holds the non-magnetic properties to a high degree of deformation in cold and in negative temperatures with 50% deformation in cold the Y.S. > 1800 MPa and there are stable non-magnetic properties
- Refractory material
- High resistance to cavitation, up to 20x higher than in 304 steel
- Higher resistance to abrasion by 30 to 80%



Fig.6.1 Pseudobinary phase diagram of the X20Cr17Mo3Mn10 steel depending on the concentration of nitrogen. Formation of nitrogen precipitates is probable for content around 0.4 wt. % N.



Fig.6.2 TTT diagram with cooling curves for steels with 17Cr, 3Mo, 10Mn and 0.9N. The occurrence of precipitates Cr_2N .

Element	BioDur® 108	BioDur 316LS	BioDur 23-13-5	BioDur734
Ni	0.05 max	13.00-15.50	11.50-13.50	9.00-11.00
N	>0.90	0.10 max	0.20-0.40	0.25-0.50
Mn	21.00-24.00	2.00 max	4.00-6.00	2.00-4.75
Si	0.75 max	0.75 max	1.00 max	0.75 max
Р	0.03 max	0.03 max 0.025 max 0.04 max		0.025 max
S	0.01 max	0.01 max	0.03 max	0.01 max
С	0.08 max	0.03 max	0.03 max	0.08 max
Cr	19.00-23.00	17.00-19.00	20.50-23.50	19.50-22.00
Мо	0.50-1.50	2.25-3.50	1.50-3.00	2.00-3.00
Cu	0.25 max	0.50 max	-	0.25 max
Nb	-	-	0.10-0.30	0.25-0.80
V	-	-	0.10-0.30	-

Table 6.3 Composition of BioDur alloys, the properties of which are on the Fig.6.3



Fig.6.3 Comparison of yield strength for four commercial BioDur alloys depending on the cold forming of wire. BioDur®108 is a nickel-free steel.

Co-Cr alloys

Co-Cr based alloy (*Vitallium*, ASTM: F75, F90) was first used in the 1930s as a cast dental alloy, and since the 1940s it has been used for orthopedic applications. Co-Cr based alloys exhibit a high mechanical properties and higher corrosion resistance the steels. Due to the highly alloyed state, there can be a galvanic corrosion in the environment of body fluids. However, the degradation is lower than in steels. Co-Cr alloys are resistant to corrosive fatigue and to stress corrosion cracking, their elongation is up to 8% and they are more resistant to fatigue failure than steels. Basically, there are two types of these alloys in applications:

- Co-28Cr-6Mo (F75) alloys cast dental alloy, joint replacements
- Co-10Ni-20Cr (F90) alloys forged in heat for highly stressed joints (knees, hips)

Metallurgical preparation of Co alloys is identical to Co super alloys: the hardening is performed by a solid solution at the presence of carbides. In shapeable alloys, it is possible to increase the toughness by hot forging, but it is necessary to lower the amount of C. The amount of Cr is decreased and the content of Ni increased to improve the workability. The amounts of elements, mechanical values of cast and forged alloys are compared to biocompatible materials in the Table 6.4 to 6.6. Further methods of preparation include precision casting, or HIP to decrease the porosity after vacuum casting or powder metallurgy, which subsequently determine the price of the products for applications.

6. Biocompatible materials

Metal / alloy		Composition (%)								
	Ni	Ti	Cr	Fe	Со	Мо	Та	С	others	
steel AISI 316	12 0		18 5	balance		30		0.08	0 75 Si [.] 0 03 P [.] 0 03 S	
51001 710	12.0		10.5	bulunce		5.0	5	max	0.75 51, 0.05 1 , 0.05 5	
cast Co-Cr	2.5		28 5	0.75	halanco	6.0		0.36	1.0 may Si	
	max		20.5	max	Dalatice		0.0		max	1.0 Max 31
wrought Co. Cr	2.5		20.0	3.0	halanco			0.15	15.2 \\/	
wrought co-ci	max		20.0	max	Dalance			max	13:3 W	
unalloyed Ti		balance		0.30				0.10	0.015 H; 0.13 O; 0.07 N	
Ti-6Al-4V		balance		0.25				0.08	6.0 Al; 4.0 V; 0.0125 H; 0.13 O	
MP35N	35.0		20.0		35.0	10.0				
		0.01		0.01		0.01	halanca	0.01	0.001 H; 0.015 O; 0.01 N;	
unanoyed Ta		0.01		0.01		0.01	balance	0.01	0.005 Si; 0.03 W; 0.05 Nb	

Tab.6.4 The composition of selected alloys and metals for surgical implants

Tab.6.5 Mechanical properties of selected alloys and metals for surgical implants

Metal/alloy	Y.S.	UTS	Α	Е
	(MPa)	(MPa)	(%)	(GPa)
Steel AISI 316 annealed	207	517	40	
Steel AISI 316 cold worked	689	862	12	200
Cast Co-Cr	450	655	8	248
Wrought Co-Cr	379	896		242
Ti Grade 4	485	550	15	110
Ti-6Al-4V annealed	830	895	10	124
Ti-6Al-4V heat treated	*	*		
Ta annealed	140	205		
Ta cold worked	345	480		
MP35N annealed	240-655	795-1000		228

Note.* the properties depend on the type of heat treatment

Tab.6.6 The influence of forging on the mechanical properties of Vitallium

	UTS (MPa)	Y.S. (MPa)	A (%)	Fatigue limit (MPa)
Treatment of alloy				/after10 ⁶ cycles, R=-1/
Wrought				
Proximal part of stem	1406.6	889.5	28.3	792.9
Distal part of stem	1506.6	1029.4	27.5	827.4-965.3
Cast (typically)	790	520	15	310

Titanium and its alloys

Ti and its alloys, the division and properties of which we have discussed in chapter 4, exhibit an excellent biocompatibility with low or no reaction with surrounding tissue. The corrosive resistance is ensured by an emerging coat of TiO_2 on the surface, which is easily restored at the temperature of surrounding tissue even in the environment of body fluids.

The composition and mechanical properties of selected Ti alloys used for biocompatible applications are listed in the Table 6.7 and 6.8. The friction and abrasion properties of titanium are different from the most of the other metals, which is a consequence of the adhesive oxide coating that stays undamaged at lower stress and at low sliding speeds (conditions in joints) However, if the coating is damaged and is not immediately restored, the abrasive wearing out will cause the formation of metal-metal contact and a cold connection. This process leads to higher rates of abrasion and wearing down. This is the reason the titanium-titanium connections (or with metal) are not used. Ti and its alloys, such as the pure Ti grade 4, Ti-6Al-4V, Ti-6Al-17Nb, Ti-15Mo, NiTi, are applied for example as femoral replacements with the joint head made of

CoCr or ceramics and the acetabulum of UHMWPE, screws, micro splints, vascular stents (shape memory alloys, see chapter 6.7). You may examine the selected application in Fig. 6.5.

Due to the effort to decrease the Young modulus in alloys used as orthopedics replacements, so that they approximate to the human bone (Fig. 6.4), the following β -alloys of Ti, which have a lower elasticity module, were selected as well for application in (Table 6.7):

Ti-15Mo	Ti-45Nb	Ti-30Ta
Ti-12Mo-5Zr-5Sn	Ti-13Nb-13Zr	Ti-35Zr-10Nb
Ti-15Mo-5Zr-3Al	Ti-16Nb-10Hf	Ti-8Fe-8Ta
Ti-12Mo-6Zr-2Fe	Ti-29Nb-13Ta-4.6Zr	Ti-8Fe-8Ta-4Zr
Ti-15Mo-2.8Nb-0.2Si	Ti-35Nb-7Zr-5Ta	

Table 6.7 Mechanical properties of titanium and selected alloys used in biomedicine

alloys	Microstructure	Young modulus E (GPa)	Y.S. (MPa)	UTS (MPa)	
CP Ti	α	105	692	785	
Ti-6Al-4V	α/β	110	850-900	960-970	
Ti-6Al-7Nb (protasul-100)	α/β	105	921	1024	
Ti-5Al-2.5Fe	α/β	110	914	1033	
Ti-12Mo-6Zr-2Fe (TMZF)	Metastable β	74-85	1000-1060	1060-1100	
Ti-15Mo-5Zr-3Al	Metastable β	82	771	812	
	aged β + α	100	1215	1310	
Ti0/20Zr-0/20Sn-4/8Nb-2/4Ta (Pd,N,O)	α/β	N/A	726-990	750-1200	
Ti-Zr	cast α'/β	N/A	N/A	900	
Ti-13Nb -13Zr	α'/β	79	900	1030	
Ti-15Mo-3Nb-0.3O (21SRx)	Metastable β + silicides	82	1020	1020	
Ti-35Nb-5Ta-7Zr (TNZT)	Metastable β	55	530	590	
Ti-35Nb-5Ta-7Zr-0.4O (TNZTO)	Metastable β	66	976	1010	
Bone	Viscoelastic composite	10-40	-	90-140	

Tab.6.8 Composition, preparation and mechanical properties of the Ti alloys for dental applications

alloy	Method of processing	UTS (MPa)	Y.S. (MPa)	A (%)	Vickerse hardness (HV)
Ti-20Cr-0.2Si	casting	874	669	6	318
Ti-25Pd-5Cr	Casting	880	659	5	261
Ti-13Cu-4.5Ni	Casting	703	-	2.1	-
Ti-6Al-4V	Casting	976	847	5.1	-
Ti-6Al-4V	Superplastic forming	954	729	10	346
Ti-6Al-7Nb	Casting	933	817	7.1	-
Ti-Ni	casting	470	-	8	190



Fig.6.4 The comparison of elasticity modules of various biocompatible alloys and the cortical bone.

Other metals and alloys

Other metals and their alloys are used as biocompatible materials as well. In the following list, some of them are mentioned together with their typical properties, advantages and limitations for applications:

- Pure tantalum corrosion-resistant, lower stiffness, high ductility and toughness, despite its price (10x higher than Ti) it is used for implants;
- Pure niobium lower density than Ta but the same properties;
- Magnesium alloys low elasticity module, biodegradable (current subject of research);
- Pure zirconium characteristics corresponding to Ti, but it is twice as expensive;
- Precious metals platinum, gold low strength (dental applications in alloyed state);
- Dental amalgams Hg + powder metals Ag, Sn, Cu, Zn (dental applications);
- Ni-Cr (crowns and bridges, dental applications).



Fig.6.5 Examples of medical applications of biocompatible materials: a) Stent from EllaCS s.r.o. [9] b) screws [10] and c) hip replacement [10]

6.3.2 **Bio-inert ceramics**

This category includes the inorganic non-metallic compounds with various combinations of ion and covalent bonds. Most of the materials in this group have a high Young modulus of elasticity, they are hard and fragile.

Application:	a) supporting structures (orthopedics and dental implants)b) coating material of metals (e.g.: hip joint head),
Materials:	oxides of Al, Zr, spinel/corundum, silane ceramics
	dental porcelain ($K_2O-Al_2O_3-SiO_2$),
	calcium hydroxyapatite (HA) (also included among biocompatible materials)

6.3.3 Polymeric materials

Biocompatible materials based on polymers are made up of small repeating units (isomers) connected to the chains. This structure is similar to the DNA. Manufacturing processes can change their mechanical properties, for example increase their strength and hardness at the expense of flexibility and elasticity.

Material:

- polyethylene (PE) depending on the preparation it may be elastic and flexible or hard and smooth Application: tubes for catheters, joint surfaces for total hip and knee replacements (smooth surfaces exhibit extremely low friction with other materials and exponentially increase the durability of artificial joints).
- silicone
- teflon, tetrafluoroethylene hardened by carbon fibers
- polymethyl methacrylate (PMMA), methacrylate resins
- polyester, polyurethane, polyvinyl chloride, polystyrene, polypropylene, polyacrylonitrile
- Gora-Tex (PTFE expanded polytetrafluoroethylene)

Application: vascular implants, angioplasties balloons, flaps, lens, membranes for dialysis etc.

Hydrogels

Polymer structures with hydrophilic crosslinking, which swell in water until creating a balance between the force of the network shrinking and the force of swelling. There are homopolymers, copolymers or multipolymers that are ionically neutral, anionic, cationic, or amphilytic.

The applications of hydrogels include a wide area according to the physical properties: contact lenses, wound covers, artificial cartilage and skin.

Biodegradable polymers

Natural and artificially prepared polymers that are biodegradable meet the requirements of temporary stability. After that, they decay (hydrolytic instability, hydratation, cleavage of the main molecular chain, the loss of molecular weight, dissolution.

Materials: collagen, chitosan, polyhydroxylalcanate (PHA), polyglycolic acid (PGA) polylactic acid (PLA), copolymers PGA and PLA and polydioxananon (PDS).

Used particularly as absorbable seams.

6.3.4 Composites

Two-phase materials consisting of a matrix and reinforcing fibers. For medical application, the polymeric matrices with carbon fibers are the most used. For more details about the nature of composite materials, see chapter 7.

6.3.5 Cements

Cements represent sealants and binders, which include for example:

- polymethyl methacrylate (PMMA) excellent mechanical adhesion to the bones and to metals as well; the most commonly used cement
- cyanoacrylate worse adhesion
- dental cements contain phosphates Zn, Si, reinforced ZnO/eugenol/EBA
- epoxy glues

ASTM	Biocompatibleí material
F55, F138	Low-carbon steel (type 316L)
F75, F90	Co-Cr alloys
F67	CP titanium
F136	Ti-6Al-4V
F451	Acrylic bone cement
F560	Unalloyed tantalum
F1713	Ti-13Nb-13Zr
F1813	Ti-12Mo-6Zr-2Fe
F2063	Ti-55.8Ni
F2066	Ti-15Mo
F4982	Ti-45Nb
F603	High purity compact aluminum oxide
F648	Ultrahigh molecular weight polyetylene (UHMWPE)
F881	Silicon gel and solid silicon

Tab.6.9 ASTM designation for the selected biocompatible materials



Important terms

Biocompatibility, bioactivity, Ti based alloys, corrosion environments of body fluids, Ni-free steels, stress shielding.



Questions

- 1. What are the basic characteristics of biocompatible materials?
- 2. Can you name the metallic alloys classed as biocompatible materials?
- 3. Which basic requirements must the biocompatible materials satisfy?
- 4. Can you select metallic alloys for orthopaedic applications?
- 5. What risks appear at application of metallic materials for implants?
- 6. How many times is lower the elastic modulus of cortical bone as compared with steel?
- 7. Can you name the materials suitable for bone or joints replacement in term of elastic modulus?
- 8. Against which type of corrosion must resist stainless steel implant applied in vivo?
- 9. What type of Ti based alloys are suitable for biocompatible application?
- 10. What elements contains the Vitallium alloy?
- 11. Why Ni-free steels are introduced in orthopaedic use?
- 12. Can you determine another beneficial properties of the Ni-free steels?
- 13. Which type of Ti alloy can be used for stents?
- 14. Do know the technological methods for preparing biocompatible materials?
- 15. Can you name some of them for Ti alloys, steels and Co-Cr alloys?

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7. COMPOSITE MATERIALS



Time needed to study: 3 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- define principle of composite effect
- describe types of matrix and reinforcement phases
- name physical and metallurgical parameters of composite materials



Lecture

7.1 Basic characteristics of composite materials

From the earlier chapters we know that materials can be classified into several groups with the basic division is represented by classification into metals, polymers and ceramics. Materials in these groups have characteristic properties as is shown on the general schematic on Fig.7.1. Metals are generally considered tough and ductile, but we also have to take into account their higher density in comparison with polymers which are light, but also shown low strength and lower mechanical properties, they can be brittle in some cases. Ceramic materials have high Young's modulus and theoretically very high strength in tension, but brittleness is their intrinsic property, so in reality they don't achieve high values of strength.



Composite materials

Fig.7.1 Schematic of basic material groups and their properties

The basic principle of composite materials is a macroscopic combination of two and more different types of materials, which usually do not mix and we can observe the interface between constitution components. If we are guided by their morphology and division of structures, we can prepare composite materials which properties are completely different from the properties of the basic components.

Composite materials are used not only for their advantageous construction properties but also for their electronic, thermal, tribologic or environmental applications. Optimization of composition and structure can lead to ensuring specific properties for given application. With regards to the fact that composite materials are today included in a large group of combined materials with different properties for a wide range of various applications, it is not easy to determine unified and simple definition which could be used in general. However, the most widespread definition is that composite materials are formed by a continual matrix joining stronger and harder reinforcing components for which it also is a carrier.

The result of a combination of two and more materials is a composite material, which characteristics are higher than an individual constitution component (matrix). Better construction (mechanical) properties are the result of decomposition of load between the matrix and the strengthening component.

Among the first modern composite materials, in use since 19th century, we can include reinforced concrete, which was formed as a combination of concrete with steel reinforcement. This group of material also includes the adobe bricks made from clay and straw which are used in house construction even today.

Another composite material is wood, which are cellulose fibers (long molecular chains, partially crystallized) and matrix based on wood and hemicellulose (amorphous component). In various climatic and soil conditions which have a significant influence on the growth rate and properties of wood, different types of trees grow which leads to significant differences in the achieved mechanical properties of wood.

7.2 Classification of composites

7.2.1 Constitution criterion

Composite materials can be divided based on a range of parameters. The basic specification is the composition of matrix and the type of reinforcing component.

a) according to the composition of the matrix

- 1. metal matrix composites MMCs, including metal foams with stabilizing component, the matrix may be pure metal or an alloy
- 2. ceramic matrix composites CMCs, the matrix may include oxides, nitrides, carbides, etc.
- 3. polymer matrix composites PMCs, (the matrix may constitute polyesters, epoxides, phenols, polyimides, melamines)
- 4. glass matrix composites GMCs
- 5. carbon-carbon composites CCCs

The selected material properties for matrices are stated in Table 7.1.

Table 7.1 Properties of materials for matrices based on polymers and alloys.

Property matrix	Density ρ (kg.m ⁻³)	Module of elasticity E (GPa)	Coefficient of thermal expansion α (10 ⁻⁶ m·m ⁻¹ K ⁻¹)	UTS σ (MPa)	Total deformation ε (%)
ероху	1.20	2.8-3.4	0.56	6.2-103	4.5
polyimid	1.43	2.8	0.51	90	7-9
polyester	1.10-1.40	3.4-5.6	0.4-0.7	21-69	0.5-5.0
polysulfon	1.24	2.8	0.56	69	50-100
polyetereterketon	1.20	3.6	0.5	69	2.0
Al alloys 2024	2.77	72	24	414	10
Ti-6Al-4V	4.43	110	9.6	924	8

b) according to the character of reinforcing component

- 1. composites reinforced by continual unidirectional fibers
- 2. composites reinforced by discontinuous (discreet) fibers or whiskers
- 3. composites reinforced by particles
- 4. composites reinforced by directional solidification of eutectic systems (in situ composites)

The first three types of reinforcing components are shown on Fig.7.2. Depending on the type and distribution of the reinforcing component, the yield strength is increased, as is shown in Table 7.2. for aluminum matrix and ceramic reinforcement. The reinforcements can be continual or discreet fibers. The yield strength increases due to dislocations which are formed due to different thermal expansion coefficients of the aluminum matrix and ceramic reinforcements.



Fig.7.2 The principle of composite materials: fibers, discreet fibers and whiskers, particles.

Table 7.2 The calculated values of the yield strength increase in a composite material compared with the values of the aluminum matrix material. The assumed particle size is $10 \,\mu m$. Volume fraction of ceramic particles is 20%.

