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Technology of special alloys

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1. Methods of preparing special alloys based on non-ferrous metals



Time needed to study: 3 hours



Learning objectives:

When you have completed this module, you will be able to:

- List the facilities and technologies for preparing special alloys
- Describe differences between induction and resistance heating
- Explain technology of arc melting
- Explain principle of skull melting
- Distinguish advantages and disadvantages of process



Lecture

1.1 Introduction

Progressive technology and hi-tech applications today are unthinkable without using specific materials, such as, e.g. superalloys, titanium alloys, highly fusible metals and their alloys, alloys on the basis of intermetallic compounds, metal glass, metal foams, composite materials with a metal, ceramic, or polymeric matrix, materials used for hydrogen storage. Among the progressive materials it is necessary to include also coatings and thin layers (films) based on the above-mentioned materials. These can, on the one hand, provide protection from an adverse environment causing damage to materials by, e.g. corrosion, high temperatures, oxidation, embrittlement by hydrogen the influence of ambient moisture, sulphuration, carburization, and other physical-chemical processes in the surface of a material. They can also perform different functions e.g. applying magnetic, electrical or biocompatible.

1.2 Basic processes of alloys preparing

Melting process includes two steps: taking a charge into the furnace and its meltdown. This process often involves refining (cleaning, using additional chemicals that trigger chemical reactions in a molten bath), and vaccination (to melt we add a small amount of a substance that will affect nucleation and the growth of solids - the crystals during solidification).

Furnace devices are powered by energy from either fossil fuels or electricity. For melting and casting metals and alloys several methods and types of equipment are available, and their appropriate selection depends on the following factors

- \Rightarrow type of melted material,
- \Rightarrow quantity of prepared material
- \Rightarrow space to place the melting equipment.

During melting, in certain cases (alloys of Ti, superalloys, alloys of metals melted at high temperatures) a protective atmosphere must be used that prevents:

- ⇒ oxidation and formation of undesirable inclusion (superalloys, alloys, etc.),
- ⇒ penetration and dissolving of hydrogen, poss. emergence of hydrides and subsequent change in properties (superalloys, Ti alloys, etc.),
- ⇒ exothermic reactions with the emergence of undesirable compounds (oxides), which can damage the furnace by overheating.

1.3 Selected technologies for special alloys preparation

1.3.1 Melting with resistance heating

Resistance heating furnaces are among the most widespread equipment, in which the processed material may be heated by resistance elements located along the walls in a furnace chamber, or by using controlled circulation of the atmosphere within the furnace. Their advantage is the possibility of heating to any temperature up to 3,000 °C with a possible automatic control of input power and temperature. Operations of these furnaces are often mechanized and automated, which makes it easier for staff to operate them and enables introducing such equipment into automated production lines. Furnaces can be hermetically sealed, and can work with a protective atmosphere or in a vacuum, so that they are able to ensure material protection against oxidation, or conversely, according to the type of special atmosphere with a gaseous medium they can ensure the chemical treatment of surfaces by nitriding or carbon restoration.

Most resistance furnaces are of an indirect type, in which electrical energy is converted into heat when the current is passing through heating elements. Heat is passed to the heating unit by heat transmission, convection, or from the circuit. Furnaces consist of a working chamber with a fibrebrick lining, which bear both the processed material and heating elements. Inner furnace space is separated from the metal core drier by thermal insulation (Figure 1.1). Other components and functional mechanisms of the furnaces are made from refractory steel, heat resistant steels, or other heat resistant materials.



Fig. 1.1 Schema of resistance heating fournace [1, 2]: 1- topné články, 2- žáruvzdorná vyzdívka, 3- tepelná izolace, 4- žáruvzdorná deska nístěje

Crucible furnaces are multi-purpose and very flexible facilities. Crucibles are vessels of refractory materials, steel or alloys, which are warming inside the furnace using resistance (or fire) heating, so that the charge is not in contact with the resistance element (with a flame). The charge is being heated by heat, which is transmitted through the wall of a crucible. Molten metal is cast directly from a portable crucible or by using a tilting device in a furnace (Figure 1.2).

1.3.2 Melting with an electric arc

Electric Arc Furnaces represent an essential type of device, which are also used for steel production (Fig. 1.3). Fundamentally the process lies in the fact that between the carbon electrodes, in this case three of them, and the charge of a desired composition an electric arc is formed, whose temperature may reach 3,000 to 4,000 °C. Furnaces are used in a foundry and also for refining metals. Liquid alloy is cast from the tilted furnaces into different forms. Melting may be carried out in a protective atmosphere, in air or in a vacuum, according to the type of material processed.

Modification of an electric arc furnace represents a device for **vacuum arc remelting** - VAR or vacuum arc-double electrode remelting -VADER, which are used for non-ferrous metal alloys. In those facilities the continuous melting of consumable electrode in a vacuum, using an electric arc, takes place. A DC current gives rise to the arc between an electrode and base of a copper crucible, chilled by water (Figure 1.4). Intensive heat, which arises through the electric arc, melts the top of an

electrode and in the chilled cup a new ingot comes into existence. During the re-melting process we maintain a high level of vacuum.



Fig. 1.3 Schema of electric arc fournace (Modified from [4])

The VAR-structure of the ingot after solidification depends on the local speed of solidification and the temperature gradient on the interface liquid/solid phase (hereinafter referred to as an interface l/s). If the primary dendrite structure is directional, a relatively large temperature gradient at the interface l/s must be maintained throughout the process of remelting. Direction of the dendrites growth

corresponds to the direction of the temperature gradient, i.e., the heat flow direction at the time of solidification in the crystallization line (l/s). The direction of heat flow is always orthogonal to the front of crystallization or, in the case of a curved interface, to the tangent of the curve. The growth direction of dendrites is therefore a function of the molten metal bath profile during solidification. With the growing speed of re-melting the depth of the bath is growing, so the angle of dendrites to the axis of the ingot is also growing (Fig. 1.4). In extreme cases, the directed growth of dendrites can stop, in which case the core of ingot solidifies non-directionally, thus with an uneven axis of grains. This case, however, leads to segregations and microshrinkings in the structure of an ingot. Micro-shrinkings also originate in directed growth, if the distance between the branches of dendrites grows.



Fig. 1.4 Schema of vacuum arc remelting fournace (Modified from [5])

The result is an optimal structure with dendrites parallel to the axis of an ingot, but the good surface of an ingot requires a certain level of power supply, which also affects the speed of remelting. Optimum melting speed and power supply depend on the size of an ingot and the purity of material, so for example, for large dimension ingots it is not possible to keep the requested low speed of remelting to form the structure parallel to the axis of the ingot.

In the re-melted ingot defects can arise despite directionally solidification, such as "tree ring patterns", "freckles" and "white spots". Such defects may be a reason for the disposal of an ingot, in particular in the case of some special alloys.

Tree ring patterns do not have a significant influence on material properties and are easy to detect with macro-etching on the cross-section of the ingot. This foundry defect represents a negative crystalline segregation, and it is the reason of fluctuations of the remelting speed. In modern VAR facilities the speed of remelting is maintained at the required value using precise computer control for the weight reduction and speed of electrodes consumption, so that there are no significant fluctuations in speed of remelting due to defects in the electrode.

Freckles and white spots affect the material properties much more significantly. Both of these defects can be a cause of premature fractures in the disk turbines of aircraft engines. After etching, freckles are black circular or nearly circular surfaces, most of which are rich in the presence of carbides or carbide-generating elements. White spots are typical defects in VAR ingots. After macro-etching they appear to be the light-coloured surface on the ingot. They contain less alloying elements, e.g. less Ti and Nb for alloy Inconel 718. In the formation of white spots different causes can play a role:

- the residues of non-melted dendrites from a consumable electrode;
- the bits and pieces of matter splashed from arc, which do not dissolve nor melt, and they harden creating an ingot;
- the pieces of the transition zone of an ingot, which are transported to the hardening interface of the ingot.

These three phenomena, whether acting on their own or in combination, are the most frequent and difficult to overcome because of white spots occurrence in a vacuum remelting, and because they are closely related to the arc melting process. To reduce the frequency of the white spots occurrence it is appropriate to use:

- a maximum speed of remelting with regard to the macro-structure;
- a short arc to minimise the generation of corona and maximize the stability of an arc;
- homogeneous electrodes without any cavities and cracks;
- an appropriate source of energy in order to reduce the extreme voltage peaks of sudden shorts.

Advantages of VAR

Basic advantages of remelting consumable electrodes in a vacuum.

- The removal of dissolved gases (hydrogen, nitrogen, CO);
- The reduction of unwanted trace elements with a high vapour pressure;
- The reduction of the oxide level;
- Achieving the directional crystallization of an ingot from the bottom to the top end, which avoids macro-segregation and reduces micro-segregation.