Ceramic	Δσ (MPa)
Al ₂ O ₃	34.37
SiC	38.69
TiB ₂	38.69
AIN	39.29
CrN	41.13
Si ₃ N ₄	40.38
Silica glass	42.57
graphite	42.57

Reinforcement materials

Continual:

Fiber composites generally have reinforcements in one direction significantly more sizeable than in others, therefore we can say that their length is often comparable with the final size of the product (part). Continual fibers can be arranged in various ways, for example all fibers in one direction without distinctive layering, groups of layers on top of each other are perpendicular (Fig.7.2) or the fibers can be intertwined like reed mats. Of course, the character of reinforcement will be dependent on the internal microstructure. Fiber composites offer high mechanical properties in the direction of the axis of the fibers. The strength of the fibers depends on their diameter; it can be generally stated that with the decreasing diameter the strength increases, because due to special production methods the occurrence and size of defects in the microstructure is minimized, also a certain orientation of these defects is achieved in the fiber axis. In non-metallic fibers, the directional character of covalent bond has to be considered, which in case of correct crystallographic orientation of fibers allows for achieving high strengths. In Table 7.3, compare properties of selected materials for reinforcing fibers. Based on the character of the fibers, they can be divided into:

- ✤ glass (normal glass, pure SiO₂)
- polymers (Kevlar 29 and Kevlar 49)
- carbon (graphite)
- $\diamond \text{ ceramic } (B, Al_2O_3, Al_2O_3 + SiO_2, SiC, Si_3N_4, BeO)$
- ✤ metal (Nb₃Sn, Be, W)
- mineral fibers or lamellae (mica, asbestos) heat-resistant (refractory) materials

Discontinual:

Reinforcing element may be in form of particles, discreet fibers or whiskers (Table 7.3). In particle reinforcement, one dimension does not exceed other dimensions and they are generally strong and thermodynamically stable compounds (carbides, nitrides, oxides, borides). Whiskers are artificially prepared long single crystal formations of e.g. oxides or carbides, their diameter may be from a few nm up to several μ m and their length from several μ m up to several mm. The strength in tension with whiskers is very good, basically at the theoretical maximum of given material (see for example the data for SiC in Table 7.3). Fracture strength of single crystal whisker is generally significantly higher than in a polycrystal fiber from the same material. An unfortunate side-effect during processing of such materials is high health risk, because whiskers are very thin and light and can be easily breathed in. Similar to asbestos, they are do not exit the lungs and are considered carcinogenous. There are many precautions that have to be upheld when processing them.

Division of discontinuous reinforcements:

- SiC, TiB_2 or Al_2O_3 in form of whiskers
- particles SiC, Al_2O_3 , TiB_2
- ✤ short or split fibers of Al₂O₃, SiC, Al₂O₃+SiO₂ or carbon

Table 7.3 Properties of metallic and ceramic fibers

	В	SiC	Al ₂ O ₃	SiC	Al ₂ O ₃	BeO
Property	fiber	fiber	fiber	whisker	whisker	whisker
Module of elasticity E (GPa)	300-420	480	500	840	2250	720
UTS (MPa)	3000-3700	2300	2000	21000	15000	6900
Elongation to break (%)	0.7-0.9	0.5	0.4	2-2.5		0.8
Density (kg/m ³)	2650	3200	4000	3200	4000	3000
Maximum operating	500-700	900	800	1600	1000	1500
temperature (°C)						

7.2.2 Practical use criterion

Another division of composite materials can be done based on their use in practise::

- a) low-temperature composites (construction and other applications in automotive or aviation industries, etc.) with metallic, ceramic or polymer matrix;
- b) high-temperature composites with matrix based on Ni, Co, Ti and others (application in automotive or aviation industry, energy industry);
- c) special composites (application as materials for bearings, sports equipment and others).

7.3 Basic physico-metallurgical parameters of composite material preparation

Every component of a composite primarily has to bring its advantageous properties, the disadvantages are superimposed by the second partner. This advantageous partnership depends on the following *parameters*, which have to be taken into consideration at preparation phase and which influence the cohesion of the matrix and reinforcements:

- 1. good wettability of the reinforcing fibers by the matrix material
- 2. minimum development of chemical reactions on the fiber/matrix phase interface
- 3. properties of the reinforcement fibers' surface
- 4. the differences in coefficient of thermal expansions of the fibers and the matrix (Table 7.4)

	Module of elasticity (GPa)	Coefficient of linear expansion (x 10 ⁻⁶ K ⁻¹)
α-Ti	105	8.8
Ti-6Al-4V	115	8.8
TiB	550	8.6
TiC	460	7.4
TiN	250	9.3
SiC	420	4.3
Si ₃ N ₄	320	3.2
TiB ₂	529	6.4
B ₄ C	449	4.5
Al ₂ O ₃	350	8.1

Table 7.4 Elasticity limit and coefficient of linear expansion for selected matrices and reinforcements

Matrices have to ensure two important roles:

- it ensures transition of mechanical tensions affecting the composite material; for optimal transition, it has to adhere to well to the fibers and the fiber shift has to be minimal; on the other hand, the matrix cannot be too hard in order not to limit the work of the fibers, its ductility being an important parameter;
- easy preparation of composite, i.e. mixing (introducing) particles, discreet fibers or continual fibers

Observed mechanical properties

Matrices have higher ductility than fibers, but its strength (Fig.7.3) and hardness are lower, so they serve as transit environment of load which mainly affects the fibers, which have much higher strength and hardness.

Composite materials have to ensure the following characteristics based on their type:

- a) high strength levels
- b) high modulus of elasticity
- c) high fatigue limit
- d) high impact strength
- e) high-temperature strength



Strain (%)

Compared to pure metal one-component materials, composites have to exhibit:

- a) higher specific strength and specific hardness
- b) better resistance to fatigue and attrition
- c) improved high-temperature properties
- d) higher strength in tension
- e) lower creep rate
- f) lower coefficients of thermal expansion

If the composite C is formed by matrix M and reinforcement component R, then its overall mass m_C is :

$$m_C = m_M + m_R \tag{7.1}$$

The overall volume of the composite V_C with regards to volume of pores and contractions V_V is given by:

$$V_C = V_M + V_R + V_V \tag{7.2}$$

Then the density of the composite material is:

$$\rho_{C} = \frac{m_{C}}{V_{C}} = \frac{m_{M} + m_{R}}{V_{M} + V_{R} + V_{V}}$$
(7.3)

If we introduce an adjustment using dimensionless weight fraction *w*:

$$w_{M} = \frac{m_{M}}{m_{M} + m_{R}} \qquad w_{R} = \frac{m_{R}}{m_{M} + m_{R}}$$

$$\rho_{M} = \frac{m_{M}}{V_{M}} \qquad \rho_{R} = \frac{m_{R}}{V_{R}} \qquad w_{M} + w_{R} = 1 \text{ also applies}$$
(7.4)

then we can put density like this:

$$\rho_{C} = \left[\frac{w_{M}}{\rho_{M}} + \frac{w_{R}}{\rho_{R}} + \frac{V_{V}}{m_{M} + m_{R}}\right]^{-1} = \left[\frac{w_{M}}{\rho_{M}} + \frac{w_{R}}{\rho_{R}} + \frac{V_{V}}{\rho_{C}V_{C}}\right]^{-1}$$
(7.5)

If we put in an adjustment using a dimensionless volume fraction of porosity f_{V} :

$$f_V = \frac{V_V}{V_C} \tag{7.6}$$

density can be expressed like this:

$$\rho_C = \left[\frac{w_M}{\rho_M} + \frac{w_R}{\rho_R} + \frac{f_V}{\rho_C}\right]^{-1}$$
(7.7)

and the volume porosity fraction is:

$$f_{V} = \left[1 - \rho_{C} \left(\frac{w_{M}}{\rho_{M}} + \frac{w_{R}}{\rho_{R}}\right)\right]$$
(7.8)

If we introduce the dimensionless volume fraction for matrix and reinforcement phase:

$$f_{M} = \frac{V_{M}}{V_{M} + V_{R} + V_{V}} \qquad f_{R} = \frac{V_{R}}{V_{M} + V_{R} + V_{V}} \qquad \text{kde } f_{M} + f_{R} = 1 \qquad (7.9)$$

we obtain density expressed like this:

$$\rho_C = \frac{m_C}{V_C} = \frac{\rho_M \cdot V_M + \rho_R \cdot V_R}{V_M + V_R + V_V}$$
(7.10)

For simplification:

$$\rho_C = f_M \cdot \rho_M + f_R \cdot \rho_R \tag{7.11}$$

In case of of fiber composite with volume fraction f_f of fibers parallel to the tension axis, the deformation in fibers f and matrix M is identical (iso-deformation $\varepsilon_{\rm C} = \varepsilon_{\rm f} = \varepsilon_{\rm M}$), then the overall tension can be calculated:

$$\sigma_c = f_f \cdot \sigma_f + (1 - f_f) \cdot \sigma_M \tag{7.12}$$

according to Hook law $\sigma = E \cdot \varepsilon$, we can write:

$$\sigma_{c} = f_{f} \cdot E_{f} \cdot \varepsilon + (1 - f_{f}) \cdot E_{M} \cdot \varepsilon$$
(7.13)

and for elasticity modulus of composite, this applies:

$$E_{c} = f_{f} \cdot E_{f} + (1 - f_{f}) \cdot E_{M}$$
(7.14)

For a composite with fibers perpendicular to the tension axis, the tension in fibers and matrix is the same, then the deformation is:

$$\varepsilon = f_f \cdot \varepsilon_f + (1 - f_f) \cdot \varepsilon_M = f_f \cdot \frac{\sigma}{E_f} + (1 - f_f) \cdot \frac{\sigma}{E_M}$$
(7.15)

and modulus of elasticity:

$$E_{c} = \frac{\sigma}{\varepsilon} = \frac{1}{\frac{f_{f}}{E_{f}} + \frac{(1 - f_{f})}{E_{M}}} = \frac{E_{f} \cdot E_{M}}{f_{f} \cdot E_{M} + (1 - f_{f}) \cdot E_{f}}$$
(7.16)

The last two equations are stated on Fig.7.4 as upper and lower limit of modulus of elasticity of the composite. Anisotropy properties are used in sports equipment (golf clubs, bars for long jump). In some cases however it is not suitable and then the fibers are put in in a "crisscross" way in order to limit possible problems.



Fig.7.4 Schematic representation of the dependence of Young's modulus on volume fraction of fibers in a composite material. Crosses mark values for particle composites for comparison (Adjusted according to [5]).



Fig.7.5 Composite material with continual fibers: curves of a) stress-strain dependence for matrices and fiber and b) strength of the composite dependence on volume fraction of the fibers (Adjusted according to [5]).

Composite materials lose their efficiency at critical deformation which corresponds to deformation at fiber fracture ε_{f} . From this point of view, the strength of the composite σ_C moves between σ'_M and σ_f , with the lower limit of strength is the matrix strength limit σ'_M . From equation (7.12) is deduced the dependence of strength limit of a composite σ_C on volume fraction of fibers f_f , with its decrease, the strength decreases as well, as is shown in Fig.7.5. If the matrix-fiber connection is to exhibit suitable properties, the volume fraction f_f has to reach critical value f_{krit} . For critical state of the material applies:

$$\sigma_M = \sigma_C \quad \text{a} \quad f_{krit} = f_f, \tag{7.17}$$

therefore

$$f_{krit} = \frac{(\sigma_M - \sigma'_M)}{(\sigma_f - \sigma'_M)}$$
(7.18)

In practice, this means that low fraction f_{krit} and high strength σ_f is required. If the matrix is strongly reinforced, the nominator increases $(\sigma_M - \sigma'_M)$ in equation (7.18) and therefore high volume fraction of fibers f_f is necessary for the required composite effect.

7.4 Metal matrix composite materials

7.4.1 Types of metal matrix composites

Metal Matrix Composites - MMC - can be further divided based on what alloys (or pure metal) forms the matrix:

- with matrix of Al or Al alloys reinforced by fibers or particles: SiC, Al₂O₃, graphite fibers, Si₃N₄, TiB₂; influence of the volume of reinforcing phase SiC on selected mechanical properties for Al matrix is given on Fig.7.6
- 2) with matrix of Ti alloy reinforced by SiC, or possibly W fibers coated by C and TiB₂
- 3) with matrix of Mg reinforced by graphite fibers, Al₂O₃, SiC, B₄C particles
- 4) with matrix of Cu reinforced by graphite fibers
- 5) with matrix of Ni based superalloys reinforced by W-Re-HfC fibers or ceramics (due to reactivity of fibers of high-melting metals with alloy, it is necessary to protects the fiber by coating)
- 6) with matrix based on IMCs (Ni, Ti and Fe aluminides)

7.4.2 Mechanical properties

Mechanical properties of composites depend on:

- 1. phase properties, i.e. their mechanical characteristics (yield strength, hardness, modulus of elasticity and others) and anisotropy of these phase properties;
- 2. volume representation of phase, their size, geometrical shape, type and arrangement;
- 3. interaction between phases and properties of their contact;
- 4. interaction with the surrounding environment;
- 5. thermo-mechanical history of the material (production technology, thermal processing, external loads, etc.).

The influence of aforementioned parameters on properties of selected composites can be compared in Table 7.5 and 7.6. It has been observed that a general trens in an increase of strength limit and ductility with decreasing particle size in particle-reinforced composites. This effect can be attributed to an increase in particle strength with the reduction in their size. It has indeed been found out that at certain particle size, the probability of tension-dependent limited yield increases. If there are relatively big particles in the composite, then they can be damaged even in the production process and do not fulfill their function. Then it can seem that composites reinforced by large particles exhibit lower strength than the basic matrices. In Table 7.5 you will find comparisons of experimentally observed contribution of 20% fraction of SiC particles in aluminum alloy to an increase of yield strength dependent on the size of their particles with values calculated. From this comparison is evident an influence of growing particle size on the decrease in contribution related to the increasing distance between particles. Experimental values were lower than the ones calculated, we can consider the irregular shape and irregular distribution of the real particles played a part in this deviation, or a possible damage of particles due to the technology of their production.

Influence of matrix composition and shape of the reinforcement on the progress of tension test is shown on Fig.7.6. If for example a Al99.85 matrix or AA6061-T6 aluminum alloy matrix is reinforced by 20 volume % of short fibers (20s) or particles (20p), we can observe an increase in yield strength and hardness limits on the tension test diagram. The influence of reinforcement character of the Ti-6Al-4V alloy matrix is given on Fig.7.7 with a progress of tension test for composite either with TiB fibers or with TiB fibers and TiC particles.

Particle size	Δσ (MPa)	Δσ (MPa)
(µm)	calculated	experimental
0.5	98.72	60
10	61.75	34
70	34.80	27
250	19.55	10

Table 7.5Influence of particle size on yield strength. Comparison of calculated and experimentally obtained values.
Volume fraction of SiC particles is 20%.

Table 7.6 Typical characteristics in tension and fracture strength of cast discreetly reinforced composite materials with Al alloy based matrices (results published by Triton System Inc., MMCC Inc. and MSE Materials Inc.).

Alloy	Reinforcement (obj.%)	Heat treatment	Young modulus (GPa)	Y.S. (MPa)	UTS (MPa)	Fracture toughness (MPa.m ^{-1/2})	Elongation (%)
2219	40 SiC	T4	-	276	345	-	0,8
Al-Si	40-55 SiC	Т6	180-200	-	300-500	10-25	-
Al-Cu-Mg	40-55 Al ₂ O ₃	Т6	170-190	-	300-500	15-30	-
Al-10Si-1Mg	20 SiC	Т6	108	334	353	15.8	0.52
Al-10Si-1Mg	30 SiC	Т6	125	-	371	14.7	0.4
Al-10Si-1Mg	40 SiC	Т6	147	270	370	-	0.4
Al-7Mg	60 SiC	-	202	441	454	15.1	0.5

Influence of the volume fraction of discreet reinforcing TiB component and type of alloy used for matrix, as for example alloys α , $\alpha+\beta$ and β , on the elasticity modulus can be observed in the graph on

Fig.7.8. α alloys with higher content of Al exhibit highest modulus for all TiB content percentages, which predetermines them for high-modulus applications.

Concrete values of selected mechanical properties alongside the method of the composite preparation depending on the matrix composition are given in Table 7.7. Yield strength depending on the matrix composition in various Ti composites with 10% TiB volume fraction compared with 21-4N steel and formed Ti alloy IMI 834 are shown on Fig.7.9. The highest yield strength values at 800°C are preserved by MMC with Ti-Al-Sn-Zr-Nb-Mo-Si based alloy matrix.



Fig.7.6 Stress-strain dependence of Al99.85 and AA6061-T6 aluminum alloy matrix and composites reinforced by particles (20p) and short fibers (20s). The arrow marks that the test of the sample was stopped before break.



Fig.7.7 Comparison of tensile test values of pure matrix Ti-6Al-4V and sintered Ti-6Al-4V composite with TiB fibers and/or TiC particles $(TiB_w + TiC_p)$ $(TiB_w:TiC_p = 1:1)$.

Anisotropy of mechanical properties exhibits in fiber composites. If the fibers in the composite material are aligned parallel to the tensile axis (0° orientation), they increase their longitudinal strength by a factor of 3. The composite with this orientation exhibits properties of the reinforcements and its strength may be several orders higher than that of the unreinforced matrix. These composites preserve their strength and stifness even at elevated temperatures.
Composition of matrix (wt.%)	Volume fraction of TiB (%)	E (GPa)	σ _v (MPa)	о_{итs} (MPa)	A (%)	Processing methods
Ti (ASTM Grade-4)	0	110	480	550	15	W
Ti-6Al-4V	10	136.6		1000	0.25	MA+HIP
Ti-24Al –10Nb (at%)	10		*	695	0	PM+HIP
Ti-6Al-4V	11	144	1315	1470	3.1	GA+HIP/E
Ti	15	139	842	903	0.4	VAR+HS
Ti-5Al-2.5Fe	15	151	*	1092	0	PM+HIP
Ti	20	148	*	673	0	PM
Ti-6Al-4V	20	154	1170		2.5	MA+HIP
Ti-4.3Fe-7Mo-1.4Al-1.4V	0	110		1080	17.5	MM+CIP+S+HS
Ti-4.3Fe-7Mo-1.4Al-1.4V	10	134		1380	7	MM+CIP+S+HS
Ti-4.3Fe-7Mo-1.4Al-1.4V	20	156		1640	3	MM+CIP+S+HS
Ti-4.3Fe-7Mo-1.4Al-1.4V	30	180		1820	1	MM+CIP+S+HS
Ti-6.4Fe-10.3Mo	34	163.2	*	737	0.49	PM
Ti-24.3Mo	34	171.2	*	1105	0.85	PM
Ti-53Nb	34	122.12	710	724	1.65	PM
Ti-6Al-4V	20	170	1181	1251	0.5	PM+E
Ti-6Al-4V	40	210		864	0	PM+E

Table 7.7 Mechanical properties at room temperature in discontinually reinforced Ti alloys with various volume fraction of TiB in comparison with 21-4N steel and IMI834 Ti alloy.

Note: abbreviations in the *processing methods*: W -welding, MA-mechanical alloying, MM -mechanical mixing, PM - powder metallurgy, GA - gaseous argon atomization, VAR - vacuum arc remelting, CIP -cold isostatic pressing, HIP - hot isostatic pressing, E -extrusion, S -sintering, HS -hot swaging.









If load is applied off-axis, the properties of the composite quickly decrease, as shown on Fig.7.10. At 90° orientation of the affecting tension to the fibers (the fibers are perpendicular to the tensile axis), the transverse strength may be around 10% of the longitudinal strengths. If we are to achieve higher strength of the composite even in perpendicular direction, it is suitable to prepare a cross-ply laminates (Fig.7.2).

The character of fracture is also very strongly dependent on strength of particles and strength of the particle/matrix interface. Fig.7.11 schematically explains this dependence. In case the strength of the interface is greater than the strength of the particle (for example in a matrix strengthened by aging), then the particles fracture before the interface. Cavities emerge in the matrix and localization of yield between the fractures particles leads to damage of the composite. Another case on Fig.7.11 is that the interface strength is

AI-2.5Li/ALO, fibers

90

a)

Al-2.5Li/Al Og fibers

test

an

6

1.2

Tensile test

much lower than the strength of the particle (for example in an over-aged matrix). In this case a cavity begins to form and grow on the interface due to decohesion of the matrix from the particle. Subsequently, a yield break occurs across the matrix itself with final damage of the composite.

500

400

Stress (MPa) 300 200 100 Fig.7.10 Stress anisotropy of Al-2.5Li composite with Al₂O₃ fibers versus strain in dependence on the applied 0 loading in the direction of the fibers (0°) or perpendicular to 0.2 0.4 0.6 0.8 Strain (%) them (90°) in a) tensile and b) compression tests. 1500 0 Compression Stress (MPa 1000 500 0 2 3 4 Strain (%) Particle fracture Void growth Elastic loading Shear fracture $\sigma_{p,f} < \sigma_{interface}$ Ductile and shear fracture Particle-matrix of matrix decohesion Fig.7.11 Two possible ways of tensile damage evolution of particle MMC: a) strength of the interface is greater than the particle's and b) strength of the interface is lower than that of the particle.

7.4.3 High- temperature behavior of composites

> O_{interface}

 $\sigma_{p,f}$

At high temperatures and affected by stress, plastic deformations occur in the materials even at stress levels that are under the yield strength limits. Therefore it is necessary to characterize materials used in elevated temperatures in terms of creep resistance. Deformation rate at creep depends on material properties, construction load, period and temperature of explosion. Depending on the size and period of the stress effect, the deformation can be so big that the part ceases its ability to perform its function.

Stages of creep

쁢

Let us quickly look at the basic processes and terms for observing creep in materials (Fig.7.12). In the initial transition stage of creep, also known as *primary creep*, (area I on Fig.7.12b) is the deformation rate relatively high, but decreases with time. This can be attributed to the mechanism of deformation strengthening, which occurs due to the movement of dislocations, their local grouping in the crystal volume and formation of some dislocation formations that prevent further movement of other dislocations. The deformation rate slowly falls to its minimum and becomes almost constant (area II on Fig.7.12b), which can be microscopically explained as a certain equilibrium between deformation strengthening on one hand and thermal destabilization on the other due to elevated temperature. This equilibrium state, which is relatively well studied, is called secondary or *stationary creep*.

If we talk of deformation speed in creep, we mean the speed in this secondary state, which is closely related to the mechanisms of creep: Nabarro-Herring creep (diffusion in the volume), Coble creep (diffusion along the grain boundaries), dislocation climb, climb assisted by yield of obstacles, thermally activated yield.

In the last stage, called *tertiary creep*, a diagonal narrowing of the parts occurs, due to which the deformation rate increases exponentially with the stress and the material finally fractures. This state is shown on Fig.7.12b as area III. This image only shows creep deformation with composite materials, which have much more complex behavior when affected by creep, depending on many parameters, among the most important of which is the nature of reinforcement, compare Fig.7.12a and b.





For metal or alloy, the dependence of stationary creep rate $\dot{\varepsilon}$ on the tension σ at medium tensions is expressed by the following function

$$\dot{\varepsilon} = A \cdot \left(\frac{\sigma}{G}\right)^n \exp\left(-\frac{Q}{R \cdot T}\right)$$
(7.16)

where A is constant, n is the tension exponent, Q is activation energy, R is universal gas constant and T is absolute temperature.

The creep process im metal alloys includes yield and climb of dislocations, viscous yield of dislocations dragged by dissolved atoms and diffusion creep. These mechanisms are usually determined by the value of exponent *n* and the activation energy *Q*. Discontinually strengthened composites with titanium matrix are characteristic for their high coefficient *n* and high activation energy *Q* (Fig.7.13). This atypical behavior requires introduction of tension threshold, which limits the creep threshold. Due to the fact that creep deformation is not controlled by the tension σ occurring but rather by effective tension $\sigma_c(=\sigma-\sigma_0)$. By introducing tension threshold, we can satisfyingly explain high values of exponent *n* in Al and Ti composites:

$$\dot{\varepsilon} = A \frac{D_{\rm L} E b}{kT} \left(\frac{\sigma - \sigma_{\rm o}}{E}\right)^{4.2} \tag{7.17}$$

$$\dot{\varepsilon} = 6.5 \times 10^2 \frac{D_{\rm L}Gb}{kT} \left(\frac{\sigma - \sigma_{\rm o}}{G}\right)^{4.3} \tag{7.18}$$

Very soon at high tension load during creep test of MMC composite with Al matrix, tertiary creep occurs. Initially only small deformation appear and then a strongly localized deformation initializes around the reinforcement. Thus we can not always conclusively attribute minimal deformation rate at load by high tension to the rate of secondary deformation at stationary creep. If the creep tests are performed under pressure of by yield, it is possible to distance the tertiary creep state and determine more precise parameters of stationary creep.



Fig.7.13 Steady-state creep rate dependence on the applied stress at 550°C for Ti and in situ Ti/TiB_w fiber composite with various volume fraction of the TiB_w fibers.

We will not look in detail at the effect of reinforcement on creep in MMCs with Al matrix. In these composites, there is a strong dependence of the rate of stationary creep on the tension in effect, exponent *n* moves within 7-25 (in non-reinforced Al alloys, *n* is approximately 4). Their activation energy of creep *Q* is more strongly dependent on temperature than in self-diffusion of Al, i.e. the value of *Q* specifically moves between 200 to 500 kJ/mol in a composite and around 146kJ/mol for Al. From this point of view, the creep behavior of composite materials can be attributed to dispersely strengthened alloys in which the tension threshold σ_0 is determined, up to which creep does not occur. In contrast with the dispersely strengthened alloys in which the critical tension is related to interaction of dislocations and fine dispersed particles, in MMC composites, this critical tension is much more complex and it is not always possible to explain it to our satisfaction. Here we have to add that the tension in effect is affecting the matrix as well as the reinforcement.

The evaluation of creep comes from an assumption that there is a deformation in the matrix due to dislocation climb. We have already stated that during creep, fractures are initiated in the surroundings. This micromechanism is describable using two components of creep - the creep occurring within the matrix and the viscous (or diffusion) creep on the matrix/reinforcement interface.

Creep within the matrix can be expressed using the following relation, where we have introduced actual tension in matrix, threshold stress for creep, volume diffusivity and properties of matrix dislocation (Burgers vector):

$$\dot{\varepsilon} \approx \{(1 - \alpha_{LT})(\sigma - \sigma_0)\}^n \exp\left[-\frac{Q}{RT}\right]$$
(7.19)

The diffusion creep rate is of similar nature and in case of Nabarro-Herring creep and is related to the transport of atoms within the matrix around the reinforcement. The rate includes stress, that the reinforcement emits, size of the reinforcement and parameters linked with the transport of matter in the surroundings of the interface (i.e. coefficients of diffusion on interface, effective width of the interface through which the diffusion process occurs and volume of the diffusion matter). Stationary creep stops in the moment when both aforementioned creep components are in equilibrium.

Continual fibers should ensure higher resistance to creep than in particle of discreet fiber reinforcements. With parallel load the fibers transport most of the stress, therefore the creep rate is related to the creep properties of the fibers. Fibers are deformed elastically and overall creep deformation of the composite ε_{c} occurs asymptotically from the immediate value $\varepsilon_{t=0}$ to the maximum ε_{max} . Creep deformation of the composite ε_{c} within a certain period *t* may be expressed using the following relation:

$$\frac{1}{\left(\varepsilon_{\max} - \varepsilon_{C}\right)^{n-1}} - \frac{1}{\left(\varepsilon_{\max} - \varepsilon_{t=0}\right)^{n-1}} = \frac{A \cdot E_{M} \cdot \left(1 - f_{f}\right)}{E_{C}} \cdot \left(\frac{f \cdot E_{f}}{1 - f_{f}}\right)^{n} \cdot t$$
(7.20)

where the creep of the matrix is given by $A \cdot \sigma^n$, $\mathcal{E}_{t=0} = \sigma/E_C$ and $\mathcal{E}_{max} = \sigma/E_f$. E_C , E_M a E_f are moduli of elasticity of the composite, matrix and fiber, f_f is the volume fraction of the fiber, σ is the stress and A and n are constants.

However, as we have stated earlier, anisotropy of mechanic properties occurs in fiber composites dependent on the orientation of fibers, i.e. the resistance to creep will be strongly dependent on the direction of the fibers related to the stress, as can be observed on Fig.7.14 and 7.15 for composites Ti-SCS-6 with Ti based matrix and continual SiC fibers. Creep rate in case of fibers parallel to the stress is very low.

In stress that acts perpendicular to the fibers, the creep rate increases, especially if cyclic temperature changes co-affect the material. Creep life is lowered when there is a yield on the interfaces, therefore for creep resistant materials, strong matrix/fiber interfaces are required..

Progress of behavior of SCS-6/TIMETAL 21S alloy with 20 volume % SiC fibers in creep at 650°C and load of 55 MPa is described by Fig.7.14. The diagram with the progress of the creep test distinguishes for distinct areas: in *stage I*, the primary creep of the matrix begins to occur with partial separation of matrix and fibers (decohesion, disconnection). *Stage II* is of linear nature and is similar to stationary creep in non-reinforced Ti alloys, we can therefore consider that in this stage, creep of the matrix occurs with the same ration of matrix separation from fibers as in stage I. In other words, the separation of matrix and fibers in no too significant and the composite can still perform its function.

In *stage III* the response of the composite to creep is no longer linear and we can assume tertiary creep occuring within the matrix. The linear nature of the following *stage IV* forces us to consider that there has to be some other mechanism for explaining why the composite has not fractures immediately after stage III. Based on experimental results, the non-linear stage III (i.e. the transition between two linear areas I and II) can be explained by a slow spread of fractures from the interface to the surrounding fiber. This then means that in stage III, the process of separation accelerates and from the original state in stage I, it moves into a state where the fibers are completely disconnected from the matrix, with the creep within the matrix continuing in the characteristic stationary creep. Linear progression of the stage IV then answers the continual stationary matrix creep occurring at the same time with the matrix and fiber separation.

The experiment on Fig.7.14 was not performed to its end and was stopped after approximately 16 day, so we cannot completely observe the final stage of creep in this composite, and thus the overall damage of the matrix and fibers. It is necessary to highlight, that this phenomenon is not applicable generally to all



Fig.7.15 Influence of SiC fiber orientation (SCS-6) on creep resistance of Ti alloy matrix composite (TIMETAL 21S). Comparison with creep resistance of fibers and matrix at 650°C in tensile test (Adjusted according to [10]).

Comparison of the answers of composite with TIMETAL 21S matrix at 650°C to a load parallel or perpendicular to its SiC fibers is shown in Fig.7.15. In case of diagonal load, appearance of three stages is characteristic. In stage I, linear elastic deformation of both components occurs and matrix-fiber interface remains connected. Stage II starts with the bending of the curve on Fig.7.15 which is in direct relation with the interface separation. During this stage, the components in the composite separate, as was shown on Fig.7.14, and the interface opens up, the matrix starts to undergo plastic deformation. In stage III, the separation of both components and opening of the interface continues, with the matrix undergoing big plastic deformation. Similar progress of creep tests in MMCs with Ti matrix has been observed in a wide interval of temperatures; we can therefore say that this progress of behavior is typical for Ti based composites.

The properties of the microstructure - of the matrix and reinforcing component as well as the overall composite - have a significant influence on creep:

- 1. Composites prepared using power metallurgy have higher creep resistance than cast composite due to presence of oxide particles in the matrix due to oxidized surface of the initial Al powder during the PM technology itself; these oxide particles prevent dislocation movement similar to precipitates.
- 2. Size of the reinforcing component if a very important factor. Small and more numerous particles contribute much more effectively to the increase of creep resistance because they are a more effective obstacle for dislocation movement and they also stabilize grain growth.
- 3. The distribution of particles within the matrix has a significant effect on creep damage. If clusters of particles appear, this leads to strong tendency to form cavities near the reinforcement and to fast composite damage. In case of isolated particles, these fractures only form on their sharp edges.
- 4. Properties of composites, whose alloy in matrix may be hardened by thermal processing (such as Al alloy of class 2xxx, 6xxx or 7xxx) will be strongly influenced by further thermal processing. If we add a strengthening component which has a different coefficient of thermal expansion than the matrix, then at cooling, dislocations occur within the matrix due to relaxation of the tension. These structural defects however then become nucleation centers for precipitation of particles of the secondary phase in the matrix, which accelerates the aging process of the alloy. In Table 7.8 you can compare how two aluminum alloys Al-Cu (class 2014) and Al-Mg-Si (class 6061) which were strengthened by an addition of 15 volume % of Al₂O₃ behave at elevated temperatures. In both cases it will be clear from Table 7.8 that the strengthening component increases creep resistance of both alloys.

Bending creep resistance in MMC materials based on Ti alloys is given in comparison with 21-4N steel on Fig.7.16. The highest creep resistance at 800°C is exhibited by the composite with matrix based on

Ti-Al-Sn-Zr-Nb-Mo-Si alloy, i.e. it is better than in the case of IMI-834 alloy and MMC with matrix of Ti-6242S. Highest creep resistance on this diagram is exhibited by an MMC composite with matrix based on intermetallic alloy Ti-33,5Al.

Fig.7.16 Influence of matrix on the bending creep resistance at 800°C in comparison with intermetallic alloy IMI-834 and steel 21-4N (strength of these materials is given on Fig.7.9)



Table 7.8 Tensile mechanical properties at elevated temperatures for two aluminum alloys strengthened by 15 vol.% of Al₂O₃ particles.

		Y.S. (MPa)	UTS (MPa)		Y.S. (MPa)		UTS (MPa)	
Temperature (°C)	2014	+ 15 vol.% Al ₂ O ₃	2014	+ 15 vol.% Al ₂ O ₃	6061	+ 15 vol .% Al ₂ O ₃	6061	+ 15 vol.% Al ₂ O ₃
22	524	531	476	503	276	324	310	365
93	434	490	393	425	262	290	283	331
149	379	434	352	388	248	269	262	303
204	310	338	283	283	221	241	228	262
260	172	214	159	159	165	172	172	179
316	76	110	62	85	90	110	97	117
371	41	55	34	43	55	62	59	69

7.4.4 Fatigue of MMC

Service life of the matrix may be extended by adding reinforcement or degraded as was found at various fatigue tests with different loads:

1. In terms of fatigue caused by stress, composites exhibit much lower overall deformation than nonreinforced alloys during cyclic fatigue. This can be explained by a higher value of Young modulus and higher strengthening rate of a composite compared to monolithic matrix, therefore the service life is extended.

2. In terms of fatigue caused by deformation, a composite undergoes higher stress during the cycle than non-reinforced alloy at comparable level of input deformation. This speeds up formation of fatigue fracture in the composite and degradation of its service life.

We can therefore state that in the first case, the increasing volume fraction of discontinual particles increases the service life of a composite due to increase of elasticity modulus and strengthening rate while it degrades it in the second case.

Size of the reinforcement also has influence on fatigue. Composites with smaller particles usually have higher service life, which can be closely related to the distance between particles and their fracture properties. If we take into consideration the fracture character of ceramic particles of the reinforcement, then the bigger particles will have higher tendency to fracture than smaller ones. Furthermore, as was mentioned earlier, preserving the same volume fraction of the reinforcement the distance between bigger particles is greater than between smaller particles. Smaller particles and shorter distances between them represent a more effective obstacles for dislocation movement. This leads to a conclusion that bigger particles will degrade the service life of a composite.

Fatigue behavior of a composite with aluminum matrix reinforced by 45 volume % of Al_2O_3 fibers on Fig.7.17 depends on the size of stress and character of the fatigue test. In high-cycle fatigue with low stress, longitudinal fracturing between fibers was the prevalent damage mechanism (Fig.7.17a). We can assume that the fracture were initialized on the fiber breakage and then grew parallel to the fiber direction. With the increasing size of cyclic tension in the transition method from high-cycle to low-cycle fatigue, the longitudinal fracturing was accompanied by diagonal cracks in the matrix between fibers. At high stresses (low-cycle fatigue), one catastrophic fracture spread perpendicular to the fibers (Fig.7.17b).

In general, the fibers in the fiber-reinforced composite cause a delay in fracturing, but the nature of the fubers, fiber/matrix interface and/or phases formed in the reaction zone near the interface may significantly influence processes of fatigue fracture growth. In composites with relatively high strength of their interface, the fracture spreads directly through the fibers (Fig.7.18a). If the interface is weak, the separation of fibers from the matrix occurs as well as diversion of fracture, bridging and subsequent ejection of the fiber (Fig.7.18b).



Fig.7.17 Mechanisms of fatigue fracture in fiber composite with aluminum matrix and Al₂O₃ fibers: a) with low stress (high-cycle fatigue) - longitudinal fracturing between fibers is the dominant mechanism; b) high stress (low-cycle fatigue) - on fracture spreads. (Adjusted according to [2]).



Cycles

Fig.7.19 Service life depending on stress and temperature in thermally processed aluminum alloys class 6xxx and composites with aluminum matrix.

7.4.5 Corrosion

Predominantly local corrosion occurs in MMC composites due to the formation of galvanic cells between the matrix and the reinforcement, crevice corrosion on the matrix/reinforcement interface and point corrosion due to the reaction of products on the interface.

Galvanic corrosion is controlled by the difference of electrode potentials of both constitution components of the composite, such as in the case of an MMC with Al matrix with graphite particles in the NaCl solution. During anode reaction, Al matrix is dissolved while the cathode reaction is strongly polarized (development of hydrogen) due to the influence of graphite. In case of a composite with the same combination of components, but the graphite is in form of fibers, the fibers swell up in the chloride environment, corrosion environment passes deeper with subsequent (exfoliation) and separating fibers from the matrix. The methods for Al-graphite composite protection include cathode protection, protective coatings and electric separation.

Al-SiC composites, both fiber and particle ones, are on the other hand sensitive to localized corrosion on the Al/Sic intervate in NaCl or acid environments. The degree of corrosion is increased with increasing content of SiC.

Corrosion of fiber composites differs from particle-reinforced, because most fibers are coated on the surface. Some fibers are prepared by deposing SiC onto the carbon nucleus and have a layer of carbon also on the surface, which changes electric properties compared with the pure component. Then in environments where particle Al-Sic composite doesn't undergo galvanic corrosion, fiber composite does corrode.

7.4.6 MMC processing

The production method is a key factor for achieving the required properties and price of a composite. The two basic requirements in MMC production are:

1) effective way of distribution of the reinforcing component in the required matrix configuration

2) strong connection between the matrix and reinforcement for good transition of load between both components without fracturing.

As a simplification, we could imagine that preparation of a suitable composite is based on correct mixture of two (or more) components, but in order to abide by requirements of its properties, it is necessary to correctly choose a suitable production technology.