1.3.3 Melting using induction heating

In the Induction Furnace an alternating current passes through a hollow copper coil cooled with water (Figure 1.5), and thus the magnetic field is induced, which allows for eddy currents to appear in the charge. These currents warm and/or melt the material. Induced current in the charge generates a secondary magnetic field (Fig. 1. 5b), which allows mechanical agitation of the molten material. The advantage of these devices is that due to the intensive agitation the material melts with both chemical and thermal homogeneity, which will affect its final structural and mechanical properties. In comparison with other devices these furnaces allow an energy-efficient, clean, and easily managed process. In foundries these devices are installed instead of cupola furnaces, as they allow to reduce the emissions of dust and other pollutants. The capacity of the facility differs as to the charge from one

kilogram up to hundred tons, and they are used for melting iron and steel, as well as copper, aluminium and precious metals. Their disadvantage of use in foundries is the limited refining, a charge must not contain oxidation products and it must have a defined composition. In addition, some of the alloying admixtures may be lost due to oxidation and must be therefore supplemented into the melt again.



Fig. 1.5 Schema of a) induction furnace and b) induced currents (Modified from [6,7])

The size of mixing depends directly on the size of an induced current, and indirectly on the square root frequency in the furnace. The inappropriate selection of frequency leads to either too small, or too intense mixing, and to a substantial limitation during melting. Excessive mixing lifts up the liquid alloy in a furnace, and exposes it to air operation. Oxygen in the air reacts with the majority of elements in the liquid alloy, and this phenomenon leads to large losses of alloys due to melt oxidation. Operating frequencies range from 50 to 60 Hz to 400 kHz or above, depending on the prepared material, the capacity (volume) of the furnace, and required speed of melting. As a general rule, the smaller the volume of melt, the higher frequencies are used in the furnace; it is given by the depth of inputs, which is a measure of the distance the AC current may penetrate below the surface of an inductor. With the same conductivity the shallower depths of penetration have higher frequencies, which means even less penetration into the melt. Lower frequencies may cause mixing or turbulence in the metal melt.

An induction furnace during the process emits various sounds, such as buzzing or purring (due to magnetostriction), their intensity can help an operator to determine whether the process is functioning properly, and whether the level of performance is correct.



During the Air Induction Melting - AIM process - the element with the highest melting temperature T_M is first melted down, because of the risk of leakage (e.g. Al) over the crucible, which could cause damage to the induction coil. Only then Al is added, causing a sudden temperature increase in a crucible up to hundreds °C. Of course, this leads to the oxidation of Al and alloying elements (Al melting loss). As an example, we can state the classic production of the intermetallic alloy IC-50 (Ni₃Al with Cr,Mo,Zr and B). Firstly, Ni is melted down with its alloys, and only then Al is added. During 1minute its temperature rises from 1,600 to 2,300 °C. After a few minutes at 2,100 °C the Al melting loss appears, since the Al oxidation (and also Zr) is the response, which is more exothermic than the aluminide formation. As a material for crucibles for induction melting are chosen Al₂O₃, Zr₂O₃ or mulites.

In the case of highly reactive metals and alloys, or highly pure materials, the induction melting may be carried out in a vacuum. In such a case the Vacuum Induction Melting - **VIM** offers other benefits, such as low losses of alloying elements due to oxidation, achieving an almost accurate composition of the material and removal of the dissolved gases. The induction furnace is this case is closed in a steel chamber (Figure 1.6), and by using a vacuum pump we can reach a vacuum of 0.133 Pa. The furnace may be loaded continuously or discontinuously (with access of air). The charges vary according to the furnaces sizes from 1 kg to 30 tonnes.

VIM technology is intended for reactions dependent on pressure (such as the reactions of carbon, oxygen, nitrogen, and hydrogen). Also a great field importance here has the elimination of harmful volatile ingredients - Sb, Te, Se and Bi in a vacuum induction furnace.

As an example of the general use of this method we can mention the deoxidization of superalloys by a strictly monitored pressure-dependent reaction of the carbon surplus.

In other alloys than superalloys the quality of materials and their specific composition may be ensured by using decarbonization, desulphurisation, or selective distillation in a vacuum induction furnace. For highly solid alloys, working at high temperatures, it may be due to the high pressure of vapours in the majority of undesirable trace ingredients that these elements are removed by distillation, during induction melting in a vacuum, up to very low levels. The vacuum level in refining depending on the product and the technology ranges between 10^{-1} to 10^{-4} mbar (10^{1} - 10^{-2} Pa). Through the VIM process it is possible to achieve high quality alloys. The purity of melts is ensured through the following steps:

- The furnace atmosphere is monitored, in particular for leaks and desorption speed;
- The selection of stable heat resistant materials for the crucible;
- Mixing and homogenization by electromagnetic stirring or by afination gas;
- The precise control of temperature, in order to avoid the reactions of melt with the crucible;
- The appropriate methods of slag flushing and during casting.
- The use of an appropriate channel or inter ladle method for better removal of oxides.

Disadvantages of VIM

Metallurgical operations to remove sulphur and phosphorus are of course limited.

1.3.4 Skull melting and casting

Skull Melting and Casting is a technology using the melting of a charge in a chilled water crucible. The molten material creates a so-called crust on the walls, and thereby stopping the direct contact between the liquid alloy and crucible, so there is no significant pollution of the resultant material. According to the type of heating it is possible to implemented this process using an electric arc or induction.

Vacuum arc skull melting

Při tomto procesu (angl. Vacuum Arc Skull Melting and Casting – ASM) se všechny operace provádí ve vakuově utěsněné komoře. Elektroda z titanu nebo slitiny titanu se přiblíží k vodou chlazenému měděnému kelímku. Mezi elektrodou a kelímkem vznikne oblouk, a protože kelímek je ochlazován vodou, vzniká na povrchu kelímku, jak bylo již napsáno výše, krusta titanu, která zamezí

přímému kontaktu taveniny s kelímkem. Jakmile je v kelímku požadované množství roztaveného kovu nebo slitiny, je provedeno odlévání do licí formy přímo ve vakuové komoře (Obr.1.8).



Obr. 1.8 Schéma moderního polokontinuálního vakuového zařízení pro obloukové tavení se studeným kelímkem s navážkou až do 1000 kg [9].

1 – systém rychlé navážky, 2 – kabely pro přívod energie, 3 – zdroj, 4 - posuvný držák elektrody, 5 – odtavná elektroda, 6 - kelímek s krustou, 7 – posuvný nosník kelímku, 8 – mezipánev, 9 – odlévací soustava, 10 – vakuovací systém, 11 – systém pro odstředivé lití

Vacuum induction skull melting

Všechny operace procesu (angl. Vacuum induction skull melting, dále jen ISM) se provádí ve vakuově utěsněné komoře. Rozdíl oproti ASM je ve způsobu ohřevu, který je zajištěn ohmickými ztrátami způsobenými vířivými proudy v tavenině. Vířivé proudy vznikají v důsledku elektromagnetického pole při průchodu proudu indukční cívkou.

Měděný kelímek chlazený vodou je segmentován, jeho palisádová stěna je tvořena z měděných trubek (obr.1.9). Indukované pole se vytvoří ve slitině uvnitř kelímku, takže kelímek se nenahřívá. Natavená slitina utuhne na stěnách segmentovaného kelímku za vzniku tenké krusty na jeho povrchu. Tavené kovy, jako např. titan, mají nízkou tepelnou vodivost, takže tato krusta izoluje roztavený kov od chladícího účinku kelímku. Efektivní příkon je tak vysoký, že roztavený kov částečně levituje (Obr. 1.10), vzniká kupole taveniny, což následně snižuje tepelnou výměnu mezi taveninou a krustou. To vede k vyššímu přehřátí a vlivem míchání pomocí indukovaných proudů je rozdělení teplot v tavenině homogenní.







Fig. 1.10 Schéma indukčního zařízení produkujícího elektromagnetického pole, které umožňuje levitaci kovu, vznik kupole taveniny a krusty na dně kelímku. Elektromagnetické míchání proudy) (vířivými vede k homogennímu rozdělení teplot složení uvnitř а (Upraveno podle taveniny [10])

1.3.5 Electron beam melting

Electron beam melting-**EBM** is a method characterized by its high refining skills and a high degree of source heating flexibility. For these reasons, it is an ideal method for melting and cleaning metals and alloys in a high vacuum, using water-cooled copper moulds. Currently this process is used in particular to manufacture highly meltable and reactive metals (Ta, Nb, Mo, W, V, Hf, Zr, Ti) and

their alloys. The process plays an important role in the preparation of sputtering targets and alloys for electronics, as well as in recycling titanium scrap.

Principle of the method

Electron guns represent the high temperature heating source, with which it is possible to exceed the melting temperature in the point of the beam impact, or even the boiling temperature of all the materials. An electron beam (Figure 1.16) can be effectively directed by the magnetic deflection and by the rapid crossing at high frequencies to focus on a target with a diverse shape, which makes it the most flexible of all remelting methods. The beam of electrons hits the target with a typical energy density of 100 W/cm². Depending on the material melted its efficiency of the power transmission ranges from approximately 50 to 80 %. EB melting is a method of heating the surface, so with achievable speeds of melting only a shallow bath appears, which may have a positive affect on the ingot structure in terms of porosity, segregation, etc. The exposure of the overheated surface of the metal bath and high vacuum environment (1-0.001 Pa) leads to superb degassing of the molten material are selectively evaporated and thus we increase the purity of a material. In some cases, however, the possibility of losses in required components must be considered in advance.