In case of composite materials with metallic matrix, we will name some of the many various technologies, which include preparation from solid, liquid or gaseous phase:

- Ingot metallurgy and casting methods are similar as in non-reinforced alloys but some modifications have to be made, such as for example an exact control of the melting temperature, careful mixing of melt for homogeneous distribution of particles, minimization of turbulence during the casting so that gases are not absorbed, melting in an inert atmosphere;
- *Powder metallurgy* mixing of the alloy and particle metal, grinding, during the grinding a substantial decrease of reinforcing particles can be achieved, pressing and sintering;
- Mechanical alloying mixing of elementary powers that form the matrix at the same time as particle reinforcement powders, grinding with consequent formation of matrix alloy, during the mechanical alloying, we can achieve substantial decrease of reinforcing particles; pressing and sintering.
- Special methods vacuum infiltration, CVD, PVD, plasma injection, layering of thin foils and sintering and others

Some components of the MMC may be prepared only by casting, others also by forming. The characteristic properties of selected MMCs with Al matrix can be compared with alloys without reinforcement in Table 7.9. Formed MMCs with aluminum matrix contain usually less than 40 volume % of reinforcements. Casts or intermediate products of powder metallurgy are subsequently forged, rolled and extruded.

Material	E	Y.S.	UTS	Α			
	(GPa)	(MPa)	(MPa)	(%)			
AI (99%)+SiC _w – pres	AI (99%)+SiC _w – pressure infiltration to preform						
Al	-	127	225	4			
Al+20 vol.% SiC	-	207	260	4			
Al+23 vol.% SiC	-	190	250	4			
Al+28 vol.% SiC	-	200	270	3.5			
Al+32 vol.% SiC	-	260	312	2.8			
Al+40 vol.% SiC	-	340	390	0.8			
A356+SiC _p – sand gra	A356+SiC _p – sand gravity casting						
A356	75.2	200	255	4			
A356+10 vol.% SiC	77.2	262	276	0.7			
A356+15 vol.% SiC	92.4	296	303	0.4			
A356+20 vol.% SiC	95.8	296	317	0.5			
F3S/F3K (AI-Si-Mg)+SiC _p – gravity casting to permanent mould T6							
A365	75.2	200	276	6			
F3K+10 vol.% SiC	87.6	359	372	0.3			
F3K+20 vol.% SiC	101	372	372	<0.1			
F3S+10 vol.% SiC	86.2	303	338	1.2			
F3S+20 vol.% SiC	98.6	338	359	0.4			

Table 7.9 Properties of selected composites with Al matrices with fibers (w) or particles (p)

Note: Composition of F3K: Al+10Si-0.3Fe-3Cu-1Mg-1.25Ni-0.2Ti; F3S: Al+9Si-0.2Fe-0.2Cu-0.55Mg-0.2Ti

7.4.7 Application of MMC

MMC composites, reinforced either continually or discontinually, are commonly used in construction applications or applications requiring resistance to wear, weight saving or for thermal economy. In common commercial MMCs, Al, Mg and Ti alloys are used as matrices reinforced by particles of SiC, Al₂O₃ or graphite.



Fig.7.20 Specific strength depending on temperature. Explanations for abbreviations: CFRP (carbon fiber reinforced polymers); GMC (glass matrix composites); GCMC (glass-ceramic-matrix composites); CMC (ceramic-matrix composites); CMC (ceramic-matrix composites); MMC (metal-matrix composites).

Overview of specific strength in various types of composite materials for applications in various high temperatures are given on Fig.7.20.

Casts from composites are prepared by exact casting with gravitational filling, they are commonly used in automotive industry, such as brake rotors, brake calipers and moveable parts in an engine or sports applications. MMC composites with Al matrix are suitable for breaks, because they are lighter and conduct heat three times more effectively than alloys.

In applications requiring abrasion resistance, composites with graphite or carbidic reinforcements are used. Addition of graphite into the matrix changes the abrasion coefficient between the composite and the opposing side, therefore the friction life of the composite is extended. Addition of hard ceramic parts increases the hardness of the composite, therefore resistance to penetration is increased and subsequent loss of materials from the product due to friction or other particles in friction environment is decreased. We have to remember hear that resistance to friction is not a material characteristic; it is the response of a system depending on internal material properties and external factors related to the friction environment. In contrast with the mechanical properties, it is not possible to generally evaluate behavior under friction, because there are no simple material parameters.

Wrough MMCs are used in bicycle frames, car shafts, sheets used in aviation and cosmonautics.

GLARE (produced by Akzo) and ARALL (produced by Alcoa) laminates combined with metalpolymer are among some of the very interesting materials for aviation industry. ARALL are composites with alternating layers of aluminum alloy 2024-T3 and fiber-reinforced epoxy adhesives. The layer with adhesives contains 50 volume % of aramid fibers with high elasticity modulus.

GLARE composites are also formed by layers of aluminum alloy 2024-T3, but instead of aramid fibers, there are 60 volume % of high-strength glass fibers in the adhesive layer oriented in one axis or two axes. Glass fibers have higher strength than aramide, so GLARE laminates are stronger when compared with ARALL laminates in both orientations (longitudinal - L and transversal LT) (comparison in Table 7.10).

Mechanical properties /orientation	GLARE 2 ^a , 3/2 ^b	GLARE 3 ^a , 3/2 ^b	ARALL 2 ^a , 3/2 ^b	2024-T3
UTS (MPa)				
L	1214	717	717	455
LT	317	716	317	448
Y.S. (MPa)				
L	360	305	365	359
LT	228	283	228	324
E (in tension) (GPa)				
L	65	58	66	72
LT	50	58	53	72
Total deformation				
L	4.7	4.7	2.5	19
LT	10.8	4.7	12.7	19
Y.S. (MPa)				
(in compression)				
L	414	309	255	303
LT	236	306	234	345
E (in compression) (GPa)				
L	67	60	65	74
LT	52	60	53	74

Table 7.10 Mechanical properties of GLARE and ARALL laminates compared with matrix based on 2024-T3 alloy (longitudinal - L and transversal LT directions)

a) GLARE 2: Al alloy 2024-T3 with unidirectional glass laminate; GLARE 3: Al alloy 2024-T3 with perpendicularly arranged 50:50 fibers in L and LT directions; ARALL 2: Al alloy 2024-T3 with unidirectional aramid fibers

b) Number of layers: 3 metallic, 2 polymeric



Fig. 7.21 Laminate material ARALL for aviation applications: a) a schematic of layering and delamination of layers, b) fatigue crack growth behaviour of ARALL depending on the number of cycles during the fatigue test compared to conventional 7075 and 2024 aluminum alloys.

The biggest advantage of GLARE is its ability to protect and self-arrest spreading of a fracture. Fatigue break in a sheet of Al can spread until the moment of total damage of a panel. In layered composite, the fatigue break spreads in the Al alloy layer. The fibers remain untouched due to their high strength and hardness. During the fracture spreading, the fibers bridge it and carry an increasing fraction of load, decrease intensity of the stress on the edge of the fracture and subsequently arrest its spread. Another advantage of both types of laminates are apart from these outstanding fracture properties also their low weight and higher

tolerance to damage than in sheets of 2024-T3 alloy. High-temperature version of these composites are formed by titanium, carbon fibers and thermoplastic resin.

For car industry, MMCs with aluminum based alloys are used. Composites can be processed by the following technologies:

- Hydroforming
- Superplastic forming
- Extrusion
- Semisolid casting methods (rheocasting, squeze casting)
- Melt stirring and casting
- ✤ Die casting
- Pressure or pressureless infiltration of liquid metal into a porous preform (consist of either discontinous or continous reinforcement
- Coating and thermal spraying
- ✤ Methods of powder metallurgyand others



Important terms

Principle of composite strengthening, fiber composites, particle composites, metal matrix composites, requierements on matrix properties, fracture mechanisms of composites, creep of particel composites, creep of fiber composites, ARALL, GLARE, fatigue behavior and corrosion properties of composites.

However, you need to repeat from previous study or eventually to get up individually: details of the creep and the creep stages, strengthening mechanisms, hardening and aging, Orowan's mechanism of dislocation bypass. (chapter 2.5.3).



Questions

- 1. What are the basic requierements on composite properties?
- 2. Can you define phase content of metal matrix composites (MMC)?
- 3. What is the principle of reinforcing of composite materials?
- 4. Can you define the main limitations of composite materials?
- 5. Do you know the basic requierements on composite matrix?
- 6. What type of materials are used for matrix purpose?
- 7. What reinforcing (strengthening) phase do you know?
- 8. How the particle size can influence the strengthening contribution?
- 9. What is the reason of that? What limitation do you find there?
- 10. How you can describe the fracture toughness of particle composites?
- 11. What type of cracking is typical for composites with higher strength of interfaces then strength of discontinual reinforcing?
- 12. What type of composite do you use for purpose of wear resistance?
- 13. For what applications are designed GLARE and ARALL laminates?
- 14. Can you describe the composition and properties of these materials?

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8. FUNCTIONALLY GRADIENT MATERIALS

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Time needed to study: 1 hours



Learning objectives:

After careful study of this chapter you should be able to do the following

- define principal concept of functionally gradient materials (FGMs).
- name exemples of material combination for processing FGMs
- propose processing method of FGMs in relation of function of product or part of device
- suggest the solution of problem coupled with distinct properties of combined materials by means of FGM concept



8.1 Definition and principle

Functionally gradient materials (FGMs) are a group of heterogeneous multi-phase systems with constitutional gradual composition and microstructure in macroscopic scope, i.e. without a clear interface that is characteristic for traditional materials. Comparisons of property change, which is characteristic for classic materials with homogeneous composition in all its volume and for gradient coating of thermal barrier are given on Fig.8.1.

	Uniform material	Functionally gradient material
 Property a) High temperature resistance b) Fracture toughness c) Compression strength, eventually hardness d) Heat or electrical conductivity 	a b c d	a, c b, d
Structure ceramics O metal		

Fig.8.1 Characteristic differences in properties of uniform and functionally gradient material for example in case of thermal barrier coatings

For high temperature applications, creep resistant materials are used such as nickel superalloys or titanium alloys, which can be further protected by a thermal barrier coating. The alloy and its coating can differ significantly in some properties, therefore the result of these differences - especially thermal conductivity, coefficients of thermal expansion, elasticity moduli and distribution of elements or phases, - are phenomena that occur on the interface of *substrate (underlying material)/protective coating* which lead to formation of residual tension and subsequent damage, cracking, peeling, etc. on the substrate/coating interface.

The concept of FGMs was started in 1984 in Japan and was initially focused precisely on solving the problems of cohesion and stability of thermal barrier coatings. Gradual transition of one material into the other is ensured by the gradient of thermal (but also mechanical, chemical, electrical or their combination) properties.

There are two ways of lowering the tension, as seen on the following schematic:



Among the basic requirements for high temperature FGMs are the following three:

- creep and corrosion resistance of the material, which has its surface exposed to high temperature and oxidizing atmosphere
- mechanical strength on the side of low temperatures
- effective relaxation of thermal stress across the material

In the following paragraphs, we will give some examples of various FGM concepts and material combinations.



Fig.8.2 Three different examples of FGM concept and possible microstructures a) continual change of composition b) discreet change of microstructure c) multi-phase change of microstructure.

(dimensions in μm)

(dimensions > 0.1mm)

As mentioned above, the first example is the continual change of composition and microstructure in ceramics/metal system (Fig.8.2a) for high temperature applications. Gradient of the microstructure can be introduced even in traditional composite materials (Fig.8.2b) for selected applications using a discreet change of volume fraction of reinforcing particles in the composite material. A much more complicated combination of more different materials in a ceramic matrix ensures gradual changes of properties due to the gradient type and the share of reinforcing phases in the ceramic matrix (Fig.8.2c).

8.2 Methods of preparing

If we can state that there are no limits to combination of materials and applications of FGM, then it is doubly so for technologies used to prepare such materials with gradual composition or microstructure. The methods used depend only on combinations of types of materials (Table 8.1) and the intended use. Basically these methods can be divided into the following groups:

1. Powder metallurgy (pressing, sintering)

Reaction sintering (Self-Propagating-High Temperature Synthesis) Layering of thin foils and sintering Layering of materials using a centrifuge and sintering Sintering by laser heating Chemical vapor deposition (CVD) (dimensions in µm)

- Chemical vapor deposition (CVD) Chemical infiltration Combination of sintering and infiltration
 Physical vacuum deposition (PVD)
- EB PVD Magnetic sputtering 4. Plasma spraying (APS or LPPS)
 - Combination of two torch Combination with CVD
- 5. Diffusion joining by hot isostatic pressing (HIP)
- 6. Galvanic and electroless coating
- 7. Thermal treatment (gradient microstructure)

 Table 8.1 Examples of combination of materials and preparation methods

phase	processing	Combination of materials			
	CVD	SiC/C, SiC/TiC, TiC/C, C/C, C/ceramics			
gaseous	Ion plating	TiN/Ti, TiC/Ti, ZrO₂/Cu, C/Cr			
0	Plasma spraying	YSZ/NiCrAlY, YSZ/Ni-Cr			
	Ion mixing	Diamond/WC, YSZ/Cu			
	Electrodeposition	Ni/Cu			
liquid	Plasma spraying	YSZ/NiCrAlY, YSZ/Ni-Cr			
	Eutectic reaction	Si/ZrSi ₂			
	SHS	TiB ₂ /Cu, TiB ₂ /Ni, TiC/Ni, MoSi ₂ -SiC/TiAl, ZrO ₂ /Ni, PZT/Ni, PZT/Nb			
solid	Powder metallurgy	YSZ/SS304, YSZ/Mo, YSZ/Nb, SiC/AlN/Mo			
	Si ₃ N ₄ /Ni, W/Cu, Ni/Al				

8.3 FGM applications

Initially, these materials were, as we have already stated in the introduction to this chapter, designed for preparation of high temperature materials for space applications. Today however there is a high diversification of applications. These include for example metal production tools, electronic parts, biocompatible materials, bearings, filters, cooling parts, etc. In the following enumeration of application fields, we can compare various concepts for solving the requirements of gradient properties:

1. aircraft and spacecraft (temperatures over 1800 °C)

- thermal barrier coatings: ZrO_2 (Y_2O_3)/Ni superalloy, SiC/C for turbine engines, motors, superchargers, combustion chambers, suction nozzle valves, front part of aircraft fuselage (aerodynamic heating), etc.

2. complex shapes of gears

- gradient composition is ensured in sintering due to diffusion of C into certain (controlled) depth

3. technical filters

- gradient porosity is prepared by a powder of austenitic steels with varying particle size

4. electrical contacts

- gradient composition in Ag contacts is achieved by gradient oxide dispersion in Ag

5. parts for high temperature loading in rapid reactors

- sodium as cooling medium induces thermal stresses in materials of primary circle, which can also be solved by gradual transition of one material on one side into the second material on the other side.

6. bearings

- gradient composition solves a combination of weldable layer with the layer with good strength and layer resistant to friction.

7. biocompatible materials

- in Ti alloys, a gradient coating of hydroxyapatite is applied.



Important terms

Principle of gradient effect, interlayers, thermal stresses, processsing methods of FGMs, basic properties.



Questions

- 1. Can you define the principle concept of functionally gradient materials?
- 2. What is the main limitation of FGM?
- 3. What basic problem was resolved by the concept of FGMs?
- 4. Can you cite the actual and potential applications of FGMs?
- 5. Can you draft some application of FGMs?.

8. Functionally gradient materials

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9. METAL FOAMS



Time needed to study: 3 hours



Learning objectives:

After careful study of this chapter you should be able to do the following

- define basic characteristics of cellular metals
- describe dictinct behavior of metal foams and dense materials
- explain distinct behavior in tension and compression of metal foams
- suggest applications of metal foams



Lecture

9.1 Basic characteristics of cellular metals

Metal foams are a new group of technical material with low density and new physical, mechanical, thermal, electrical and acoustic properties. In terms of their internal structure, they are cellular metal materials with high porosity, usually between 40 to 90 volume % (Fig.9.1 a 9.2).

An interesting characteristic of theirs is their high hardness related to very low specific mass or high strength in stress combined with good energy absorption. The study of metal foams is attractive both in terms of basic scientific research, but also in terms of their industrial applications, be it as a material for light construction, for energy absorption or for thermal economy.



Fig.9.1 Cross section of metalic foam (image of X-ray tomography) (LKR Ranshofen).



Fig.9.2 Sandwich panel from metalic foam.

Even if the interest in this type of material is on the rise, there still are certain disagreements about the name "metal foam", often used in general terms for describing a material which in fact is not a foam. When determining the properties of metal foam, the differences stemming from the following characteristics have to be taken into consideration (Fig.9.3-9.8):

Cellular metal: this term generally applies to metallic bodies in which any pores (cavities) are distributed that formed due to the presence of gas in the melt. Metal phase divides the space between enclosed cells, which contain gaseous phase.

- *a) Porous metals*: a special type of cellular metal limited only to a certain type of porosity. Cavities are usually round and isolated from each other. Porosity is usually lower than 70%.
- *b)* (*Solid*) *metal foams*: a special group of cellular metals prepared from liquid metal foams which have limited morphology depending on the material preparation method. Spherical or polyhedric cells are enclosed and separated by a thin layer of metal.
- c) Metal sponges: the morphology of cellular metals usually with open and interconnected cavities.



Fig.9.3 Aluminum foam (IFAM).



Fig.9.4 Cellular structure of an Fe based material, stretched in one direction (MER Corp.).



Fig.9.5 Bronze sintered powder, i.e. sintered porous material (so-called metal sponge).



Fig.9.6 Aluminum sponge, so-called cellular structure with enclosed cells.



Fig.9.7 Nickel sponge (Inco).





Fig.9.8 A characteristic morphology of metal foams: a) open cells, b) closed cells.

9.2 **Properties of metal foams**

With the development of more and more challenging requirements for impact energy absorbtion of a material, preparation of a material which would be able to absorb high deformation energy has been the object of interest. The assumption that metals with uniformly distributed porosity allow achieving uniform impact properties without compromising their strength under pressure, lead to the development of porous structures, despite the fact that porosity and its distribution as well as the deformation properties of metals are still not entirely homogenous. A big advantage of these materials is the reproducibility of impact energy absorption of every product.

From the mechanical properties, in metal foams, the real elasticity modulus and strength related to the fraction of sample size and cell size is observed. These properties can of course be influenced by the state of the sample's surface and method of the sample's fix into a device and loaded.

The progression of deformation behavior of metal under stress is schematically shown on Fig.9.9 and comparison with the classic non-foamed material is shown on Fig.9.10. From these graphs, a large energy absorption ability W_V in metal foam is evident under the plateau of stress σ_{pl} in the area of plastic deformation. Metal foams are able to absorb much greater deformation energies (5-7 times higher) and exhibit higher strength under stress than polymer foams, as seen on Fig.9.11, which shows the development of strain curve for aluminum (Al-Cu4) and polyethylene (PE) foam.



Fig.9.9 Energy absorbed during deformation: stress- strain behavior for metal foam: E-Young modulus, σ_{pl} – stress at plateau, ϵ_D – densification strain. Area below the flat part (plateau) represents energy W_V per unit volume, what can be absorbed by the material.



Fig.9.10 Schematic comparison of deformation behavior and energy absorbtion at impact in metals and metal foams.



Fig.9.11 Comparison of strain and strength of aluminum (Al-Cu4) and polyethylene (PE) foams.

The behavior of a foam at initial load is an analogy of elastic behavior, the dependence however is not linear and the vector of the curve is smaller than the real modulus of elasticity E, because some cells are plastically deformed even in small loads. Local character of plastic behavior under stresses lower than the overall yield strength of the foam requires the real elasticity modulus E to be measured either dynamically or from the curve vector at unloading after loading the foam into the plastic area (Fig.9.12).

Mechanical properties are investigated by different tsets: uniaxial tensile or compression tests (Fig.9.12 and 9.13), shear tests, at multiaxial state of stress, fatigue, creep or indentation (measurement of hardness) tests. Young's modulus E, shear modulus G and Poisson's ratio are functions of density according to the following relations:

$$E \approx \alpha_2 E_s \left(\frac{\rho}{\rho_s}\right)^n \qquad G \approx \frac{3}{8} \alpha_2 G_s \left(\frac{\rho}{\rho_s}\right)^n \qquad \nu \approx 0.3$$
 (9.1)

where n is within 1.8 to 2.2 and α_2 between 0.1 and 4, depending on the metal foam structure.

In case of open cell structure, the plateau on the deformation-stress dependence (Fig.9.9, 9.18, 9.19) is rather flat, the behavior of foams with closed cells is more complicated and rise of stress with rising deformation can occur because the walls of the cells transport membrane tension. The plateau in both cases continues until the deformation compaction ε_D , after which the structure of the material is compact and stress rises steeply. The stress plateau σ_{pl} and compaction deformation ε_D is a function of density based on the following relations:

$$\sigma_{pl} \approx (0,25 \div 0,35) \sigma_{y,s} \left(\frac{\rho}{\rho_s}\right)^m \qquad \varepsilon_D \approx \left(1 - \alpha_1 \frac{\rho}{\rho_s}\right) \tag{9.2}$$

where ρ and ρ_s is the density of metal foam and compact metal, *m* is between 1.5 and 2.0 for common metals and the coefficient α_l moves between 1.4 and 2.

The behavior of metal foams at deformation differs based on if the load is a pressure or a tension (Fig.9.14). The value of Young's modulus E in tension is typically 10% higher. The anisotropy of cells can cause significant differences (up to 30%) of moduli in different directions. The vector of the stress-deformation curve until the yield strength of the foam is lower than E, which points to a significant microplasticity even at small deformations. Above the yield strength (σ_y) the metal foal strengthens up to the maximum stress in tension σ_{ts} , over this point, it fractures as stress corresponding to deformation ϵ_t (elongation until fracture in tension).



Fig.9.12 Mechanical uniaxial stress test of square sample from aluminum foam with closed cells (Alporas with 8% density): a) up to 5% of deformation, b) up to 70 % of deformation.



Fig.9.13 The development stress-strain curve in uniaxial tensile test of cylindrical sample from aluminum foam with closed cells (Alporas with 8 % density).



Fig.9.14 Total tensile strain for Alulight foam.

Fig. 9.15 Comparison of deformation behavior of foams Alporas (16 % density) and Duocel (7.1 % density) in uniaxial and multiaxial load (rate of strengthening depending on the stress applied).



Fig.9.16 Compression and hydrostatic stress-strain behavior for Alporas and Duocel foams (strengthening occurs faster for hydrostatic pressure in Alulight and Alporas 13 %)



Fig.9.17 Sound absorption measured in a planewave impedance tube for a) glass fiber,b) Alporas foam in the as-received condition and after 10% compression to rupture the cell walls.



Fig.9.18 Compression strain-stress behavior with significant plateau for foams a) Cymat and b) Alporas



Fig.9.19 Schematic of energy absorption during compression of metal foams to the densification of metal material

The damping effect of metal foams is typically five to ten times higher than of a given compact metal. This property is suitable because the loss factor is still lower than in the case of polymer foams. Metal foams also exhibit good acoustic absorption even if the polymer foams and fiberglass achieve higher values in general (Fig.9.17).

Same as in other materials, metal foams can also be damaged by fatigue in cyclical load. Therefore in high-cycle fatigue tests, the fatigue limit $\Delta\sigma_c$ is determined, which determines the range of stress at which the material can last for 10^7 cycles.

Fracture strength of metal foams is determined by standard methods. Based on an empirical rule, the initial fracture strength depends on density:

$$J_{IC} \approx \beta \sigma_{y,s} l \left(\frac{\rho}{\rho_s}\right)^p \tag{9.3}$$

where *l* is the cell size with p = 1.3 to 1.5 and $\beta = 0.1$ to 0.4.

Properties of metal foams at creep, whether in uniaxial or multiaxial pressure are still an object of research.



Fig.9. 20 Energy absorption in compression test: a) a load – deflection curve and b) a stres- strain curve. Energy under plateau represents energy W or energy per unit volume W_V absorbed at impact or deformation.

Ashby's diagrams on Fig. 9.21 and 9.22 show selected properties of metal foams depending on their density. Based on these diagrams, the suitable material for practical use may be chosen.

Properties of some metal foams and other cellular metal structures depend on the properties of the metal, relative density and topology of the cells (i.e. if they are closed or open cells, their size, etc.). The selected properties of five metal foams in commercial use are given in Table 9.2. During the study of structural properties of foams, the classic optical or raster electron microscopy (SEM) is used. Lately, the options of x-ray tomography (CT) have also been used for observing the microstructure - with this method, we can obtain a 3D image of the structure. Unlike the medical devices, their image resolution is limited to 0.7 mm, industrial CT scans achieve magnification of structure of up to 200 μ m. This device can therefore observe the internal space of closed cell and using the sequential capture also find distortion of cells during deformation.



Fig.9.21 Young's modulus E vs. density ρ for common metal foams / Output from CES3.1 with the MetFoam '97 database/



Fig.9.22 Compressive strength σ vs. density ρ for common metal foams / Output from CES3.1 with the MetFoam '97 database/

	Open-cell foams	Closed-cell foams			
Mechanical properties					
Young's modulus E (GPa)	$E = (0, 1-4)E_s \left(\frac{\rho}{\rho_s}\right)^2$	$E = (0,1-1,0)E_s \left[0,5 \left(\frac{\rho}{\rho_s}\right)^2 + 0,3 \left(\frac{\rho}{\rho_s}\right) \right]$			
Shear modulus G (GPa)	$G \approx \frac{3}{8}E$	$G \approx \frac{3}{8}E$			
Bulk modulus K (GPa)	$K \approx 1,1E$	$K \approx 1,1E$			
Flexural modulus E_f (GPa)	$E_{f} \approx E$	$E_f \approx E$			
Poisson's ratio v	0,32-0,34	0,32-0,34			
Compressive strength σ_c (MPa)	$\sigma_{c} = (0, 1-1, 0) \sigma_{c,s} \left(\frac{\rho}{\rho_{s}}\right)^{3/2}$	$\sigma_{c} = (0,1-1,0)\sigma_{c,s} \left[0,5 \left(\frac{\rho}{\rho_{s}}\right)^{2/3} + 0,3 \left(\frac{\rho}{\rho_{s}}\right) \right]$			
Tensile strength σ_t (MPa)	$\sigma_t \approx (1, 1-1, 4)\sigma_c$	$\sigma_t \approx (1, 1-1, 4)\sigma_c$			
Endurance limit σ _e (MPa)	$\sigma_e \approx (0, 5 - 0, 75) \sigma_c$	$\sigma_e \approx (0, 5 - 0, 75)\sigma_c$			
Densification strain $\epsilon_{\rm D}$ (MPa)	$\varepsilon_D = (0,9-1,0) \left[1 - 1,4 \left(\frac{\rho}{\rho_s} \right) + 0,4 \left(\frac{\rho}{\rho_s} \right)^2 \right]$	$\varepsilon_D = (0,9-1,0) \left[1 - 1,4 \left(\frac{\rho}{\rho_s}\right) + 0,4 \left(\frac{\rho}{\rho_s}\right)^3 \right]$			
Loss coefficient η	$\eta \approx (0.95 - 1.05) \frac{\eta_s}{\rho / \rho_s}$	$\eta \approx (0.95 - 1.05) \frac{\eta_s}{\rho / \rho_s}$			
Hardness H (MPa)	$H = \sigma_c \left(1 + 2 \frac{\rho}{\rho_s} \right)$	$H = \sigma_c \left(1 + 2 \frac{\rho}{\rho_s} \right)$			
Iniciation toughness J _{IC} (J.m ⁻²)	$J_{IC} \approx \beta \sigma_{y,s} \lambda \left(\frac{\rho}{\rho_s}\right)^p$	$J_{IC} \approx \beta \sigma_{y,s} \lambda \left(\frac{\rho}{\rho_s}\right)^p$			
Thermal properties	· · · · · · · · · · · · · · · · · · ·				
Melting point T _m (K)	As dense metal	As dense metal			
Max.service temperature T _{max} (K)	As dense metal	As dense metal			
Min. service temperature T _{min} (K)	As dense metal	As dense metal			
Specific heat C _p (J.kg ⁻¹ .K ⁻¹)	As dense metal	As dense metal			
Thermal conductivity $\lambda (W.m^{-1}.K^{-1})$	$\left(\frac{\rho}{\rho_s}\right)^{1,8} < \frac{\lambda}{\lambda_s} < \left(\frac{\rho}{\rho_s}\right)^{1,65}$	$\left(\frac{\rho}{\rho_s}\right)^{1,8} < \frac{\lambda}{\lambda_s} < \left(\frac{\rho}{\rho_s}\right)^{1,65}$			
Thermal expansion coefficient α (10 ⁻⁶ K ⁻¹)	As dense metal	As dense metal			
Latent heat L (kJ.kg ⁻¹)	As dense metal	As dense metal			
Electrical properties					
Resistivity R (10 ⁻⁸ ohm.m)	$\left(\frac{\rho}{\rho_s}\right)^{-1,6} < \frac{R}{R_s} < \left(\frac{\rho}{\rho_s}\right)^{-1,85}$	$\left(\frac{\rho}{\rho_s}\right)^{-1,6} < \frac{R}{R_s} < \left(\frac{\rho}{\rho_s}\right)^{-1,85}$			

Table 9.1 Relations for selected mechanical, thermal and electrical metal foam properties

Product (producer) Property (symbol /unity)	Cymat	Alulight	Alporas	ERG	Inco
Material	Al-SiC	Al	Al	Al	Ni
Relative density $\rho/\rho_{\rm S}$ (-)	0.02-0.2	0.1-0.35	0.08-0.1	0.05-0.1	0.03-0.04
Structure (-)	Closed cell	Closed cell	Closed cell	Open cell	Open cell
Density ρ (10 ³ .kg/m ³)	0.07-0.56	0.3-1.0	0.2-0.25	0.16-0.25	0.26-0.37
Young's modulus E (GPa)	0.02-2.0	1.7-12	0.4-1.0	0.06-0.3	0.4-1.0
Shear modulus G (GPa)	0.001-1.0	0.6-5.2	0.3-0.35	0.02-0.1	0.17-0.37
Bulk modulus K (GPa)	0.02-3.2	1.8-13.0	0.9-1.2	0.06-0.3	0.4-1.0
Flexural E _f (GPa)	0.03-3.3	1.7-12.0	0.9-1.2	0.06-0.3	0.4-1.0
Poisson's ratio v (-)	0.31-0.34	0.31-0.34	0.31-0.34	0.31-0.34	0.31-0.34
Compressive strength σ_{c} (MPa)	0.04-7.0	1.9-14.0	1.3-1.7	0.9-3.0	0.6-1.1
Tensile elastic limit σ_y (MPa)	0.04-7.0	2.0-20	1.6-1.8	0.9-2.7	0.6-1.1
Tensile strength σ_t (MPa)	0.05-8.5	2.2-30	1.6-1.9	1.9-3.5	1.0-2.4
MOR σ_{MOR} (MPa)	0.04-7.2	1.9-25	1.8-1.9	0.9-2.9	0.6-1.1
Endurance limit σ_e^c (MPa)	0.02-3.6	0.95-13	0.9-1.0	0.45-1.5	0.3-0.6
Densification strain ε_D (-)	0.6-0.9	0.4-0.8	0.7-0.82	0.8-0.9	0.9-0.94
Tensile ductility $\varepsilon_{\rm f}$ (-)	0.01-0.02	0.002-0.04	0.01-0.06	0.1-0.2	0.03-0.1
Loss coefficient η^{c} (%)	0.4-1.2	0.3-0.5	0.9-1.0	0.3-0.5	1.0-2.0
Hardness H (MPa)	0.05-10	2.4-35	2.0-2.2	2.0-3.5	0.6-1.0
Fracture toughness K ^c _{IC} (MPa.m ^{1/2})	0.03-0.5	0.3-1.6	0.1-0.9	0.1-0.28	0.6-1.0
Melting temperature T _m (K)	830-910	840-850	910-920	830-920	1700-1720
Max. service temperature T _{max} (K)	500-530	400-430	400-420	380-420	550-650
Min. service temperature T _{min} (K)	1-2	1-2	1-2	1-2	1-2
Specific heat C _p (J/kg.K)	830-870	910-920	830-870	850-950	450-460
Thermal conductivity λ (W/m.K)	0.3-10	3.0-35	3.5-4.5	6.0-11	0.2-0.3
Thermal expansion coefficient $(10^{6}/K)$	19-21	19-23	21-23	22-24	12-14
$\frac{(10-1)}{10}$	255 295	280.200	270.280	280 205	280.210
D atistical L (KJ/Kg) D osistivity P (10^{-8} O m)	90-3000	20-200	210-250	180-450	300-500
Resistivity R $(10^{-8} \Omega.m)$	90-3000	20-200	210-250	180-450	300-500

Table 9.2 Physical, mechanical, thermal and electrical properties of commercially used metal foams

9.3 **Processing methods**

One of the significant properties of metal foams used for energy absorption is their ability to be shaped depending on various ingot shapes. This allows production of complex shapes similar to alloys. This way, parts for existing constructions can be produced not only in terms of the ability to absorb energy, but also in terms of reinforcing a construction in general.

The processes of metal foams preparation (foaming) are schematically shown on Fig.9.23 and can be classified into four groups depending on if the foams are:

- a) prepared from a gaseous phase
- b) applies electrolytically from water solutions
- c) prepared by a process from melted state
- d) prepared in solid state

Nine different metal foam preparation methods are used currently, five of which are used commercially:

1) blowing a gas through an Al, Mg melt or their alloys such as Al-SiC or Al-Al₂O₃;

- 2) mixing the foaming agent (most commonly TiH₂) into the melt of an alloy (most commonly Al or Al alloy) and directing pressure during cooling;
- 3) compressing the metal powder (most commonly Al alloy) with particles of foaming agent (most commonly TiH₂) with subsequent heating up to a mushy consistency, when the foaming agent releases hydrogen and expands the material. It is also used in the production of foams from Al, Zn, Fe, Pb and Au.
- 4) production of ceramic form using pre-form from wax or polymer foam, which then burns and melted metal or the metal powder mash is introduced by pressure into the form which is then sintered. The method is used in preparation of foams from Al, Mg, Ni-Cr, stainless steel or Cu.
- 5) deposition of metal from gaseous environment or electrolytically into a preform from polymer foam, that subsequently burns out. It is used in production of foams from Ni and Ti.
- 6) capturing the inert gas at high pressure in pores by the method of hot isostatic pressing (HIP) of powdered metal or alloy, with subsequent expansion of the gas at further thermal processing. The method is used in preparation of foams from Ti and Ti alloys.
- 7) sintering hollow balls prepared by a modified process of atomization; sintering of balls made of oxide or a hydride of a metal with subsequent reduction or decomposition; the deposition of metal from gaseous environment into polymer balls. Used in preparation of foams from Ni, Co and Ni-Cr alloys.
- 8) concurrent pressing of powdered metal with leachable powder; pressure infiltration of liquid metal into the deposition of leachable particles with subsequent leaching; Used for Al and salt as the leachable powder.
- 9) Dissolution of gas (most commonly of hydrogen) in liquid metal at high pressure with subsequent controlled solidification and release of gas. Used to prepare foams from Cu, Al and Ni.

Two factors are usually taken into consideration when developing a suitable structure of metal foam: high quality and low price.



Fig.9.23 Processes of metallic foams preparation

9.4 Advantages of metal foams

- amount of complex shapes for various requirements
- possibility to prepare foams into an existing shape (without requiring a special form)
- various impact strength
- independence of shape
- economically and ecologically suitable solution
- easy change and adaptability of existing production technologies
- less economic difficulty compared with other high-load packaging materials (such as bubble wrap)
- if the material is not damaged by impact, it can be re-used and is fully recyclable
- metal foam has 5-7 times higher capacity for energy absorption compared with non-foamed metals

The quality and price of products depends on the method of production, the price is currently around 7-12 thousand dollars for a kg.

9.5 New directions and applications

Despite the development of metal foams having a relatively long history (first data come from the 1950s), there is still no process able to prepare a foam material comparable with polymer foams. We encounter difficulties in many areas:

- lack of knowledge of basic mechanisms of metal strengthening, knowledge remains more or less speculative and some points are unexplained.
- insufficient ability to produce foam with constant quality and with predefined parameters.
- difficulties with finding application for metal foams. Apart from certain opportunities in commercial matters, there is still no real industrial use for metal foams, because their physical properties are disproportionate, data of their properties is insufficient, transfer of research results into construction engineering is insufficient or the foams are too expensive

Applications

Currently, foams find more applications based on the type of their porosity (Fig. 9.24) in the following areas :

- bumpers and panels in car and transport industry (reducing noise, impact and vibrations)
- impact damping on platforms
- sound attenuation
- special packaging technology for heavy loads
- ♦ filters
- ◆ light construction at high volume (mechanical strength relative to specific mass is high) ⇒ potential for wide spread in car, aviation and construction industries
- batteries (Pb, Ni foams)
- jewelry and art decorations
- heat exchangers
- catalyst carriers
- biocompatible components in medicine



Fig. 9.24 Aplications of metal foams dependent on their porosity character



Important terms

Cellular metal, foaming agent, delayed process, open cell, closed cell, tension and compression behavior, desification strain, energy absorption, damping capacity.



Questions

- 1. Can you define basic classification of cellular metals?
- 2. Can you explain the term of metal foam?
- 3. What are the basic characteristics of cells in metallic foam?
- 4. What advantageous properties show the metallic foams?
- 5. Can you determine characteristic differences between dense (unfoamed) and foamed metals?
- 6. What basic parameters differenciate the processing methodof metal foams?
- 7. Can you explain why the properties of metal foams are different in compression and tensile test?
- 8. For what applications is this difference favorable?
- 9. What property of metal foam is requiered for crash zones?
- 10. For what application do you suggest the open-cell metal foam?
- 11. And conversely, for what application the closed-cell metal foams are suitable to use?
- 12. What processes perform at stress plateau under loading of metal foam?



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10. METALLIC GLASSES



Time needed to study: 4 hours



Learning objectives:

After careful study of this chapter you should be able to do the following:

- define principles of metallic glass features
- describe basic properties of metallic glasses
- determine basic distinction of properties between amorphous and conventional crystalline materials
- explain crystallization process of metallic glasses
- define basic glass forming condition
- name applications of metallic glasses in the industries
- evaluate basic limitations of metallic glasses in engineering use



Lecture

10.1 Basic properties of metallic glasses

Metallic glasses represent a relatively new type of materials with unique properties. Unlike traditional metals and alloys, which crystallize upon solidifying from the melt to reach the structural state with the lowest energy i.e. the formation of crystalline lattice, the metallic glasses keep their disordered state due to the fast cooling and/or a suitable composition. This state can be unstable above a certain temperature and may become stable if the temperature rises (crystallization).

Traditional metallic materials with a regular arrangement of atoms into a periodic lattice are characterized by mostly metallic bond, which is non-directional and collective, while the valence electrons are easily released and are in fact "common" for all the atoms of the material. Melted metal or an alloy of a metal is unstable under the melting temperature that is why it crystallizes in a few microseconds. Under normal solidification conditions, a polycrystalline material with varying shape and grain size is formed and their boundaries are a weak link of optimal atoms arrangement, resulting for example in the intercrystalline fracture and corrosion. Metallic materials usually exhibit a certain plastic properties (depending on the type of lattice and the slide systems), mostly good thermal and electrical conductivity and sensitivity to the effects of the corrosive environment.