Fig. 1.16 Princip elektronového ohřevu [12]

- 1 kov ve formě tyče určený k přetavení (anoda),
 - 2 roztavená zóna, 3 fokusátor,
 - 4 wolframová kruhová katoda

1.3.6 Electroslug remelting

In contrast to the VAR, which needs a vacuum for refining, in this method of Electroslag remelting - ESM - the consumable electrode is immersed in a bath of slag using the water chilled mould (Figure 1.16). An electric (usually alternating) current passes through the slag, between the electrode and emerging ingot and overheats the slags, so there is a thin layer of liquid metal emerging at the top of the electrode. Molten metal drips off the electrodes, passes through slags, where it is cleaned from non-metallic admixtures through chemical reactions with the slag or using flotation, it drops to the bottom of the water chilled mould, where it hardens. The remaining inclusions are of a very small size and they are spreading in the melted ingot.

The molten slag is shifted upwards with the emergence of an ingot. The new ingot of the clarified material is growing slowly in the direction from the bottom of the mould and it is

Fig. 1.17 Průmyslová elektronová pec

homogeneous, directionally crystallised and without a centrist dividing plane, which is typical for traditionally cast ingots, hardening from the external surface to the centre.

Slag composition varies according to the melted material, it may contain e.g. CaF₂, CaO and Al₂O₃, eventually also MgO, TiO₂, and SiO₂. Slag must show some properties:

- a melting temperature lower than the melting temperature of the processed metal;
- electrically conductive;
- the chemical composition should ensure the required refining chemical reactions;
- a suitable viscosity at melting temperature



Fig. 1.21 Schéma pece pro tavení metodou ESR [8]: 1, 2- zařízení pro posuv elektrody, 3- nastavitelná podpěra pece, 4- siloměr, 5- píst elektrody, 6- čep elektrody, 7komora s ochrannou atmosférou, 8lázeň strusky, 9-ingot, 10-kokila, 11, 12- přívod energie, 13ovládací systém pístu elektrody, 14- platforma pro obsluhu

Advantages of ESR

Generally, ESR provides a very high, consistent, and predictable quality of the product. Controlled solidification improves the integrity of the product concerning its defects and structure. Surface quality of an ingot improves also thanks to a thin layers of stiff slag between the ingot and the wall of a mould during the melting. For this reason, the ESR method is preferred for highly solid superalloys to be applied in aviation, the nuclear energy, and for the large forgings. Ingots are achieving purity, which was unthinkable a few years ago. The surface of an ingot with a thin layer of slag does not need any special treatment before forging. Consumable electrodes may be used in a cast condition.

Structural casting defects

In melted ingot there may appear, despite directionally solidified processes, various defects, such as tree ring patterns, freckles, and white spots. The causes of these defects are similar to those for the VAR method. White spots do not commonly occur in ingots after using the ESR method.

Summary of terms

Induction melting, resistancce heating, induction skull melting, electroslag remelting, vacuum arc remelting, electron beam remelting



Question to the topic

- 1. Can you explain the principle of heating in arc remelting process?
- 2. Can you name the advantages of vacuum induction melting?
- 3. Which processes proceed during electroslag remelting?

What resources can you use to help?

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2. Preparation of alloys based on nickel and superalloys



Time needed to study: 3 hours

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Learning objectives:

When you have completed this module, you will be able to:

- Define basic methods of superalloys preparing
- Describe principles and parameters of proecesses
- Explain formation of possible casting defects

Lecture

2.1 Technology for superalloys preparation

Superalloys are special alloys based on Co, Ni and Fe-Ni, which are intended, concerning their excellent properties, for specific applications. The majority of these alloys shows high resistance to creep at elevated and high temperatures (up to 800° and some even above 1,000 °C). Therefore, they are used as high temperature materials in aviation, power engineering, the automotive industry, etc. Most of these alloys contains a large amount of alloying ingredients, and therefore they require specific procedures of preparation, which are discussed below.

2.1.1 Melting superalloys in electric arc furnace

Some superalloys, in particular those based on Co and Fe-Ni, are melted using various methods, which can also be used for stainless steel (Tab. 2.1), such as Electric Erc Furnace/Argon Oxygen Decarburization - EAF/AOD process. The process EAF/AOD was originally developed in the 1960s for the effective melting of stainless steel with a high content of Cr (11.5 and more % of Cr). For many superalloys based on Fe-Ni we can essentially say that they are special types of stainless steels and others, in particular based on Ni, showing a high content of Cr; therefore, they may be melted similarly to stainless steel. In this case, there is, as is the case of many other regular melting processes, the most expensive item the charge of this technological operation. We must, however, note that the raw materials used for EAF/AOD operations, are rather cheaper than that of the other types of superalloys. The process can enter scrap without any prior melting, and also a limited amounts of entry element oxides (such as Nb and Mo), as a replacement of more expensive elemental metals. These advantages make the process EAF/AOD the cheapest melting technology for superalloy production.

2.1.2 Vacuum induction melting of superalloys

Nevertheless, most superalloys based on Ni and Fe-Ni contain reactive elements, such as aluminium and titanium, and therefore they must be prepared by melting using the **VIM** method. Vacuum allows you to remove harmful trace elements, unwanted gases, and volatile elements. Induction heating ensures the agitation of melt and homogenisation, as we have mentioned in Chapter 1. After VIM is carried out, casting into the shape of an ingot or another required form is performed.

Melting superalloys based on Co do not generally require complex vacuum processes. AIM is normally used, but for the preparation of material for further forming the Co superalloys are melted also using VIM, VIM+VAR, or ESR. Alloys with Al or Ti (e.g., J-1570) and TA or Zr (e.g., MAR-M 302 and MAR-M 509) must be melted using VIM. Vacuum melting of other Co superalloys may improve their properties through the increased purity and the controlled composition of properties, such as strength or drawability.

2.1.3 Vacuum arc remelting of superalloys

Many alloys, in particular for forming, are then re-melted using VAR, in order to achieve higher purity and better foundry microstructures. Ingot (usually after VIM) forms the cathode, which, as soon as the vacuum arc starts to burn, begins to melt. Emerging drops drip through a vacuum and purifies. The molten alloy falls into the water chilled copper form. In the liquid bath further floatation purification of solid impurities (oxides, nitrides) takes place toward the surface. Solidified metal has the required directed structure. The VAR process reduces the content of elements with high pressure vapours in the alloy. Bismuth and lead, which may be present in the alloy even after VIM, are as to the influence on superalloys properties, highly undesirable, but their content can be significantly lowered using VAR. The magnesium content that is desirable in terms of improving its formability, and which is added during preparation with VIM, is also reduced, but not completely eliminated.

The comparison of relations between an electrode, the hardening ingot, and the shape and depth of the solidification line for VAR and ESR is illustrated in the Fig. 2.1. With VAR the first to solidify on the wall of crucible chilled with water is the alloy, which is deprived of a dissolved element. The upper part of this solidified layer is formed by the melt, which spurted out from the bath melt, and it is called the "crown".

After the crown is melted again by the continuous line of molten metal, the layer of deprived metal remains on the outer side of the ingot and creates the so-called shelf. During remelting the oxides and nitrides contained in the VIM electrode travel across the upper part of the molten bath into the shelf. The distance between the wall of the electrode and the wall of the crucible constitutes an annulus, which is an important parameter of this process. This distance between the lower part of the electrode and the upper part of the molten bath represents an arched space. Between the ingot and the water cooled crucible a space occurs during solidification, due to contraction, into which gaseous He is introduced, particularly for alloys sensitive to segregation, intended for better heat transfer, reducing the depth of the molten bath. From the schematic comparison we can see that the releases heat concentrates near the upper part of the molten bath. VAR is a process with low thermal inertia and any change in input will cause a rapid response (change in the shape of bath).

Defects in casting structure after VAR:

Freckles are not the only structural defects associated with a secondary melting, even though they belong among the most serious. Segregation combined with the deprivation of an alloying element reflects in the macro-etching as *a discreet white spot*, and it may have several different reasons. The most frequent mechanism of this is the shelf intersection by an arc. Shelf pieces, which drip into the bath, may not be completely melted and create the so-called "drop-in" defects. The result of this phenomenon is the emergence of areas with the chemical composition of a shelf, which may also contain thin layers of oxides or nitrides. Another possible mechanism of white spots areas occurrence may be the in-drop of dendrites which form the porous areas of the electrode. If the electrode is cracked, even bigger bits than dendrites can fall into the bath. Light spots then are not discreet structures, but they also contain darker areas (a residual foundry structure), so these large complex areas are called *dendritic white spots*.

Although optimization of the VAR process can minimize the frequency of those discrete white spots occurrence, it cannot be completely prevented due to the inner instability of the arc . Constructions using the components produced from material which were re-melted via the VAR process must take into account the frequency of white spots occurrence given by the process or type of alloy used.

Monitoring and process control is carried out by two different criteria:

- 1. bath depth and shape (checking the structure of solidification)
- 2. stability of the arc (the control of undesirable defects).