On the other hand, in conventional glasses there is no regular special arrangement and the most of their properties are given by the covalent bond, which highly directional and the electrons in the atoms are tightly bonded. Classic glasses have such a low rate of crystal nucleation and growth kinetics that the melt can be easily supercooled far below their melting temperature and the glass state can be hardened without crystallization. Atoms retain the amorphous distribution, in other words the random filling without arrangement over long distances. Consequently, the glasses are fragile, they are typically good insulators and are resistant to corrosion.

The structure of the metallic glasses is much more closer to the structure of normal glasses than to the structure of metals, but many properties typical for metals remain. Based on the above mentioned characteristics, we may easily imagine that the properties of metals and glasses are merged in metal glasses. This view is not entirely correct, because new properties arise due to the extreme disorder of atoms.
10. Metallic glasses

Metallic glasses can be defined using the following parameters:

- 1) Due to the composition of identical or almost identical atoms they are structurally simpler than silicate or polymer glasses
- 2) They are considerable more homogeneous than crystalline metals because they do not contain faults such as grain boundaries, twins and layering errors
- 3) They are crystallographically isotropic
- 4) They maintain a metallic character

As a result of the above mentioned characteristics the metallic glasses have a great technical importance from the point of their useful properties, especially mechanic and magnetic characteristics:

- An unusual combination of low elasticity module and high yield strength (Fig. 10.1)
- High strength (2 to 5 GPa) and fracture toughness (up to 20-60 MPa.m^{1/2}) (Fig.10.2)
- Ferromagnetism, small coercive force, high permeability
- Formability (limited) in cold
- High corrosion resistance and abrasion resistance
- Resistance to high doses of radiation etc.



Fig.10.1 The dependence of yield strength σ_y on Young modulus E for 1507 metals, alloys, composite materials (MMC) and metallic glasses (composition in at.%). The contours represent the limit of elastic deformation (σ_y/E) and resilience (σ_y^2/E) (Adapted according to [3])

10. Metallic glasses

Material	Vit1	Al alloys	Ti alloys	Steels
Property				
Density (g/cm ³)	6.1	2.6-2.9	4.3-5.1	7.8
Tensile yield strength (GPa)	1.9	0.1-0.63	0.18-1.32	0.5-1.6
Limit of elasticity strain ϵ_{el} (%)	2	0.5	0.5	0.5
Fracture toughness K _{IC} (MPa·m ^{1/2})	20-140	23-45	55-115	50-154
Specific strength (GPa/(g·cm ³))	0.32	< 0.24	< 0.31	< 0.21

TABLE. 10.1 The comparison of mechanical properties of metallic glass (Vitreloy-Vit1) with other materials



Fig.10.2 The comparison of the strength and elasticity of classic glasses, wood, polymers, steels, and Ti alloys and the metallic glasses.



Fig.10.3 The development of critical thickness of metallic glasses during the 50 years of development of these alloys.

A little from the history of the development of metallic glasses

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First amorphous metallic alloys were prepared already more than 50 years ago by rapid quenching (cooling rate of 10^5 - 10^6 K/s) of melted alloys Au₈₀Si₂₀ into a thin strip (P.Duvez, 1959). Other metallic glasses were prepared by rapid quenching of metallic vapors on the substrate cooled by liquid He (steaming techniques, sputtering or the use of electrolytic deposition).

Research during the 1970s and 1980s was mainly focused on magnetically soft material for cores of transformers and magnetic equipment. Early in the 1970s it was shown on the Pd-Cu-Si alloy that the cooling rate of melts can be lowered by a suitable alloy composition down to 10^3 K/s. In the early 1980s the cooling rate of Pd-Ni-P amorphous alloys was lowered even further down to 10^2 K/s. Turnbull and his associates have proven in this alloy that the reduced temperature T_{gr} (will be defined hereinafter) is of the value $\approx 2/3$, which is close to the value for silicate glasses. A considerable faster progress started after that in the research of these materials and by the end of 1980s first large-size so-called bulk metallic glasses – BMGs were made. The composition was various (based on Mg, Zr, La, Ti and others) and the thickness ranged from 1mm to 1cm and the cooling rates of 10^2 K/s. Further progress was made in 1993, when it became possible to cast alloys with complex composition based on Zr-Ti-Be into bars with the diameter of several centimeters and the cooling rates of only 1 K/s.

The result of intensive research of metallic glasses for the last forty years came in the form of materials with new composition (Table.10.2) that can be prepared using methods with lower critical cooling rates (from 1 to 100 K/s), thus increasing the dimensions of castings (to several centimeters), as shown in the alloys overview on the Fig. 10.3.

Metallic	Composition (at.%)	Critical diameter	Preparing	Year
base		(mm)	technology	
Dal	$Pd_{40}Ni_{40}P_{20}$	10	Fluxing	1984
Pa	Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	72	Water quenching	1997
7.	Zr ₆₅ A _{I7.5} Ni ₁₀ Cu _{17.5}	16	Water quenching	1993
21	Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	25	Cu mold	1996
Cu	$Cu_{46}Zr_{42}AI_7Y_5$	10	Cu mold	2004
Cu	$Cu_{49}Hf_{42}Al_9$	10	Cu mold	2006
K\/7	Y ₃₆ Sc ₂₀ Al ₂₄ Co ₂₀	25	Water quenching	2003
KVZ	La ₆₂ Al _{15.7} Cu _{11.15} Ni _{11.15}	11	Cu mold	2003
Μα	$Mg_{54}Cu_{26.5}Ag_{8.5}Gd_{11}$	25	Cu mold	2005
IVIS	Mg ₆₅ Cu _{7.5} Ni _{7.5} Zn ₅ Ag ₅ Y ₅ Gd ₅	14	Cu mold	2005
	$Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	12	Cu mold	2004
Fe	$(Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2}C_{15.8}B_{5.9})_{98.5}Y_{1.5}$	12	Cu mold	2004
	$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16	Cu mold	2005
Со	$Co_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	10	Cu mold	2006
Ti	$Ti_{40}Zr_{25}Cu_{12}Ni_3Be_{20}$	14	Cu mold	2005
Са	Ca ₆₅ Mg ₁₅ Zn ₂₀	15	Cu mold	2004
Pt	Pt _{42.5} Cu ₂₇ Ni _{9.5} P ₂₁	20	Water quenching	2004

Table.10.2 Composition and preparation methods of metallic glasses of selected compositions

10.2 Formation conditions and stability

Two criteria are very important for the preparation of metallic glasses, which are in metastable state (Fig.10.4) from the thermodynamic point of view:

1) Ease of formation of the amorphous state of GFA, in other words the glass-forming ability-GFA

2) Stability of metallic glass (resistance to crystallization)



Fig.10.4 Schematic representation of possible thermodynamic states of alloys in the diagram according to the size of Gibbs free energy (G) and the change of structure: a) unstable equilibrium, b) metastable equilibrium c) stable equilibrium and d) unstable state of imbalance

Conditions for the formation and stability of the metallic glasses

Formation and stability of metallic amorphous materials are conditioned by the following factors:

- Cooling rate
- Interaction between atoms
- Suitable mutual geometry of coexisting atoms of elements (the ratio of the radii of coexisting elements)
- In some systems the lowering of the symmetry of the electron orbits f (stabilization of the melt structure)
- Multicomponent alloys composed of three or more elements: with increasing complexity and size
 of elementary crystalline cell, there is a decrease in energetic advantage for the formation of
 ordered structure with periodic order larger than the distances of the atomic interactions
- Difference of atomic radii between the elements $(\Delta r/r)$ higher than 12 % leads to a higher density of ordering and lower free volume in the liquid state, therefore needing a higher increase of volume for crystallization
- Negative mixing heat between the main elements increases the energetic barrier on the liquid/solid border and decreases the diffusivity of atoms (increases the equilibrium melt viscosity by three orders higher than in binary alloys); this slows down the local ordering of atoms, decreases the rate of nucleation of crystals, and widens temperature range of melt supercooling
- Alloy having a eutectic composition creates a melt that is stable at low temperatures
- Slower crystallization enables the lowering of critical cooling rate and creation of a stable volume metallic glass and its preparation using traditional casting methods

It is obvious from the list of factors influencing the formation of metallic glass, that the cooling rate is not the only parameter influencing the suppression of crystalline phase nucleus. There are effects of other factors, which lead, apart from other things, to an increase of viscosity and

stabilization of the melt structure. In the following text we are going to further demonstrate the basic characteristics that are monitored for determining of the GFA:

- 1. Critical cooling rate R_c
- 2. Reduced glass transition temperature T_{rg}
- 3. Supercooled liquid region ΔT_x
- 4. Parameter γ

The formation of metallic glasses is influenced by thermodynamic and kinetic factors. In the Fig. 10.5. there are the characteristic DSC curves for the bulk metallic glasses with the critical temperatures when heating the metallic glass and subsequent slow cooling down. This diagram illustrates that the temperatures, which are monitored in metallic glasses, are recorded in the form of slow changes (broad peaks).



Fig.10.5 Two typical DSC curves for bulk metallic glasses with defined temperature characteristics T_g; T_x and T₁ measured upon heating and T_s measured upon cooling down.



Fig.10.6 TTT diagram for melt cooling to form metallic glass: R_c – cooling rate, T_x - temperature of crystallization, T_l – temperature of the melt, T_g – temperature of the transition to glass condition.

In the crystalline phases, the melt-solid state transition takes places at the melting temperature T_m , which characterizes the thermodynamic equilibrium between the two states. During this transition (a type of cooling) all the changes of order in the structure can take place and the obtained state of the material (energetically stable) is of a crystalline type. In metallic glasses, the liquid temperature T_1 is defined more often. Under this T_1 temperature there is a T_g temperature, at which the movements of atoms are restricted and they occur at a distance lower than their size. At these conditions, the changes of atomic order are impossible in real time. If we heat the melt over the T_1 temperature and subsequently cool down (freeze) at the rate over R_c to the T_g temperature or lower, an non-equilibrium condition of material is created and it preserves the atomic structure of the starting melt, thus creating a metallic glass.

To be able to imagine how high the critical cooling rate \mathbf{R}_{c} has to be for the formation of metallic glass, we will show a diagram of the time-temperature-transformation diagram (TTT-diagram) on the Fig.10.6. We already know its form from the study of phase transformations in steels (IRA diagrams). The curve \mathbf{A} in the shape of the letter C (C-curve) defined the time necessary until the beginning of crystallization depending on the temperature below the T₁ temperature. Crystallization starts to take place between T₁ and T_g. Therefore, to eliminate the creation of a crystalline structure, the system has to be cooled down at a rate higher than R_{c} , while the temperature of the given system must lie outside of the location of the C curve. If an amorphous metal is heated isochronously at a constant heating rate, the process of crystallization starts at a certain temperature \mathbf{T}_{x} . We can define the critical cooling rate as:

$$R_{c} = \Delta T_{x} / \Delta t \tag{10.1}$$

in other words as a crossing through a certain supercooling interval ΔT_x over a certain period of time Δt . At the rate lower than R_c , the material may completely or at least partialy crystallize, at higher rate it will reach the glass condition. In silicon glasses and a variety of glasses from organic polymers, the "nose" in the dependence of T-transformation is moved towards the long periods, meaning that the preparation of amorphous material is easy.

For most metallic systems, which do not have directional bonds, the movement of atoms is relatively easy and the location of "the nose" is moved towards very short periods (longer than milliseconds but newer longer than several milliseconds). The result is the necessity of high cooling (freezing) rates. First materials were therefore prepared using cooling rates of around 10^5 - 10^6 K/s. The process of cooling down, in some cases very quick, must therefore take place in the temperature interval:

$$\Delta T_{\rm x} = T_{\rm l} - T_{\rm g}, \tag{10.2}$$

The ratio of T_g and T_l temperatures is very important for the formation of metallic glasses:

$$T_{rg} = T_g / T_1 \tag{10.3}$$

This ratio defines the so-called *reduced temperature*. The ratio reaches the value of 2/3 in some silicates and polymers, the value of 0.25-0.5 originally in metallic systems, and nowadays the values is 0.6 in some systems. Reduced temperature T_{rg} , similarly to T_g is associated with the frequency of atoms skipping and varies for various metallic systems (Table.10.3).

For the above-mentioned characteristics it is possible to generalize the assumption that for the quick transition through the critical temperature interval ΔT_x during the melt cooling down period, we need the difference between T_1 and T_g to be minimal, in other words, the reduced temperature T_{rg} should have the highest possible values.

The influence of T_{rg} on the attained rate of nucleation can be seen on the Fig. 10.7, where the dependence of nucleation rate on reduced temperature $T_{rg}(=T_g/T_l)$ is shown for three values of T_{rg} . For $T_{rg} < 1/2$ the maximum of rate of nucleation is so high that the formation of metallic glass is very

difficult for all the cooling rates, in some cases it is even impossible. On the other hand, for the $T_{rg} > 2/3$ the rates of nucleation of crystals are very low for all the cooling rates.

From the viewpoint of glass forming ability (GFA), another temperature ratio is important apart from the above mentioned parameters (R_c , ΔT_x and T_{rg}). This ratio expresses the normalized temperature of crystallization T_x and is referred to as γ :

$$\gamma = \frac{T_x}{(T_x + T_i)} \tag{10.4}$$

Fig.10.7 Dependence of nucleation rate on the reduced temperature T_{rg} (= T_g/T_l) for three values of T_{rg} .



The *a* and *b* curve in the IRA diagram on the Fig.10.8 define the time t_x necessary until the beginning of the crystallization dependi ng on the temperature T_x under the temperature T_l ; the following applies for the periods and temperatures: ${}^at_x < {}^bt_x$ a ${}^aT_x < {}^bT_x$. Crystalline structure is not created if the temperature of the given system lies outside of the location of the "nose". The *a* curve represents classic metallic glass with high cooling rates, the *b* curve represents the bulk metallic glasses, in which the cooling temperatures do not need to be so high due to the influence of suitable composition of elements, which support the transition into glass state. The general view of the connections between the critical cooling rate and reduced temperature T_{rg} with regard to the composition of the alloys can be seen on the Fig.10.9.



Fig.10.8 IRA (TTT) diagram showing the dependence of the crystallization temperature T_x measured during continual heating for various melts with similar liquidus temperature T_1 and the temperature of transition to glass state T_g . The melt 'b' with higher bT_c (${}^aT_c < {}^bT_c$) exhibits a lower cooling rate bR_c (${}^bR_c < {}^aR_c$)

Glasses, whether metallic or non-metallic type, are not only in the out of balance state, but they also cannot be assigned any *"defined thermodynamic state"*. From the viewpoint of thermodynamics, the transition to glass state at T_g (creation of metallic glass) could be included among the second order transformations, because as opposed to crystallization from a melt, which represents a transformation of the first order, the changes of thermodynamic quantities (energy, volume) take place continually. However, some experimental evidence has demonstrated that such inclusion is not so easy and the difficulty of transition into glass state is nowadays explained using several phenomenological concepts:

- 1) Melt relaxation model,
- 2) Free volume model,
- 3) Interactions model.



Fig. 10.9 Relations between the critical cooling rate R_c, reduced temperature T_{rg} and the thickness t max (mm) for various alloys that create metallic glasses.

It is important to have a good knowledge of thermodynamics and kinetics of the process of crystallization to be able to understand the ability to create glass state. As was already mentioned before, the key parameter is the reduced temperature T_{rg} . If the melt is cooled below the melting temperature, than the difference of free energy between the melt and crystals becomes the driving force of the nucleation of crystals, while the creation of the melt/crystal border means a positive surface energy, which does not support the nucleation. These two effects lead to the creation of an energetic barrier ΔG^* that needs to be overcome by the local change so that a nucleus can be created. For the growth of embryo, the atoms in the melt must rearrange and the speed of transfer of atoms is described by the diffusion coefficient **D**, or viscosity **\eta**. The resulting rate of crystals nucleation I_v per a unit of volume is a result of multiplication of thermodynamic component, which depends on the probability of the overcoming of the nucleation barrier by the change and the kinetic component, which depends on atoms diffusion (or viscosity).

10. Metallic glasses

The rate of homogeneous crystal nucleation I_{ν} is given by the following expression:

$$I_{\nu} = \frac{A_{\nu}}{\eta(T)} \cdot \exp\left(-\frac{\Delta G^*}{k_B \cdot T}\right)$$
(10.5)

where A_v is a constant of 10^{32} Pa·s/(m³·s) order

 k_B is the Boltzmann constant.

The value of critical barrier for the formation of a critical spherical nucleus is given by the following expression:

$$\Delta G^* = \frac{16}{3} \frac{\pi \cdot \sigma^3}{\left[\Delta G_{xl}(T)\right]^2} \tag{10.6}$$

where ΔG_{xl} is the change of free energy per unit of volume during the transformation and σ is the energy of the border between melt and nucleus. Temperature dependence of the change of Gibbs energy can be considered in the first approximation as a function of undercooling:

$$\Delta G_{x1} = \alpha(T) \cdot \Delta S_{m} \cdot (T_{1} - T)$$
(10.7)

where $\alpha(T)$ is a thermally dependent correction factor (which decreases slowly from 1 at T₁ to approx. 0.7 at T_g) and ΔS_m is the melting entropy per unit of volume of the melt (generally 8-9 J/(mol·K)). The maximum controlling force for the crystallization at T_g is therefore approximately:

$$\Delta G_{\rm xl}^{\rm max}(T_{\rm g}) = 0.7 \cdot \Delta S_{\rm m} \cdot (T_{\rm l} - T_{\rm g}) = 0.7 \cdot \Delta H_{\rm m} \cdot (1 - T_{\rm rg})$$
(10.8)

where ΔH_m is the total enthalpy of alloys melting and this last relation implies the critical role of reduced temperature T_{rg} . In alloys that form bulk metallic glasses at slow cooling rates, it is true that $T_{rg} \approx 2/3$ (Fig. 10.7), which was predicted earlier by Turnbull.

The kinetic factor that influences the formation of the glass is viscosity (or diffusion). Viscosity η and diffusivity *D* are often related through the Stokes–Einsteinova relation:

$$D = \frac{k_B \cdot T}{3\pi \cdot \eta \cdot l} \tag{10.9}$$

Where *l* is the mean atomic diameter.

The viscosity of the liquids η is commonly described by the modified Vogel–Fulcher–Tammanovou (VFT) equation:

$$\eta(T) = \eta_0 \cdot \exp\left(\frac{D^* \cdot T_0}{T - T_0}\right) \tag{10.10}$$

where D* is the parameter of brittleness ($1 \le D^* \le 100$), T₀ is the VFT temperature and η_0 is a constant indirectly proportional to the molar volume of the melt. At the temperature T₀ the barrier becomes infinite due to the flow. The brittleness describes the degree of deviation of the supercooled liquid viscosity from the Arrhenius behavior. The liquid is considered to be "brittle", if D*<10 and "strong" if D*>20. Strong liquid exhibits a high equilibrium viscosity of the melt and higher Arrhenius temperature dependence of viscosity than the brittle liquid. For pure metals, the values of D* is approximately single digit, while for SiO₂ glass, which is a typical example of material with a strong tendency to create glass, the D*=100 and its viscosity exhibits Arrhenius temperature dependence. The rate of crystal nucleation is considerably influenced by the melt temperature, VFT temperature and brittleness. If we use the relations for

$$T_r = T/T_l,$$
 (10.11)

$$T_{r0} = T_0/T_1$$
 (reduced VFT temperature) (10.12)

and introduce the substitution for the parameter A involving a critical barrier for the formation of critical nucleus

$$A = \frac{16\pi \cdot \sigma^3}{\left[3k_B \cdot \alpha^2 \cdot T_l^3 \cdot \Delta S_m^2\right]}$$
(10.13)

then the rate of nucleation of a homogenous I_v crystal is given by the following relation

$$I_{v} = \frac{A_{v}}{\eta_{0}} \cdot \exp\left(-\frac{D^{*} \cdot T_{r0}}{T_{r} - T_{r0}}\right) \cdot \exp\left(-\frac{A}{T_{r} \cdot (1 - T_{r})^{2}}\right)$$
(10.14)

and the growth rate *u* by the following relation

$$u = f \frac{D}{l} \left[1 - \exp\left(-\frac{n \cdot \Delta G_{xl}(T)}{k_B \cdot T}\right) \right]$$
(10.15)

If we consider a stable nucleation and a tri-dimensional crystal growth, then the time t for the crystallization of a certain detectable volume ratio of x crystals (e.g. 0.5%) during the isothermal annealing is given by the following relation:

$$t = \left(\frac{3x}{\pi \cdot I_{\nu}(T) \cdot [u(T)]^3}\right)^{1/4}$$
(10.16)

This last equation is the base for the formation of a TTT diagrams (Fig. 10.6 and 10.8).