Bath depth and shape are regulated by the intake and exhaust of heat. Heat supply is determined by the speed of the electrode melting, which is monitored and changed in short intervals of time by adjusting the melting stream (the speed control of melting). During the melting process the mean speed of melting can be maintained using a constant jet intensity. Heat dump depends on the ratio of the surface/volume of the ingot (the size of ingot), which is processed. Bigger ingots are worse in

dumping the heat (low surface area/volume), and they must be melted with a slower rate, in order to avoid occurrence of big areas with liquid alloys+solids, and thus the emergence of unacceptable positive segregations. The high speed of melting can support at a given size of ingot positive segregation; on the contrary too slow melting may lead to the occurrence of structural phenomena associated with the reduction of a dissolved element. The mechanism of white spots solidification occurrence has not been fully explained yet, as it differs from the discrete white spots described above. These structures are not accompanied by drop-in defects, originating in the shelf or electrodes, and therefore do not contain layers of oxides or nitrides. Solidifications of white spots are also very serious defects of material, limiting the possibility to control the growth of grains in the following process.

The stability of the arc is actively controlled through the distance of the arc during the melting of an electrode, when the annular is constant for a given standard process. To melt superalloys the arc distance is maintained as a constant, the electrode is immersed either quickly or slowly (the reciprocating drive) in line with the variation of voltage, which take place when the arc distance changes the resistance of the system.

2.1.4 Electroslag remelting of superalloys

ESR superalloys are carried out similarly to the VAR process, but the bath is covered by a molten slag layer with a thickness of 10 cm (CaCO₃, Al₂O₃ a CaF₂). An ingot processed with the VAT method creates an electrode, which is in contact with a slag of a large electrical resistance, it heats and melts, and its temperature exceeds the melting temperature of the metal electrode. This electrode tip melts, the metal drops through the slags into the bath with a liquid alloy on the bottom, and thus the alloy refines. For alloys used for critical applications such melting is carried out twice or more times.

Melting speed is controlled through the input power and heat release by the size of the ingot. By ensuring the balance between the parameters of melting and solidification, we can maintain the depth and angle of the area (1+s), so the undesirable segregation defects in casting do not appear.



Fig. 2.1 Schématické srovnání procesů tavení VAR (vlevo) a ESR (vpravo) (Upraveno podle [1])

With ESR it is not possible to remove the elements using high vapour pressure, so we can maintain the content of Mg higher with VAR (which has a positive influence on thermal formability). A favourable effect on formability is represented also by the possible removal of sulphur, done by a chemical reaction within the process. Major changes in the composition may take place during the response of reactive metals, in particular in Al and Ti with the slag components.

Oxides, which are contained in the electrode are removed effectively during the melting, and the ingot is usually of a higher purity than in VAR. The ingot structure is controlled during solidification by the same rules as that of the VAR, but one significant difference in comparison with VAR is the nature of the heat transfer (through the oxidic coating of an ingot), and the existence of a thermal pocket (molten slag) in the upper part of the ingot/molten bath. The already mentioned scheme in Fig. 2.1 represents relations between an ESR electrode, hardening ingot, and the shape and depth of the molten bath. A characteristic feature of a solidification with ESR is that between the surface of an ingot and the wall of crucible, where an oxidic membrane occurs. Similarly as in the case of VAR, also during this process the annulus occurs between the wall of the crucial and the side of the electrode. An important parameter of this process is the depth of the slag bath, with which we control the electrical resistance of the system. The immersion depth of the electrode in the slag represents a parameter that influences the shape of a molten bath. Heat released during the ESR process is much larger than in the case of VAR (Fig. 2.1), but due to the influence of insulation characteristics of the slag coating the heat dump is less effective than for the VAR. Therefore, the ESR process has high thermal inertia and a slow response to the changes in input, in terms of the bath shape changes. The presence of a slag coating on the ingot improves not only the quality of the ingot surface, but also significantly reduces the presence of the shelf layer with reduced dissolved elements. Oxidic particles from the electrode are dissolved in the slag and they do not gather on the ingot surface. If a shelf does not form on the surface of the ESR ingots, then the emergence of undesirable internal defects (white spots) is also limited. However, the internal defects in the electrode may be a source of white spots occurrence in the solidified ingot after ESR.

Basic differences between ESR and VAR technologies, which are listed in Fig 2.1, can be summarised as follows:

- 1) The ESR bath is deeper and in the shape of V, unlike the VAR bath with the shape of U.
- 2) The deeper bath encourages dark spots occurrence, which may be controlled by using an ingot of a smaller size. Therefore, the maximum size of the ESR ingot is always less for any ESR device in comparison with VAR.

Monitoring and control of the ESR process is carried out by two different criteria:

- 1. bath depth and shape (checking the structure of solidification)
- 2. emergence of a sufficient slag layer on the ingot.

Similarly as in the VAR, also in this case the depth and shape of the bath are primarily controlled by the speed of melting (input power). The ESR process shall be carried out using the continuous setting of melting speed, in order to maintain the equal speed of melting. Due to a high thermal inertia of the process, as we have mentioned on the previous page, the response to changes of input are slower than in VAR, so that there are bigger fluctuations in the melting speed. Secondary control of the depth and shape of the melt is provided by using a shallow dive of electrodes into the slag. The transition of molten metal drops through slags affects the resistivity of the slag, and thereby also the voltage of the system. That is why the working voltage is given as a band of values. The range of this band is called *the voltage fluctuation*. Immersion of the electrode is directly proportional to the voltage fluctuations, i.e. the electrode is shifted with the help of a piston holder, so that the voltage does not exceed the specified band of fluctuation.

The creation of a sufficient *slag layer* on the ingot is not controlled during melting actively, but by selecting appropriate parameters, such as the melting speed, the depth of the molten bath, and the selection of the slag composition. Higher speeds of melting will enable achieving better surfaces of ingots, but a high speed of melting increases the depth of the molten bath, and shifts the process closer to the conditions for dark spots emergence. Therefore, it is critical for the process to have correct and well balanced parameters chosen.

Slag is particularly made of fluoride CaF₂ with the addition of oxides CaO, MgO, Al₂O₃, which reduce the temperature of slag melting and alters its resistivity. Commercially pure CaF₂ contains a certain quantity of SiO₂. During the melting of alloys with a Ti content there is a reaction between Ti and SiO₂ from the slag; the slag enriches the TiO₂, and in contrast, the content of Si grows until the balance is achieved. In order to minimise such undesirable changes some commercial slags are deliberately enriched with added TiO₂.



EAF/AOD, VAR, VIM, ESR, directional solidification, single crystal microstructure, odlévání lopatek, white spots, freckles, homogenization, precipitation



Question to the topic

- 1. Why some siperalloys are melted under protective atmosphere?
- 2. Can you specify basic differencies between VAR and ESR processes?
- 3. How the control of the processes could be realized?
- 4. Can you describe the differencies in the microstructures after VAR and ESR?
- 5. Name the type of defects in superalloys castings.



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3. Preparation of alloys based on titanium



Time needed to study: 2 hours



Learning objectives:

When you have completed this module, you will be able to:

- Define reactivity of titanium
- Describe methods of titanium alloys preparing
- Explain formation of possible casting defects in titanium alloys
- List the advantages of ISM method in preparing of titanium alloys



Lecture

3.1 Production of ingot titanium

Titan has excellent qualities which allow it to be used in such applications where other metals do not meet the requirements: aviation, space industry, chemical industry, and high-strength constructions. During the last two decades, titanium gradually became a common technical metal. There is an obstacle to its widespread use in our industry, however, that is its relatively high price. Even in its cast state it is several times more expensive than steel.

For production of all titanium semi-products, as well as for alloying special steels, stabilised using titanium, the basic material is the titanium sponge together with a certain dose of a recycled material. Pollution from the Kroll process (the reduction of chloride Ti by magnesium) can be reduced by a multiple re-melting of the sponge, and it also removes the volatile impurities (chlorides), and changes the morphology of the metal. Where appropriate, it is possible to add alloying ingredients during remelting to prepare a titanium alloy. Depending on the type of melting process there may be prepared various castings, ingots or slabs, with the required quality for further processing.

During the first step the titanium sponge (with a density 1.2 - 3 g cm⁻³⁾ is pre-melted using hydraulic pressing. The extrudes are subsequently connected into electrodes for the melting process. For any specific composition of alloys the extrudes are in addition alloyed by foundry alloys or elements. Into the extrudes small pieces of waste material can be also added. Due to the high affinity of titanium to oxygen the extrudes must be welded into the final consumable electrode in the chamber of plasma welding, with a low pressure of argon. By welding electrodes with a weight of 13 tonnes it can be prepared. Electrodes are in the normal case re-melted twice in a vacuum arc furnace. Between an electrode and metal sawdust on a water chilled bottom of a crucible an arc is ignited. The high energy of the arc melts the electrode, it is consumed, and an ingot arises in the crucible. This process takes place in a vacuum, the temperature is controlled by a computer, and data on melting processes are stored on the grounds of preparation materials for specific or critical applications.

Semi-products in the form of slags are also prepared using other methods, e.g. using electron or plasma melting, induction or arc melting in a cold crucible. For critical applications (the highest quality or disk quality for space industry) the final re-melting must be carried out in a vacuum arc furnace.

3.2 Melting and casting of titanium alloys

Titanium alloys are so reactive with oxygen, nitrogen, hydrogen and carbon, so that they must be melted, cast and cooled in a vacuum or in an inert atmosphere. Titanium and alloys react with the crucible material, so they are processed in water-cooled copper crucibles, in order to avoid their melting at the temperature of molten titanium (alloy), i.e. around 1,700 °C. If there was contact of molten titanium with the cooling water, there would be a risk of a very serious explosion in the furnace area. For this reason the melting aggregates for titanium alloys are very complex engineering equipment, in terms of ensuring their safety.

3.2.1 Preparation of alloys using VAR

VAR requires the emergence of an arc between an electrode of Ti alloy and pieces of the same alloy (the ends of electrodes, etc.). This electrode melts quickly and at a sufficient amount of molten metal it is pulled out, the crucible is tilted to cast the metal into a mould. The whole process takes place in a water-cooled copper crucible.

Casting must be carried out in special non-reactive forms, which are expensive due to those special oxidic materials for crucibles (typically zirconium ZrO₂) used. To cast titanium is a very difficult process, and it is often necessary to rework the castings and refine them. Usage of material is low, as recycling of the returnable material (pads and defective castings, which can be otherwise normally remelted) and of the waste is complicated.

3.2.2 Preparation of alloys using ISM

A relatively new method in the preparation of the titanium alloys is **ISM**, which we have discussed in more details in Chap.1. The ISM process may be followed either by casting or subsequent crucible titanium gas atomisation - TGA.

Advantages of ISM:

- Ability to melt almost all alloys of Ti. (It was used for more than 3,000 different reactive alloys, not only Ti)
- The charge may be in any form: ingots, plates, tubes, sponge, powder, reusable waste. Ideal charge chopped plates of scrap, which represents the high quality input of a raw material at a price of scrap. Typically 30 % returnable waste, 70 % of the primary raw material
- It is not necessary to prepare material in the form of an electrode, as the charge is melted using the magnetic field
- The water cooled copper crucible allows more than 10 thousand heatings (meltings) one producer reported more than 100 thousand heatings.
- 100 kg of Ti and its alloys are commonly melted. Higher weights are also considered.
- Ideal for small charges (for research) with castings of 1 kg.
- Controlled content of oxygen TiO₂ can be added into the melt, in order to control the strength characteristics of castings (higher content of O→with higher strength of Ti). Castings with a reproducible oxygen content for different melts.
- It allows more freedom in the input of charges and alloying; material can be added directly to the melt, which enables the prevention of melting losses of alloying elements (e.g. volatile Mn etc.), or the keeping of material in a melted state for a longer period of time, in order to dissolve high temperature melting alloying metals W, Ta).
- The resulting thin layer (skin, crust) on the surface of a crucible can be quickly removed, which ensures flexibility in the preparation of various alloys, e.g. 120 melts of several different alloys can be performed in 18 hours one cycle with a casting in 6 minutes!).
- Power input allows quick melting \rightarrow 20 minutes for 30kg and 35 minutes for 100kg
- Continuous agitation due to eddy currents→ the homogeneous distribution of concentrations and temperatures in melt
- A higher overheat of melt and more homogeneous temperature distribution \rightarrow facilitates casting.
- The possibility of precise casting

Casting methods

Use of traditional forms leads to an unacceptable surfaces of castings and large porosity, creating deep fragile reaction layers, with very difficult workability (large hardness); it leads to the

initiation and promotion of cracks in high tenacity alloys (e.g. Ti-6Al-4V). That is why precision casting (with investment casting) is more suitable. Traditional materials for forms are used as for the

other materials, such as Al₂O₃-SiO₂ are not appropriate for casting Ti and alloys. Melted Ti (alloy) reacts with oxides and dissolves Al, Si, and even the oxygen. Ti alloy consumes the form, and in extreme cases there can be a spillage of Ti into the furnace area. Therefore, the form shall be prepared from special, highly stabilised materials: ZrO₂, ThO₂ and Y_2O_3 . The ash content in wax sweeps must be controlled, because the ash (carbon!) will cause complete destruction of the а casting. Other possible materials for casting forms are listed in Table 3.4. melt has The Ti low-flow characteristics, so that the castings using the traditional gravitation method show the defects as a result of contraction, gasification, nonleaking of the melt; therefore, it is necessary and convenient to use, e.g. centrifugal casting (Fig. 3.4).



Fig. 3.1 Proces TGA pro přípravu práškového materiálu z titanu nebo jeho slitin [4]



Fig. 3.2 Gravitační a protigravitační lití lopatek pro turbíny (Upraveno podle [8])

Although ISM method makes it possible to prepare an alloy with a high purity, the main disadvantage of this process is the possibility of low overheating of the melt for subsequent casting into a form, due to thermal losses in a water chilled crucible. As a result, there are problems in casting thin-walled casts and the occurrence of casting defects.



Summary of terms

Reactivity of titanium, treatment of titanium sponge, casting of titanium alloys, induction skull melting, limitation of VAR method, casting defects.



Question to the topic

- 1. Jak se zpracovává titanová houba na ingotový titan?
- 2. Jakými metodami tavení je možné připravit titanové slitiny?
- 3. Jaká jsou omezení metody VAR?
- 4. Jaké jsou výhody použití metody ISM?
- 5. Jaké metody pro odlévání slitin Ti znáte?
- 6. Jaká jsou omezení při odlévání slitin Ti z hlediska jeho reaktivity?
- 7. Jaké materiály kelímků a forem se při ingotové metalurgii slitin titanu používají?
- 8. Jaké typy vad se ve slitinách titanu mohou vyskytovat po tavení a odlití?



What resources can you use to help?

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4. Preparation of alloys based on intermetallic compounds





Learning objectives:

When you have completed this module, you will be able to:

- Describe preparing methods of intermetallic alloys
- Explain principle of ExoMelt process
- Explain the principle of reaction of Ni and Al



4.1 Overview of technological processes

Intermetallic compounds IMC and intermetallic compounds based alloys are characterised by various unique properties (electrical, magnetic, mechanical, high temperature, corrosion resistivity, etc.), and so they are used in various fields of expertise, e.g. as superconductors, structural materials in the aircraft and automotive industries, magnets, the electrodes of battery power (batteries), hightemperature equipment, or as materials for the hydrogen industry. Intermetallic phases are characterised by a high organization of diverse atoms in the lattice, and thus they differ from the lattices with one-generic atoms of pure metals, and from the disordered solid solutions of conventional alloys. This orderliness affects the physical and mechanical properties. The organized structure of intermetallic phases may arise either directly duringn the solidification of a melt with a given composition, or during its phase transition into the solid phase, in the transition of a ordereddisordered state.

Since the 1980s these applications of alloys, based on nickel aluminides, expanded into many applications areas, due to their high content of Al, which allows the allows to resist oxidation or carbon restoration in an environment containing oxygen and carbon at high temperatures (up to 1,100 °C). Alloys are successfully used for the structural components of the furnaces used for heat treatments or for hardening other materials, especially in the automotive industry.

Intermetallic compounds and alloys are produced from the second half of 1980s, the first license was given to the ORNL laboratory (USA). Options for IMC preparation vary as to the material processed, they are carried out either using ingot metallurgy, or powder metallurgy methods. Depending on the composition of intermetallic alloys, i.e. whether they are for example aluminides, silicides, or whether they contain reactive titanium, you can select suitable preparation technology. All methods have their advantages and limitations.

4.2 Melting of IMC alloys

4.2.1 Factors with effect on the melting process

Conventional melting includes the already mentioned methods: AIM or VIM, VAR or VADER. Material prepared by these methods achieves different purity levels and different microstructures. Even though AIM is an economically advantageous method, a more preferred process preparation is VIM, in particular for aluminides, as it enables limiting the occurrence of porosity.

Nickel aluminides are to be prepared by traditional melting, so that you add aluminium into the molten nickel at a temperature 1,600 °C, which cannot be melted at the same time with nickel, as at the temperature 800 °C and above it can leak through the crucible in its liquid state and drop into the induction heat space of the furnace, and thus harm or even endanger the safety of this equipment's operation. When adding aluminium into the nickel melt, however, due to the influence of the exothermic character of combining nickel and aluminium the temperature in the crucible may rise by up to several hundreds degrees. It is the major issue in the production of aluminides using conventional melting, as it leads to the oxidation of aluminium and other ingredients contained in the melt, the so-called melting loss. Using conventional melting with the possible modification of the process, it is also possible to prepare titanium aluminides (e.g. γ -TiAl).

With induction melting of IC - 221M alloy, based on Ni₃Al, in zirconic crucible we add individual alloying elements such as Cr, Mo, Zr and B into the nickel melt, in order to prevent their oxidation. After adding aluminium at 1,600 °C into the melt, the temperature will increase up to 2,300 °C in one minute due to an exothermic reaction, then as a result of Al oxidation the temperature in the crucible will be keep at 2,100 °C for several minutes. The temperature may be increased not only by adding aluminium, but also zirconium.