10.3 The composition of the alloys

Alloys that are suitable for the preparation of the amorphous structure are usually composed of transition metals (Fe, Ni, Co, Pd, Pt, Cu, Zr etc.) with eventual additives inhibiting crystallization, such as B, Si, C a P (Table.10.3). The composition is usually selected according to specific needs for applications (high strength, hardness, ductility, elasticity, magnetism, corrosive resistance). An important role for the development of bulk metallic glasses was played by the alloying or microalloying by elements, which influence the formation of the glass, thermal stability, crystallization, and properties of these materials.

Elements that support the formation of amorphous state have also other effects:

Phosphorus improves the conditions of production technology, but it also leads to increased susceptibility to embrittlement after the thermal processing and it lowers the level of magnetic saturation;

Boron increases the stability of metallic glasses;

Carbon improves the conditions of production technology, it supports the development of the relaxing processes upon the thermal processing of the metallic glass;

Silicon increases the stability of metallic glass and improves its characteristics as a magnetically soft material.

Table.10.3 Composition of selected alloys for the preparation of bulk metallic glasses and their characteristic properties

Alloy	D _{max}	Tg	T _x	T _I (K)	ΔT _x	T _{rg}	γ	R _c
	(mm)	(K)	(K)		(K)			(K/s)
$Pd_{40}Cu_{30}Ni_{10}P_{20}$		586	660	856			0,458	0,1
$Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$		574	660	834			0,469	0,067
$Pd_{42.5}Cu_{27.5}Ni_{10}P_{20}$		584	665	871			0,457	0,083
Pd ₄₀ Cu _{32.5} Ni _{7.5} P ₂₀		568	654	932			0,436	0,133
Pd ₄₀ Cu ₂₅ Ni ₁₅ P ₂₀		596	668	910			0,44	0,15
$Pd_{45}Cu_{25}Ni_{10}P_{20}$		595	675	884			0,456	0,1
$Pd_{45}Cu_{30}Ni_5P_{20}$		577	659	861			0,458	0,083
$Pd_{37.5}Cu_{30}Ni_{12.5}P_{20}$		572	647	929			0,431	0,133
Cu ₅₀ Zr ₄₃ Al ₇	4	721	792	1176	71	0,613	0,418	
Cu ₄₇ Zr ₄₃ Al ₇ Ag ₃	5	716	795	1156	79	0,619	0,425	
Cu ₄₇ Zr ₄₃ Al ₇ Be ₃	6	715	798	1139	83	0,628	0,430	
Cu ₄₃ Zr ₄₃ Al ₇ Ag ₇	8	710	797	1125	87	0,631	0,434	
$Cu_{43}Zr_{43}Al_7Be_7$	12	710	813	1126	103	0,631	0,443	
$Mg_{65}Cu_{25}Gd_{10}$	8	408	478	755	70	0,540	0,411	0,33
Mg ₆₅ Cu ₂₅ Y ₁₀	4	413	473	760	60	0,543	0,403	0,33
$Pr_{60}Cu_{20}Ni_{10}AI_{10}$	5	409	452	718	43	0,570	0,401	0,17

Note: D_{max} is the thickness of prepared material

So far prepared metallic material with amorphous structure can be divided into two main groups:

1. *metal-metalloid*, which includes alloys of transition or noble metals with approximately 20% metalloids (e.g.: $Fe_{80}B_{20}$, Fe_{40} Ni₄₀B₂₀, $Pd_{40}Cu_{25}Ni_{15}P_{20}$). The easiest preparation of amorphous state is with alloys, which are composed of one or more elements (metalloids, elements of 4th or 5th group of the periodic table of elements) that are similar to metals thanks to their properties. The metallic glasses are usually of 3 to 5 components and mostly the ratio of 70-80% between the metallic elements and metalloids is maintained.

2. *metal-metal*, such as alloys based on Cu-Ni, Nb-Ni, Zr-Ni, (Ti,Zr)-Be, Al-Cu, Mg-Zn, Mg-Y-Cu, Zr-Ni-Cu-Al, Ti-Zr-Be-Ni-Cu, which can be divided into:

- *a*) alloys of the transition metals of the 8th and 1st group with the transition metals of the 3rd to 7th group
- *b*) alloys of alkali metals or alkaline earth metals
- c) alloys of rare earth metals (lanthanoids) or actinoids

The examples of critical temperatures and cooling rates for selected alloys can be studies in the Table.10.3 and on the Fig.10.9.

The following empirical criteria were determined for the formation of metallic glass:

- Criterion of deep eutectic
- Criterion of different size of atoms
- Criterion of different crystalline lattice

Criterion of deep eutectic

Experimental research has proven that in metallic systems, the temperature T_g strongly depends on the composition and that the formation of the glass will be most probably near the eutectic composition. The "deeper" the eutectic or the steeper is the adjacent liquidus, the higher the tendency of metallic glass formation. Deeper eutectic means higher stability of the liquid and relatively lower degree of undercooling necessary for the glass formation.



A note on the role of amorphous structure controlling the behavior of a supercooled melt during the formation of a metallic glass

In the diagram of the dependence of free energy (G) on the composition, the intersections of the G curves of the supercooled melt with the curves of crystalline phase determine the glass-forming range - GFR during the polymorphous process of cooling without segregation (partition-less), as, for example in the melt spinning technology, as schematically shown in the phase diagram on the **Fig.10.10**. This diagram depicts only the left part of the binary diagram consisting of solid solution on the left side and the intermediary β phase on the right side, which at first forms an eutectic on the side adjacent to the element A (with solid solution).

In order to be able to predict the GFR, we have to search for the range of composition in the moment, when both the T_0 curves (dashed) cross the temperature of transition into glass state T_g (solid line). On the T_0 curve in that moment, the free energies of both existing phases depending on the temperature and composition are the same. The T_0 curve between the liquid and solid determines the minimal undercooling of the melt for the solidification of solid phase with the same composition without segregation. The G curve of the melt will reach "deeper" if the short range ordering – SRO – is created in the melt, therefore the enthalpy becomes more and more dominant member of the G energy with the rising temperature and the T_0 curves will decrease more steeply.



Fig.10.10 A cut of the left part of the schematic equilibrium phase diagram for a binary system A–B. a) For a symmetrical eutectic system with eutectic composition X_{eu} approximately in the center of the GFR line and almost identical to $X_B^{T^0}$; b) For a non-symmetrical system, where GFR and $X_B^{T^0}$ are clearly out of the eutectics.

Dashed lines T₀ intersect at the composition $X_B^{T^0}$. The range of transition into glass state (GFR) is given by the intersection of the T₀ lines with the T_g line: it is obvious that for the case on the Fig.10.10a (symmetric eutectic system) the eutectic composition X_{eu} occurs at approximately the center of the GFR line and is almost identical to $X_B^{T^0}$; while in the case on Fig.10.10b (non-symmetrical system) the GFR and $X_B^{T^0}$ occur clearly out of the eutectics.



Fig.10.11 Structure of alloys (Fe₇₂Mo₄B₂₄) ₉₄Dy₆ cast into a bar with 3 mm diameter: a) the TEM picture and the corresponding SAED figure; b) HRTEM picture of the area in the white frame a) with the imposition of atoms.(Note.: SAED selected area electron diffraction; HRTEM – high resolution transmission electronic microscopy)



Teplota (°C)

Fig.10.12 Equilibrium phase diagrams of selected binary systems, in which it is possible to prepare metallic glasses for certain eutectic compositions (adjusted according [8]).

The depth of the eutectics can be defined as the deviation of the liquid temperature from the mean melting temperature of pure component, or as negative deviation of the liquid temperature from the ideal solution liquid. This depth is quantitatively related to the ability to create glass phenomenon in various systems, however, various empirical relations had to be define. One of the assumptions is that a strongly negative mixing heat support the creation of glass state. Similarly, higher values of above-mentioned reduced temperature T_{rg} are associated with the good ability to form glass state.

From the experimentally observed mixtures of various phases in the microstructure after casting under various technological conditions and for various compositions, it has been possible to determine the range of compositions for which the formation of the glass state is real in the systems. The microstructure of the glass state can be examined on the picture from the high resolution transmission electronic microscopy (HRTEM) (Fig. 10.11). The lines in the upper part of the binary diagrams shown on the Fig.10.12. represent the areas of composition for which the metallic glass state formation is possible.

10.4 Structural properties of metallic glasses

In the case of ideal amorphous alloys there is no regular arrangement of atoms over a long distance, the distances between nearest neighbors are not precisely defined and these distance are often larger by up to 5% than those we can observe in crystalline phases. Nevertheless, we can say that there is a certain topological short-range order in the metallic glass. This order has to be relatively tight, because the weight of alloys in the glass state is just a few percent lower compared to the crystalline phase. Simply, it is possible to compare the metallic glass structure to the structure of solidified melt. However, as mentioned before, in this state there is a certain arrangement and there have been several models proposed, explaining the metallic glass structure. We will talk about these models in the following paragraphs.

10.4.1 Microscopic model

It explains the metallic glass structure in a metal-metalloid system (with the composition of around 20% metalloid and 80% metal). It is based on the idea that atoms of the metallic component are arrange in a so-called tight irregular arrangement. The mentioned arrangement is based on the application of atoms arrangement according the "hard spheres" model and corresponds to the initial idea of Bernal, describing the structure of a melt composed of one type of atoms.



Fig.10.13 Types of atomic arrangement according to Bernal – eight convex deltahedra (polyhedron, whose faces are all equilateral triangles): a) regular tetrahedron; b) triangular bipyramid with 6 faces, c) regular octahedron with 8 faces, d) pentagonal bipyramid with 10 faces, e) snub disphenoid f) triangular prism, g) gyroelongated square bipyramid h) regular icosahedron

It has been determined that the TNU is actually composed of 8 types of atomic arrangement (Fig.10.13). The most frequent is the tetrahedral arrangement (Fig.10.13a). Some types of arrangement (Fig.10.13 c-h) have large internal cavities that may be occupied by atoms of the metalloid. Local arrangement (short distance) of various types of atoms take places in the melt and leads to the stabilization of the melt structure resulting in favorable conditions for the formation of amorphous structure after a rapid cooling (solidification). The physical base of the ability to form metallic glass is the weak resistant potential of the AB atomic pair in comparison with AA and BB pairs. The distances between closest neighbors r_{AB} may vary in a broad range, as it is required by the formation of amorphous structure, without causing a significant change in potential energy. When the crystalline structure is formed, there is a slight drop of energy.

10.4.2 Model of local chemical arrangement

The existence of an irregular distribution of metalloid atoms corresponds with the irregular distribution of larger cavities in the "Bernal structure" (Fig.10.13c-h). The irregular arrangement of the metal atoms in the metallic glass of the $Fe_{40}Ni_{40}B_{20}$ type has been experimentally demonstrated using the ion microscopy. The emergence of areas with local arrangement is a result of mutual interaction of various types of atoms and their structure in many cases approximated to the corresponding intermetallic phases. Their formation influences the ability to form the metallic "structure". The created agglomerates of atoms with characteristic configuration and composition (Fig.10.14) could act as a potential nuclei for the nucleation. Then the ability to retain the amorphous structure in the solid state is a function of concentration of the given system, lying between the composition correspondent to the pure component and the composition of agglomerates of atoms with characteristic composition.

The tendency to form metallic glass is usually highest in the area of concentration lying between two stable crystalline phases, which corresponds to a lowmeltable eutectic.

Fig.10.14 Tri-dimensional model of atomic structure of a metallic glass based on Ni81B19. The purple atom in the center of each cluster is a dissolved B, which is surrounded by green Ni atoms. The bonds of B were omitted from this picture for more clarity. These quasiequal clusters exhibit a different schemes of linking: connection through the top, sharing over the wall, connection through the corner and without a connection.



10.4.3 Model of microcrystalline structure

It is based on the idea that when a melt is rapidly cooled, the size of emerging crystals decreases with the decreasing substrate temperature, in other words with the rising cooling rate. The amorphous state then represents a limiting case of the crystalline state under conditions of extremely high nucleation rate and zero value approximating to the nucleation rate. Microcrystalline models are based on the crystal size that is comparable to the size of elementary cells in simple crystalline structures. The consent experimental results of observation (diffraction characteristics of the scattering X-rays) and the results of theoretical analysis is significantly smaller than in the case of the model mentioned in 10.4.1. The transformation between the amorphous and crystalline state it was found that the process of crystallization does not take place by the growth of microcrystalline areas, but through the discontinual nucleation of particular crystalline particles in amorphous matrix Fig.10.15.

The comprehensive analysis of obtained experimental results suggests that in most cases, it is possible to successfully apply the ideas according the TNU model.

Základní kov	At.poloměr (nm)	Kovový systém	Slitina	ΔT _x	T _{rg}	D _{max} (mm)	R _c (K/s)
Kov-kov							
La	0.274	Ln-Al-LTM	$La_{55}-AI_{25}-Ni_{20}$	69	0.68	7	100
			La_{55} -Al ₂₅ -Ni ₅ -Cu ₁₀ -Co ₅	98	0.70	9	
Zr	0.216	Zr-Al-TM	Zr ₆₀ -Al ₂₀ -Ni ₂₀	77	0.64	30	1-10
		Zr-Ti-TM-Be	Zr _{41.2} -Ti _{13.8} -Cu _{12.5} -Ni ₁₀ -Be _{22.5}	25	1-10		
Mg	0.172	Mg-Ln-LTM	Mg ₆₅ -Y ₁₀ -Cu ₂₅	70	0.59	7	200
			$Mg_{65}\text{-}Y_{10}\text{-}Cu_5\text{-}Ag_5\text{-}Pd_5$	35	0.62		
Kov-meta	loid						
Pd	0.179	Pd-LTM-P	Pd ₄₀ -Ni ₄₀ -P ₂₀	50			1.28
			Pd_{40} - Cu_{30} - Ni_{10} - P_{20}	95	0.71	40	1.57
			Fluxováno			72	0.1
			Pd _{42.5} -Cu ₃₀ -Ni _{7.5} - P ₂₀				0.067
Fe	0.172	Fe-(Al,Ga)-metaloid	Fe_{72} -Al ₁₅ -P ₁₁ C ₅ B ₄ -Ge ₂	60		2	10
		Fe-TM-B					

Table.10.3 The list of metallic glasses with critical temperatures and rates

Note.: Ln – lanthanoids, LTM – late transition metal – transition metals from the right half of the periodic table of elements, TM – transition metals in general, R_c – critical cooling rate, T_{rg} – reduced temperature and D_{max} – the thickness of the casting.

10.4.4 The crystallization process of metallic glasses

The undesirable phenomenon that limits the use of metallic glasses is the possibility of **crystallization (devitrification)**, which is accompanied by a severe and *irreversible change of physical and mechanical properties*. For the application of metallic glasses, it is necessary to consider the following crystallization characteristics:

- a) Temperature of crystallization
- b) The time period of exposition at given temperature
- c) Heating rate





The Fig.10.15 and 10.16 illustrate the temperature dependencies of the change of electrical resistance of metallic glass of the $Pd_{81}Si_{19}$ type in comparison with the process characteristic for the crystalline state (for metals and their alloys it is true that the electrical resistance increases with rising temperature).

Fig.10.16 Change of free energy, specific heat, viscosity and density depending on the temperature related to the transition from the glass to crystalline state.

In terms of evaluation of the thermal stability of metallic glasses, we must emphasize that the given type of material is in **unstable state and its creation temperature is under the T**_g **temperature**. That is why upon heating this type of material, the heat activated process start immediately. These processes are similar to, for example, the tempering treatment of solid solutions. It is possible to divide these processes into three types according the temperatures:

a) At the temperature $T < T_g$ *the process of relaxation*, takes place. It is characterized by the changes in atomic arrangement of the amorphous matrix over a short distance. Diffusion processes are ongoing in the amorphous matrix.

b) At the temperature $T_g < T < T_x$ the changes in amorphous state take places as well as the *processes of demixing*, which leads to, for example, reaching the so-called metastable (quasi-equilibrium state) state of the metallic glass.

c) At $T > T_x$ *the process of crystallization* of metallic glass takes place, in other words the transition to crystalline state, which can take place in various steps until it reaches the equilibrium crystalline state.

The process of crystallization may be very different. The diagram of Gibbs free energy curves in a binary system is on the Fig.10.17 and it depicts how a glass or an amorphous material may decrease its energy through the following steps:

- a) Dissolution into two amorphous phases
- b) polymorphous crystallization to a supersaturated solid solution α ,
- c) polymorphous crystallization to a metastable compound β
- d) polymorphous crystallization to an equilibrium phase γ ,



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- e) primary crystallization α ,
- f) eutectic crystallization to α and metastable β ,
- g) equilibrium eutectic crystallization to α and γ



Fig.10.17 The diagram of equilibrium in a binary system upon formation of various phases.

In some cases, the **emergence of two amorphous phases** (the **a** area on the Fig.10.17) is observed in the first phase of the transformation in the metallic glass. This phase takes place before the crystallization process itself.

 $\begin{array}{ll} (\text{amorphous}) \ \text{AuSi} \ \rightarrow \ \text{Si} \ + \ \text{Au}_{75} \text{Si}_{25} & (\text{both phases amorphous}) \\ \downarrow & \downarrow \\ & \text{Si} \ + \ \text{Au}_3 \text{Si} & (\text{both phases crystalline}) \\ \downarrow & \\ & \text{Au} \ + \ \text{Si} & (\text{both phases crystalline}) \end{array}$

Polymorphic crystallization takes place with the change of concentration. It is associated with the local change of atoms arrangement, giving rise to a metastable or stable crystalline phase with the same composition as glass (areas **b**, **c** and **d** on Fig.10.17):

$Fe_{75}S1_{25} \rightarrow Fe_3S1$	(stable)
$Fe_{75}B_{25} \rightarrow Fe_{3}B$	(metastable)
\downarrow	
$Fe_2B + Fe(\alpha)$	(stable)

Primary crystallization of metallic glass (area e on Fig.10.17) may take place in **two stages**, first the decay of matrix will take place with the emergence of two phases, one of which is amorphous:

 $\begin{array}{rcl} & & & & \\ & &$

In the next stage, the dispersive crystalline phase Fe (α) operates as preferential nucleation center with the following crystallization of the amorphous matrix Fe₃B.

Eutectic crystallization (areas **f** and **g** on Fig.10.17) represents a process of simultaneous crystallization of two phases in a discontinual reaction. The resulting phases are both crystalline (they may both be stable or one of them can be metastable):

 $\begin{array}{rcl} & & & & \\ & & & 370^{\circ}C \\ Fe_{80}B_{20} & \rightarrow & Fe\left(\alpha\right) + Fe_{3}B \end{array}$

10.5 Methods of preparation of metallic glasses

It possible to use various methods to prepare materials in amorphous state. In this chapter, we are going to mention the three most common that were so far used to prepare alloys from more than a hundred of binary systems:

- 1) Quenching the melt
- 2) Ion mixing
- 3) Mechanical alloying



Fig.10.18 Four different methods of metallic glass preparation by quenching the melt.