Traditional ingot metallurgy has been facing many problems that complicate the preparation process of IMC, and must take into account the proper selection of equipment, crucibles, and forms for casting. When melting aluminides the following factors must be taken into account:

- 1) The difference between the melting temperatures of aluminium and transition metals (Ti, Nb, Ni, Fe, Co,.).
- 2) A large content of aluminium (up to 30 % and more)
- 3) The exothermic character of IMC
- 4) In some cases higher melting temperature resulting from IMC in comparison with Al or transition metals
- 5) Reactivity and the vapour pressure of alloying elements in the environment (air, vacuum) at a melting temperature

4.2.2 Reaction melting

The process in which the strong exothermic reaction induced by melting aluminium is used, was patented under the name Exo-MeltTM and named reaction melting. It is used to produce Ni₃, Al and FE₃Al alloys. Today, the melting and casting of Ni₃Al and Fe₃Al is provided by more than a hundred various enterprises and they are able to prepare and cast even 100kg melts.

$$xNi + yAl = Ni_xAl_y + Q \tag{4.1}$$

where Q ... teplo and for x = y = 1 is valid $Ni_xAl_y = NiAl$

In the production of Ni_3Al using the Exo-Melt process the key factor of the success is the sequence of raw materials charges, in order to create a strong exothermic reaction. Charges into the furnace follow the two basic rules: in the upper part combined Ni and Al is inserted, and nickel goes into the lower part. Alloying ingredients of alloys such as Cr, Zr, Mo, B, etc. are placed on the layer of nickel. Reaction melting takes place in the furnace, whose scheme concerning the charge is shown in Fig. 4.1. For pre-melting we use the heat of exothermic reaction, and control the energy consumption. This method can be used not only to melt the above mentioned IMC, but also other compounds based on Ti-Al and Fe-Al.

During the reaction melting the heating is carried out using induction heating coils, so that the exact temperature of each segment depends on their properties. Ni, whose melting temperature is 1,455 °C, is heated to around 800 °C, and as soon as Al starts to melt at 661 °C, it gets into contact with it. As a result of the exothermic reaction between Ni and Al, the NiAl compound appears and releases a large quantities of heat. Drops of NiAl compounds, whose melting temperature is 1,639 °C, roll down along the non-reacted molten aluminium. Overheated NiAl melt dissolves alloying elements in itself, non-reacted Al further combines with the heated Ni during the emergence of further NiAl, which responds to Ni on the bottom of the crucible, and there the Ni₃Al compound arises.





Summary of terms

Process EXO MELT, reaction melting, reaction heat, formation enthalpy

Question to the topic

- 1. Jaká jsou omezení při klasickém tavení IMC, zejména aluminidů?
- 2. Vysvětlete charakter reakce mezi Ni a Al.
- 3. Jaký je princip a průběh procesu Exo-Melt?
- 4. Vyjmenujte výhody procesu.

What resources can you use to help?

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5. Preparation of alloys by means of mechanical alloying



Time needed to study: 2 hours



Learning objectives:

When you have completed this module, you will be able to:

- Define basic parameters of the process
- Describe milling mechanisms
- List the mill devices
- Define the effect of parameters on final product of alloying



5.1 Basic characteristics of the process

Mechanical alloying - MA as one of the powder metallurgy methods allows for the preparation of homogeneous materials from the initial mixture of elementary powders. This process is carried out mainly in a dry environment of high-energy ball mills (*English* High energy Mechanical alloying - HE-MA) and it is being used for the preparation of both commercial and experimental materials.

Mechanical alloying enables:

- \Rightarrow the preparation of fine disperse particles by secondary phases (usually oxidic)
- \Rightarrow the extension of solubility limits in their solid form
- \Rightarrow the reduction of grain sizes to the nm scale
- \Rightarrow the synthesis of new crystalline or quasi-crystalline phases
- \Rightarrow the development of new amorphous phases (metallic glass)
- ⇒ splitting the organised state of intermetallic phases (IMC)
- ⇒ alloying elements difficult to alloy
- \Rightarrow the invocation of chemical reactions at low temperatures
- ⇒ reproducible and controlled process

5.2 Process parameters

At the beginning of the mechanical alloying process the required charge with a precise ratio of elementary powders is prepared, which is placed inside the grinding equipment together with the grinding medium (e.g. steel balls). The powder mixture is ground for a certain period of time, until a steady state is achieved, when the composition of each powder particle corresponds to the ratio of the starting charge. The ground semiproduct is then densified into a compact shape and heat-processed, in order to obtain a desired micro structure and properties.

5.2.1 Raw materials

Raw materials used for mechanical alloying are widely available technically clean powders, with particle sizes in the range 1-200µm. The size of particles in powder is not so crucial, only their size should be less than the size of the grinding balls, as the particle size of the powder reduces exponentially with time, and they reach the size of several microns after a few minutes of grinding. Raw material can be a wide range of materials from pure metals, foundry alloys, pre-alloyed powders, and highly meltable compounds. Dispersionally solidified materials usually contain the ingredients of carbides, nitrides, and oxides, from which the oxides are the most common (the oxides of dispersion solidified alloys). Originally, one of the raw materials used in mechanical alloying was malleable

metal, which worked as a bond, but in recent years the only ones successfully prepared were the mixtures for alloys of completely brittle materials.

At present, they prepare various types of alloys using ground powders mixtures: malleable - malleable, malleable - brittle, and brittle.

5.2.2 Types of grinding equipment

For the preparation of mechanically alloyed powders different devices are used for the highenergy grinding. They differ as to their capacity, grinding efficiency, and additional equipment for the cooling, heating, etc. In the next section a more detailed analysis will be given, but only for selected types.

Vibrating mills, such as SPEX, grind around 10-20 g of powder at one time. They are the most commonly used for the aboratory research of alloys.

A general mill type has one vessel, containing the sample and grinding balls, which is fixed in a holder that vibrates effectively there and back, driving a thousand times per minute. This vibrating movement there and back draws, in combination with lateral movements, a trajectory of eights. At each vibration of the vessel the balls hit the vessel wall, which leads to grinding and sample mixing. Thanks to the amplitude (about 5 cm) and the speed (about 1,200 rpm) of this vibrating movement, the speed of ball is also high (about 5 m/s), and as a result the intensity of the balls, their collisions are unusually large. Therefore, these mills belong to high-energy types.

The latest types of mills are designed to ensure a greater production capacity by grinding powder in two vessels. For SPEX mills the vessels may be of different types of materials, for example of hardened steel, corundum, tungsten carbide, zirconium oxide, stainless steel, silicon nitride, agate, plastic or methacrylate.



Fig. 5.2 Laboratorní planetární kulový mlýn s nádobkami, schéma mlecího procesu [1]

One mill, often used for mechanical alloying in laboratories, is the *planetary ball mill*, in which we can grind powder from just a few to hundreds of grams simultaneously. A planetary ball mill owes its name to the movement of vessels, which resemble the movement of planets. Vessels are arranged on a support rotary disk with a special propulsion mechanism, ensuring circular motion around its own axis. Centrifugal forces produced by a vessel rotating around its own axis and the rotation of a support disk operates on the container content, thus on the raw material and on the grinding balls. The vessels and the supporting disk rotate in the opposite directions, and centrifugal forces work alternately in the same and in the opposite directions. As a result, the grinding balls move on the containers walls and the material is ground on one side thanks to the frictional effect (Fig. 5.2) and on the other side by their impact effect when the balls hit the opposite wall of the vessel.



A traditional *ball mill* consists of torque horizontal cylinders, half-filled with small steel balls. During rotation of the cylinder the balls hit the milled metal powder; the grinding speed will increase with the speed of rotation. At high speeds, however, the centrifugal force acting on steel balls exceeds the gravitational force and the balls are pressed against the wall of the drum (Fig. 5.3 and 5.4). At this point, the grinding activities stop.

Fig. 5.3 Srážka dvou koulí s částicemi prášku (Upraveno podle [2])



Fig.5.4 Tři možné stavy pohybu koulí: a) nedostačující energie pro srážky při nízké rychlosti otáček mletí, b) optimální rychlost otáčení pro srážkový proces a c) koule přitisknuty na stěnu nádoby při příliš vysoké rychlosti otáčení [3]

Friction mills consist of a vertical cylinder with spinning stirrers inside the cylinder (Fig. 5.5). A powerful engine revolves the stirrers, which gradually move the steel balls in the cylinder.

In friction mills large quantities of powder (from 0.5 to 40 kg) can be ground at a time. The speed of the grinding charge movement is much lower (about 0.5 m/s) than that of planetary balls or vibration mills, as a result of the low energy of friction. Grinding vessels are either of stainless steel or stainless steel coated inside with corundum, silicon carbide, silicon nitride, zirconium oxide, rubber or polyurethane. Various milling media types are also available - aluminium silicate, silicon carbide, molybdenum carbide, corundum, zirconium oxide, stainless steel, carbon steel, chromium steel, and tungsten carbide.



Fig 5.5 Schéma dle [2] a foto průmyslového (MIKRONS®) třecího mlýnu [4]

The friction process is provided as follows: a charge of powder is inserted into a vessel with a grinding medium, the mixture is put into motion by rotation stirrers of a high velocity (which is approximately 250 revolutions/min), which leads to the action of the grinding medium on the material using forces of shear and impact.

5.3 Process variables

Mechanical alloying is a complex process, which includes the optimization of a large number of variables to achieve the required phase or microstructure. The final morphology and the powder particles composition is influenced by the most significant variables of this process:

5.3.1 Speed of grinding

Faster rotation of the mill can increase the energy input into the powder, but the increase of the rotation speed is limited by the mill design. For example, with a traditional ball mill the increase of revolution speed causes the increase of balls spinning. Overcoming the critical speed will cause the balls to be pressed to the wall of the vessel and not tobe dropping down, which means no impact force. Therefore, the highest speeds should be set under this critical value, so that the balls are falling from the maximum height with a maximum impact force.

Another limitation to the high speeds is the fact that during such high speeds or the high intensity of grinding the temperature of vessel can reach critical values. In case the diffusion it is required for the homogenization or alloying of the powder, and the increased temperature can be beneficial. However, in some cases the increased temperature brings a fast transitional process, which results in the decay of the oversaturated solid solutions and other metastable phases during grinding.

5.3.2 Time and ratio of BPR

Grinding time is the most important parameter. Required times vary in accordance to the type of mill used, the intensity of the grinding, ball-to-powder ratio, and the temperature of grinding. With times longer than required the level of pollution increases and unwanted phases can appear. That is why it is advisable not to prolong the time of grinding.

The BPR ration marked as a charge ratio (CR) is an important variable within the milling process. Various authors determined various ratios ranging from 1:1 up to 220:1. When grinding the powder using the e.g. SPEX mill with a low capacity, the commonly used ratio is 10:1. On the other hand, when using a mill with a large capacity, e.g. a friction mill, the BPR ration used is 50:1 or even 100:1.

The BPR ratio has a significant influence on the time required to achieve each phase during the grinding of powder. The higher the BPR, the shorter the time required for the grinding (Fig. 5.5). For example, when grinding the powder Ti with at. 33% Al in the SPEX mill, an amorphous phase is achieved after 7 h with the BRP ratio 10:1, after 2h with BPR 50:1, and after 1 h with BPR 100:1. For a very large BPR the process of alloying takes place more quickly, because the weight ratio of balls increases, and thus increases the number of collisions at a time, and as a result, more of the energy is transmitted to the powder particles. Thanks to this higher energy more heat is produced, which can also change the composition of powder. If this temperature exceeds the critical limit, the formed amorphous phase may even crystallise.

5.3.3 Grinding atmosphere

During grinding there is a significant influence of the grinding atmosphere, in particular with the powder pollution. Therefore, the grinding of powders shall be carried out in a vessel, which has been either evacuated, or filled with some neutral gas, such as argon or helium. Highly pure argon is the most commonly used protective environment against oxidation and powder pollution.

For specific purposes different types of atmosphere are used in grinding, such as nitrogen atmosphere or ammonia for nitriding, hydrogen for hydrogen charging and formation of hydrides. If air is present n the vessel, oxides and nitrides can arise in the powder, in particular if they are powders of reactive metals.

5.3.4 Temperature of grinding

The temperature of grinding is another important parameter affecting the composition of the milled powder. During the grinding there is a diffusion, so whatever arises a solid solution, intermetallic compound, nanostructural or amorphous phase, the temperature of grinding will be the

decisive factor. It is possible to reduce the grinding temperature by inserting liquid nitrogen into the grinding container or, on the contrary, increase temperature in grinding containers using electric heating.

The intensive mechanical deformation of the powder leads to the occurrence of crystalline disorders. This process, together with the emergence of the bonds while cold, and breaking of particles, significantly affects structural changes in the powder.

Temperature within the grinding system can significantly increase for two reasons. The first parameter that can significantly increase temperature in the system, is the kinetic energy of the grinding media (balls). The second phenomenon that significantly affects temperature, is the heat release during the exothermic reaction, which is ongoing during grinding. In practice, if the temperature increases are found in a container, it is probably the influence of both cases. The grinding process is a dynamic process, so it is not easy to measure local temperature during grinding; temperatures may be evaluated using either an appropriate modelling, or by using indirect evidence from the studies of microstructural or crystalline changes during grinding.

5.4 Mechanism of alloying

During high-energy grinding the particles are repeatedly flattened, split, and connected. During the collision of two steel balls a certain amount of powder wedges between them, and we can assume that during each collision (Fig. 5.6) approximately 1,000 particles are wedged, with a cumulative mass of about 0.2 mg. Influenced by impact balls, the powder particles are plastically deforming, which leads to mechanical reinforcement and refraction. Newly created surfaces allow particles to stick together, which leads to an increase in the size of the particles. In the initial stage of grinding the particles are fine and tend to stick together and to build large particles or clusters. Emerging particles have a large range of size. For particles at this stage stratified composition is characteristic, formed by different combinations of initial components (Fig. 5.7). As this deformation continues, particles strengthen due to the deformation mechanisms and they break, thus the created fragments get smaller and smaller. At this stage there is an overriding trend to break particles over their bonding.



Fig.5.7 Různé typy srážek mlecích koulí při procesu mechanického legování (Upraveno dle [2])

Due to the influence of the continuous impact of balls the structure of particles constantly refines, the distance between the layers is declining, and the number of particles increases. The efficiency of the grinding process in normal mills is very low for the reduction of particles size, around 0.1 %. In case of a high-energy mill it makes around 1 %, but the remaining energy is converted mostly to heat, a small amount is used for elastic and plastic deformation of the powders particles. At a certain moment an equilibrium state between connections occurs, which leads to an increase of average sized particles, and between the fission, which reduces the particle size, the speed between the two actions become equal.

Smaller particles are able to withstand the deformation without fission and they have a tendency to form larger pieces. During mechanical alloying large deformations are inserted into particles, which will manifest itself in the presence of various crystalline disorders, e.g. dislocations, vacancies, layered errors, and an increased number of grain boundaries. The presence of these disorders will increase the

diffusivity of dissolved basic elements in the matrix. A refined microstructure reduces diffusion distances. To diffusion also contributes a moderate increase of temperature during grinding, and the result is the actual alloying between the basic elements.

This process generally takes place at room temperature, but sometimes it is necessary to anneal the powder after mechanical alloying sufficiently at an elevated temperature, in order to complete the alloying. This procedure is used in particular for the preparation of intermetallic phases.

5.5 Contamination

Important parameters in the process of mechanical alloying are the properties of metal powders and the content of impurities in the powder, which get into the powder and contaminate it. During mechanical alloying, when the powdered particles are captured between the grounding medium, they undergo strong plastic deformation, they are fragmented, and new surfaces result. The small sizes of powder particles, large surfaces, and the emergence of new surfaces during grinding contributes to a growing pollution of the powder due to friction of the grinding system, since the collisions occur between the balls, as well as between the grinding balls and the vessel.

The size of contamination has an impact on time, intensity, and the atmosphere of grinding. If the grinding is carried out in a steel grinding system, the majority of the ground powders shows normal pollution of 1 - 4 hm. % Fe. In some cases, there may be a very significant pollution, such as in the case of the mixture W-5Ni ground 60 h in SPEX mill, it was found to be at 60 %. Fe. Other impurities, such as oxygen and nitrogen, are entering the powder, as it has been already mentioned above, from the grinding atmosphere. Other dangers of contamination from the ground material are represented by the addition of the process control agent - **PCA**, which restricts the processes of clustering and welding in cold conditions. From these agents, according to their chemical nature, carbon may release into the ground powder, as well as oxygen, nitrogen, and other elements. The presence of these impurities is particularly harmful for the reactive metals such as titanium or zirconium. Oxygen and nitrogen may significantly affect the ratio of resulting crystalline and the amorphous phase, e.g. in Ti-Al alloys, carbon and the subsequent emergence of carbides.

Nevertheless, this method of mechanical alloying is very perspective, and products prepared via this process are subsequently used in many areas (Fig. 5.8)

Summary of terms

Parameter of process, types of mills, studený svar, ratio BPR, contamination, collision of particles, alloying.



Question to the topic

- 1. Které parametry procesu mechanického legování znáte?
- 2. Které typy mlecích zařízení znáte?
- 3. Co je podstatou mletí v planetárním kulovém mlýnu?
- 4. Jaký je význam parametru BPR?
- 5. Vysvětlete mechanismus mechanického legování. "
- 6. Proč dochází při mletí ke znečištění a co je jeho zdrojem?



What resources can you use to help?