On the Fig.10.18 there are schemes of preparation processes of metallic glasses from melts. In essence, all of the cases consist of preparation of thin strips by quenching the melt on a cooled substrate, be it on one cylinder or between two spinning cylinders, injection of melt into cooling liquid in a planar cooled surface.

In the manufacturing of the hard magnetic materials based on Fe, the optimization based on TTT diagram, which is listed on the Fig.10.19, is performed.



Fig.10.19 TTT diagram for the optimization of conditions of manufacturing the permanent magnets Nd-Fe-B in glass state.

10.6 Properties of metallic glasses and the areas of the technical use

Metallic glasses are being considered to be a suitable material in various areas of material engineering based on their extremely favorable combination of properties such as their magnetically soft properties and high strength properties, including good formability (magnetic shielding, magnetoelastic sensors, and substitutes for the crystalline magnetically soft materials of the Fe-50% Ni type). Another excellent property, as mentioned already in the introduction, is their ratio of yield strength and elasticity modulus. Thanks to this property, these material based on Zr, Ti, Cu etc. of non-magnetic alloys are applied in sports and biomedicine applications. Among other uses there are thin abrasion resistant and protective coatings.

10.6.1 Mechanical properties

Over the last few decades, the bulk metallic glasses were the subject of great interest because of their unique properties, which were defined above. Strange and very attractive combination is the high strength and high limit of elastic deformation, such as in Vitreloy alloys in the Table.10.5. From the viewpoint of density and compressibility, the amorphous metals practically do not differ from the crystalline metallic material of the same composition. However, there is a number of characteristic differences in the level of obtained mechanical properties. Examine the diagram on the Fig.10.20, which compares the yield strengths depending on the E module for selected types of materials and alloys in amorphous state. This diagram clearly shows that the properties of metallic glasses reach higher levels than the crystalline materials. Also the Table.10.6 compares the selected properties including the price of amorphous and traditional crystalline materials based on Al, Fe, Ti a Zr.

Note on the elastic properties of metallic glass

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Search and watch the video on youtube under the keyword "Liquidmetal ball". The balls made of steel, titan and metallic amorphous material (Liquidmetal) are put into glass cylinders and are left bouncing on a hard surface until that movement is naturally stopped. Steel and titanium ball almost immediately stop their movement (approx. after 10 s), the ball made of metallic glass bounces for more than a minute. The defects in lattice in crystalline materials absorb the plastic reflection and change the plastic energy quickly to heat. Homogenous composition of amorphous structure makes possible for the 99% of the energy of the collision to be returned to the surface and allow the ball to accelerate its upward movement.

Property	Value
Elastic strain limit ϵ_{el}	2%
Tensile yield strength σ_{y}	1.9 GPa
Young's modulus Y	96 GPa
Shear modulus G	34.3 GPa
Poisson's ratio v	0.36
Vickers hardness	534 kg/mm ²
Fracture toughness K _{Ic}	55-59 MPa·m ^{1/2}
Thermal expansion coeficient α	10.1.10 ⁻⁶ K ⁻¹
Density p	6.11 g/cm ³

Table.10.6 Properties of alloys based on Al, Ti, Zr and Fe in amorphous and crystalline state

Materials	Strength (MPa)	Young's modulus (GPa)	Density (g/cm⁻³)	Fracture toughness (MPa.m ^{1/2})	Plastic strain to fracture (%)	Cost (USD)	
Conventional alloys *							
Al alloys	200-300	60-80	3-4			2-5	
Ti alloys	300-1000	100-120	4-5	~ 20-120 High values	2-50 Typical high for all loaded geometries	15-30	
Fe alloys	300-2000	150-200	7-8			0.6-10	
		Bulk	amorphou	is alloys (BMG) **			
Al alloys	800-1500	60-80	~ 3-4	~ 20-60	Large in confined geometry.	2-5	
Zr alloys	1600-2000	80-105	~ 6	High values can be increased using 2nd phase	Limited (to 1%) in unconfined geometry. Can be extended to 5%	25-40	
Fe alloys	2000-3500	140-160	7-8	additions	or more using 2nd phase additions	1-10	

Note: * preparation by traditional casting, forging, heat treatment extruding, machining to precise shapes etc. increases the price of the product

** pressure casting into metallic molds, thermoplastic molding (in supercooled state), very precise shapes, without thermal treatment, minimal or none additional processing, which decreases the price of the product

Amorphous metals exhibit a higher yield strength and higher limit of elastic deformation than the crystalline materials. Generally, however, they have a low toughness and fatigue strength. The creation and movement of dislocation is not possible, because there is no crystalline arrangement over long distances. Amorphous metals therefore reach higher yield strength and higher elastic deformation limit than crystalline alloys with the same composition. With the rise of deformation to about 2%, the oblique shear bands start to form in the amorphous metals with the rising critical tensile stress.

Due to the localized deformation shear bands, the elastic deformation of the bulk metallic glasses is non-homogeneous at room temperature. The mode of macroscopic elastic deformation of the bulk metallic glasses is often closely associated with the single shear band along the main shear plane. As a result of this, the bulk metallic glasses will slide at the angle of 45° to the axis of strain with the plastic deformation of < 2% in compression and they have essentially zero tensile ductility.

The formation of these macroscopic shear bands, which have the thickness of only 10 to 20 nm and are created very fast, predominates during the whole process of plastic deformation until fracture. The bands restrict the subsequent deformation (non-homogenous flow).



Fig.10.20 Schematic dependence of yield strength (metals, composites and polymers) or flection (ceramics) on the Young modulus (Adapted according to [10]).

The metal has lower density and lower strength in the shear bands than in their surroundings (softening) and it behave more as a viscous liquid. The continuing deformation quickly leads to the fracture along the shear bands. The morphology of the fractures of bulk metallic glasses is characterized by the typical vein-like formations along the whole surface of the fracture. The reason of these formations may be the lowering of the viscosity inside the shear band during the catastrophic fracture.

As we have mentioned above, the ductility of the metallic glasses is low. At low rates of deformation and/or mildly increased temperatures, the metallic glasses may be considerable deformed by creep, which is manifested by pure viscous flow.

Although the testing conditions during the evaluation of mechanical properties on the material in form of strip with thickness of $30-50 \ \mu m$ can be considered critical, the obtained mechanic and metallurgical characteristics can be summarized into several points:

- When tested in tension, the amorphous metals behave as macroscopically brittle. At the same time, with the beginning of plastic deformation the fracture of the material occurs, the plastic deformation is therefore very small. A typical sign of the deformation of amorphous metals is the formation of strongly localized small shear bands. A totally different behavior is manifested by the amorphous metals under pressure. In these conditions, it is possible to obtain a reduction to 50%, for example by rolling.
- 2) The tape made of a wide range of alloys (with a typical thickness of 40 μm) can be bent by 180°, without breaking. Metallic glasses are extremely resistant to cyclical bending stress, this is the reason why they are used as reinforcing fibers in the preparation of composite materials.

Massive construction material cannot be directly produced due to the specific conditions of their preparation. However, it is possible to produce tubes or cylinders from the thin amorphous tape using the winding technique. Semi-finished products prepared like this can be then manufactured further to create compact construction parts, for example, using the technique of mutual welding of the wound tape or connecting the wound tape using the amorphous powder, while preserving the amorphous state with all the mechanical and metallurgical advantages.

The viscous flow increases the density of the material, therefore with the continuing creep, the viscosity rises. Amorphous materials manifest a quick decrease of creep rate at constant stress and temperature. The fatigue strength of amorphous material is low in general, cyclical tensile stress causes the formation of shear bands, which lead to a more rapid fatigue fracture than in the crystalline metals under same conditions.

The low ductility and fatigue strength of the amorphous metallic materials may be increased by partial devitrification. The material basically creates a composite structure, which is a mixture of amorphous and nanocrystalline structures. In this case, the crystalline phase acts as a barrier preventing the spreading of the shear bands and the subsequent ruptures. This leads to increased ductility and toughness.

The secondary phase may be introduced from outside as well (for example the C or W fibers in an amorphous matrix). This type of composites will keep their high yield strength of the amorphous phase but at the same time increase the reliability and strength up to the fracture point of the material.

An important technological characteristic of the technical materials is their formability. Ceramic glasses are easily formed into various shapes when they are heated to a temperature, at which their viscosity decreases so much that a plastic flow is possible. Similar attitude can be used towards bulk metallic glasses, therefore we arrange a suitable formability. If a metallic glass with high GFA is heated, the following transformation will occur:

Amorphous metal \rightarrow transition through the glass temperature \rightarrow supercooled liquid \rightarrow crystallization \rightarrow melting.

In the temperature range of the supercooled liquid, the metallic glass deforms more probably through a simple viscous flow of liquid than through the shear bands. In that case, great deformations may be performed without disrupting the metal. The viscosity is an exponential function of the temperature, therefore the strength of the metal can be adjusted by selecting a suitable temperature. For example, in alloys based on Zr (Vitreloy-1) very good formability can be achieved at approximately 400°C and that makes the supercooled liquid available for forging or extruding. This process is much easier for amorphous alloys with high GFA than the processes of traditional casting and molding. The operations are carried out at lower temperatures and stress, the shrinkage is less frequent, there is no porosity, the surface is typically shiny and this eliminates the additional finishing

and polishing. The material is therefore treated as easily as a thermoplastic polymer and also remains in the amorphous state during molding and subsequent cooling to 20 °C.



Fig.10.21 Stress –deformation dependence: a) Zr50Cu50, b) (Cu50Zr50)96Al4, c) (Cu50Zr50)95Al5, d) (Cu50Zr50)94Al6 and e) (Cu50Zr50)92Al7Gd1 under stress with the deformation rate of $8 \cdot 10^{-4} \text{ s}^{-1}$.

Table.10.6 Maximal critical	dimension, therma	al stability and 1	mechanical p	roperties for Fe	-Co-B-Si-Nb
and Co-Fe -Ta-B ba	ased alloys (bulk m	netallic glasses i	in the form of	f rods)	

		Thermal stability			Mechanical properties		
Alloy	Diameter Ø (mm)	Т _g (К)	ΔT _x (K)	T _g /T _I	HV	E (GPa)	σ _f (MPa)
Based on Fe-Co and Fe-Co-Ni							
$[(Fe_{0.9}Co_{0.1})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	2	832	45	0.570	1150	190	3900
$[(Fe_{0.8}Co_{0.2})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	2.5	830	50	0.580	1225	205	4170
$[(Fe_{0.7}Co_{0.3})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	3.5	828	50	0.586	1245	210	4200
$[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4	825	50	0.586	1250	210	4250
$[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	5	820	50	0.587	1220	210	4210
$[(Fe_{0.8}Co_{0.1}Ni_{0.1})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	2.5	818	55	0.606	1230	208	4225
$[(Fe_{0.6}Co_{0.1}Ni_{0.3})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	3	792	60	0.608	1170	205	4070
$[(Fe_{0.6}Co_{0.2}Ni_{0.2})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4	800	65	0.611	1210	210	4160
[(Fe _{0.6} Co _{0.3} Ni _{0.1}) _{0.75} B _{0.2} Si _{0.05}] ₉₆ Nb ₄	4	813	65	0.613	1240	210	4200
Based on Co							
$Co_{43.5}Fe_{20}Ta_{5.5}B_{31.5}$	2	910	72	0.600	1455	268	5185
(Co _{0.535} Fe _{0.1} Ta _{0.055} B _{0.31}) ₉₈ Mo ₂	1.5	915	75	0.586	1693	282	5545
$[(Co_{0.535} Fe_{0.1}Ta_{0.055} B_{0.31})_{0.98}Mo_{0.02}]_{99}Si_1$	2.5	895	82	0.593	1450	238	4915
[(Co _{0.535} Fe _{0.1} Ta _{0.055} B _{0.31}) _{0.98} Mo _{0.02}] ₉₈ Si ₂	3	890	82	0.597	1314	227	4454

The mechanical properties of the metallic glasses can be improved by adding alloying elements, which we can clearly demonstrate on the alloys based on Fe, Co and CuZr in combination with various elements. The influence of these alloying elements on the basic parameters and mechanical values of metallic glasses are listed in Tab.11.7 and 10.8. The comparison of the behavior of selected alloys based on CuZr (Table.10.8.) alloyed by other elements during a stress test can be examined on Fig.10.21, from which you can read the optimal composition of the alloys to increase their strength and plastic deformation. In the case of $(Cu_{50}Zr_{50})_{95}Al_5$ alloys, we may observe the behavior of highly solidifying metallic glass up to 18% of deformation (pink row in Table.10.8.). Fracture strength during static and dynamic stress in bulk metallic glasses based on Zr-Hf can be examined on Fig.10.22. The picture shows that for both contents of Zr+Hf (52.5 or 57 at.%) the fracture strength is higher under

quasistatic than under dynamic stress, meaning that the material is not sensitive to the deformation rate in both compositions.



Fig.10.19 The fracture strength of bulk metallic glasses based on $(Zr_xHf_{1-x})_{52.5}Ti_5Ni_{14.6}Cu_{17.9}Al_{10}$ and $(Zr_xHf_{1-x})_{57}Ti_5Ni_8Cu_{20}Al_{10}$ under static and dynamic stress: higher fracture strength under quasistatic than under dynamic stress implies the negative sensitivity to deformation rate for both compositions

Table.10.7 Mechanical properties of CuZr alloys under pressure depending on the addition of other elements –Al and Gd

Slitina	Modul of elasticity E (GPa)	Yield strength σ _y (MPa)	Elastic deformation ε _γ (%)	Ultimate strength o _{max} (MPa)	Plastic strain (to break) ɛ _f (%)
Cu ₅₀ Zr ₅₀	84	1272	1.7	1794	7.9
(Cu ₅₀ Zr ₅₀) ₉₄ Al ₄	88.7	1611	2.1	2068	5.4
(Cu ₅₀ Zr ₅₀) ₉₅ Al ₅	87	1537	2.0	2265	18.0
(Cu ₅₀ Zr ₅₀) ₉₄₃ Al ₆	92.4	1636	2.1	1999	2.8
(Cu ₅₀ Zr ₅₀) ₉₃ Al ₇ Gd ₁	90.6	1774	2.0	2249	1.1

10.6.2 Corrosive properties

Amorphous metals based on Fe and Ni have high corrosion resistance, if they also contain chromium, which create a passivation layer of Cr_2O_3 on the surface. A similar layer causes and increased resistance in crystalline materials, but in the case of metallic glass, the basic material is homogenous without precipitates and grain borders, which can be potentially the location of preferred corrosive attack. This is the reason why the corrosive resistance is higher in alloys even without adding chromium.

10.6.3 Magnetic properties

The amorphous structure of metallic glasses creates the conditions for reaching extraordinary magnetic properties. One of the basic characteristics of amorphous metals is the very easy magnetization.

The reason could probably be the ideal isotropic nature of amorphous metals, because from the macroscopic point of view, all directions in amorphous material are equal. The change of magnetization is therefore possible with small energy requirements. In fact, there is a little anisotropy in metallic glasses related to internal tension induced and "frozen" in the material during rapid cooling during their preparation.

Due to the fact that there are no grain borders in an amorphous material, the movement of the domain walls (borders between the areas with different magnetization characteristics) is not restricted. Therefore, another process that makes the magnetization difficult is not present.

Another advantage is the high electrical resistance (approximately 3 times higher than in crystalline materials with similar chemical composition), which is attributed to the irregular atomic arrangement of amorphous material. When the magnetization is change rapidly in amorphous metals, the magnetization losses associated with the heating of the material are very low. That is why it is possible to use these materials for systems working at higher frequencies.

Amorphous alloys based on Fe and Co manifest excellent soft magnetic characteristics, mechanical strength and corrosive resistance. For example, the Fe60Co8Zr10Mo5W2B15 alloy is amorphous up to 800 K of temperature and has an extremely narrow hysteresis loop BH, hardness according to Vickers HV=1360, strength under stress 3800 MPa and can be inserted in aqua regia for an hour without any loss of weight. The amorphous metals serve as suitable starting materials for the preparation of nanocrystalline soft magnetic materials and hard permanent magnets. Large dimensional magnetic material with the highest productivity is the $Nd_2Fe_{14}B$. This intermetallic compound is widely commercially used, for example in electric engines and speakers and is frequently manufacture by the casting method of melt spinning in amorphous ribbons, which can be devitrified to nanocrystalline permanent magnets. Very fine grain size of 14-50 nm, which were obtained through transition amorphous state, increase the coercivity.

Applications

✤ Sporting equipment

The high yield strength and elastic deformation limit imply the modulus of deformation energy that is up to 25 times higher than in crystalline materials with similar chemical composition. This considerably increased ability to accumulate and disperse energy of elastic deformation makes the metallic glasses an ideal material for spring and sporting equipment such as golf clubs, tennis rackets, baseball bats or bows that are able to bounce or shoot an object with a higher force and to a greater distance.

Tools and equipment casings

High hardness and ease of formability of selected amorphous alloys is ideal for application in surgical instruments, knives, computer and equipment cases. Due to their hardness and high corrosion resistance they can also be used in jewelry of for coating of various containers, pumps, valves, filters and electrodes, which work in corrosion liquids.

Metallic foams

In melted state, the alloys with high GFA (glass forming ability) are two to three time more viscous than traditional alloys which makes it easier for them to be used for the preparation of metallic foams by bubbling gas through melt and injecting the resulting foam into the mold. This technology was used to prepare amorphous alloys with 99% porosity.

***** Diffusion barriers in microelectronics

At intermediate temperature, the predominant mechanism of diffusion is the transport along the grain borders, which means that the diffusion is much slower in metallic glasses than in crystalline materials. The absence of grain borders in metallic glasses make it possible to use them in diffusion barriers of microelectronic devices.

Projectiles with high penetration

10. Metallic glasses

Limited deformability of amorphous materials is advantageous for their use in armor piercing projectiles. Compared to missiles based on Pb alloys, which are deformed and flattened, a missile from magnetic glass breaks into self-sharpening shrapnel upon impact. If the munitions from the metallic glass is reinforced with tungsten, its efficiency is comparable with the missiles made of depleted uranium.

Limits of applications

Wider applications of materials based on metallic glasses have two significant limits:

Their *limited toughness* is the greatest limit for the most of the structural applications. The research on optimization is ongoing, as we have mentioned above, and it is focused on the preparation of composite materials combining the glass and crystalline state. Therefore, it is possible to expect some new applications.

The second great limit is the so far common high price of these alloys – around 35 USD for a kilogram. To be able to manufacture metallic materials with high GFA, it is necessary to use highly pure metals. A great challenge for the decrease of prices and therefore further application is the development of alloys, which would be less sensitive to the content of impurities.

Important terms

Glass transition of metals, devitrification or crystallization, structure and ordering of metallic glasses, corrosive properties, magnetic properties, thermodynamics of glass transition, critical cooling rate.

However it is needed to repeat thermodynamics of solidification, nucleation, critical nuclei, TTT diagrams.



Questions

- 1. Can you define the basic characteristics of metallic glasses?
- 2. What most important parameters are requiered to know for preparing and using metallic glasses?
- 3. What thermodynamic and structure parameters controll the transition to glass condition?
- 4. What are the reason of high corrosion resistance of metallic glasses?
- 5. What elements form the Vitreloy?
- 6. What basic requierements are needed for metallic glasses?
- 7. What main limitation do you name for metallic glasses?
- 8. What processing methods of metallic glasses do you know?
- 9. Can you name the application area of metallic glasses?



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