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6. Production technology of metallic glasses



Time needed to study: 2 hours

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Learning objectives:

When you have completed this module, you will be able to:

- Define structure of metallic glass
- Define basic parameters of transition to glassy state
- Explain the term of deep eutectic
- Describe the technologies of preparing metallic glasses

Le Le

Lecture

6.1 Basic characteristics of metallic glass

Metallic glass belongs among new types of materials, and it has very interesting physical and mechanical properties. The organization of atoms in the solid state rather reflects a liquid layout arrangement than normal crystalline materials (Fig. 6.1), and we talk about the amorphous state of structures. In the early applications, roughly 40 years ago, these amorphous metal materials were prepared only in the form of thin stripes using rapid solidification. Only at a later stage there could have been used , based on the change in the composition of alloys, other methods of preparation, with much lower speeds of solidification. Currently, metallic glasses can achieve even greater thickness. In these cases we already talk about bulk metallic glass - BMG.

Metallic glass represent a unique combination of different atoms, which are mixed in certain atomic proportions, and by melting and mixing we ensure an even distribution of constitutional atoms. In this amorphous state the alloy have different properties than metals and alloys in crystalline states.



Fig.6.1 Atomic structure and corresponding Xray graphs for a) crystalline and b) amorphous structure

In contrast to the crystalline structure, for an amorphous state it is not possible to detect any shapes typical for an organized structure (Fig. 6.1). In the case of crystalline material the boundaries of the grain and jogs in a plane of the crystalline lattice are the weakest links to achieve the limit properties.

Gradual evolution in the preparation of large volume metallic glasses is given in Tab. 6.1. So far, the most famous is the commercially used Liquidmetal material, which was invented in California Institute of Technology. It is manufactured by the Liquidmetal Technologies, Inc. This material was quickly used for *applications* in various sectors, such as the precise surfaces in the control systems for aviation and aerospace sector, sports equipment, nearly indestructible rims, durable knives from non-ferrous alloys, surgical instruments, safe from the point of magnetic resonance imaging, high tenacity liners for drilling tools, and others. Fig. 6.2 shows a comparison of the yield points and melting temperature of the traditional alloys of non-ferrous metals, alloy LM-001 based on Zr, Ti, Cu, Ni and Be.

BMG systems	Year of
	development
Pd-Cu-Si	1974
Pt-Ni-P	1975
Au-Si-Ge	1975
Pd-Ni-P	1982
Mg-Ln-Cu	1988
Ln-Al-TM	1989
Zr-Ti-Al-TM	1990
Ti-Zr-TM	1993
Zr-Ti-Cu-Ni-Be	1993
Nd(Pr)-Al-Fe-Co	1994
Zr-(Nb,Pd)-Al-TM	1995
Cu-Zr-Ti-Ni	1995
Fe-(Nb,Mo)-(Al,Ga)-(P,C,B,Si,Ge)	1995
Pd-Cu(Fe)-Ni-P	1996
Co-(Al,Ga)-(P,B,Si)	1996
Fe-(Zr,Hf,Nb)-B	1996
Co-Fe-(Zr,Hf,Nb)-B	1996
Ni-(Zr,Hf,Nb)-(Cr,Mo)-B	1996
Ti-Ni-Cu-Sn	1998
La-Al-Ni-Cu-Co	1998
Ni-Nb	1999
Ni-(Nb,Cr,Mo)-(P,B)	1999
Skelné kompozity na bázi Zr	1999
Zr-Nb-Cu-Fe-Be	2000
Fe-Mn-Mo-Cr-C-B	2002
Ni-Nb-(Sn,Ti)	2003
Pr(Nd)-(Cu,Ni)-Al	2003

Table 6.1 Systems forming bulk metallic glasses

Note.: Ln- lantanide, RE-rare earth metal, TM-transition metalsv

6.2 Stability of metallic glass

From the basic characteristics it is clear that metallic glass is an amorphous structure, and under normal conditions it may not be so stable material. The emergence and stability of metallic glasses are characterized by two basic criteria

- 1) glass-forming ability hereinafter GFA, in other words the ease of amorphous state creation
- 2) the stability of metallic glass (resistance to crystallization)

If normal alloys in their melted state are cooled below the melting temperature T_m , which is characterised by a thermodynamic equilibrium between a liquid and solid state, the atoms try to get into the equilibrium state. If the equilibrium conditions are met, the atoms place themselves in certain positions during solidification, and they form a crystalline organization, while they produce a large amount of crystals (grains). An alloy in amorphous state is thus, from the thermodynamic point of view, in a metastable status (Fig. 6.3 b).

The specific ratio of elements is slowing crystallization down, so if the alloys are sufficiently quickly cooled, the amorphous (glazed) status is maintained. Another important requirement for the preparation of materials of so specific properties, as we have mentioned above, is their high purity. Thus, we monitor the contents of such impurities as oxygen, hydrogen, nitrogen, and carbon, which can act as initiation centres for the nucleation of crystals during solidification, and they may provoke the local crystallizations of alloys. There are also high demands to meet the requirements for specified composition, as a little deviation can manifest very quickly by a higher speed of crystallization and destroy the required properties.



Fig.6.4 TTT diagram pro ochlazování taveniny za vzniku kovového skla: R_c - rychlost ochlazování, T_x - teplota krystalizace, T₁ - teplota taveniny, T_g - teplota přechodu do skelného stavu (Upraveno dle [1])

Unlike differences in ordinary crystallized structures, for metallic glass we define the melting temperature T_m rather than the temperature of melt T_1 , under which there is a certain temperature $T_{g,n}$ at which the movements of atoms are limited to a distance shorter then their size. Under such conditions changes in the organization of these atoms cannot take place in real considered time. During the cooling of melt from a temperature higher then T_1 at a speed bigger then R_c to the temperature T_g (or lower), a matastable state of material occurs, which conserves the atomic structure of the initial melt and metallic glass forms.

Cooling the melt with a critical rate \mathbf{R}_{c} is illustrated in the chart of dependence time-temperaturetransformation (diagram TTT) in Fig- 6.4. We know an analogical diagram from our studies of the phase transformations in steels (diagrams IRA). Curve **A**, in the shape of the letter C (C curve, or also sometimes so-called "nose"), defines the time required to start the early stage of crystallization, depending upon the temperature under t₁ temperature. Between temperatures T₁ and T_g crystallization begins to occur, so if the occurrence of a crystalline structure is to be prevented, the system must be cooled with a speed higher than R_C and the temperature of the given structure must lie outside this C curve. The crystallization process occurs in amorphous metal at a certain temperature **T**_x, during heating using a constant speed.

$$R_{c} = \Delta T_{x} / \Delta t \tag{6.1}$$

With a speed less than R_c this material may be entirely or at least partially crystallised, and with greater speed it will transfer to glass. With silicon glass and a whole range of organic polymers the "nose" depending on TTT is postponed to the long periods, i.e. the preparation of an amorphous material is easy. For most metallic systems, which do not show directional links, the movement of atoms is relatively simple and the position of "nose" is therefore shifted to very short periods (longer than milliseconds, but never more than a few milliseconds). As a result the first materials prepared using high-speeds of cooling (freezing), range approximately 10^5 - 10^6 K/s.

The emergence of a glass state for metallic glass shall be assessed by so-called *reduced* temperature T_{rg} , which is the ratio of temperatures T_g and T_1 :

$$T_{rg} = T_g / T_l \tag{6.2}$$

If we are to define the essential requirements for GFA, then concerning the fast transition over the critical temperature interval ΔT_x during cooling of the melt, we need the difference between T₁ and T_G to be minimal, i.e. the reduced temperature T_{rg} should have the highest possible values. Graphically, the dependence of the critical cooling speed on the reduced temperature T_{rg} is shown in Fig. 6.6a, the maximum thickness, which is possible to prepare for the selected glass systems depending on T_{rg} and R_c, is shown in Fig. 6.6b.

The difference in speeds of cooling for classical metallic and for the new bulk volume glass shown in Figure 6.8.

$$\gamma = \frac{T_x}{(T_g + T_l)} \tag{6.3}$$

6.3 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.

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.6.10**. 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.

Dashed lines T_0 intersect at the composition $X_B^{T^0}$. The range of transition into glass state (GFR) is given by the intersection of the T_0 lines with the T_g line: it is obvious that for the case on the Fig.6.10a (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.6.10b (non-symmetrical system) the GFR and $X_B^{T^0}$ occur clearly out of the eutectics.



Fig.6.10 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.



Fig.6.11 Structure of alloys ($Fe_{72}Mo_4B_{24}$) $_{94}Dy_6$ 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)

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.



Fig.6.12 Equilibrium phase diagrams of selected binary systems, in which it is possible to prepare metallic glasses for certain eutectic compositions (adjusted according [8]).

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. 6.11). The lines in the upper part of the binary diagrams shown on the Fig.6.12. represent the areas of composition for which the metallic glass state formation is possible.

6.4 Methods of metallic glass production

From the 1980s up to the present day new technologies for the production of metallic glass have been developed, based on different mechanisms for creating and maintaining their amorphous structures. The most common, by means of which alloys from more than a hundred binary systems were prepared, include the following methods:

At the end of 1980s in Japan (Inoue et al., Tohoku University) multi-components systems from common metal elements were found, showing the lower critical speeds of cooling, which triggered another stage in the process of development technologies for the preparation of metallic glasses. Gradually, as the systems with favourable GFA have been found (ternary, and quaternary, and quinary systems with rare earth metals, e.g.La-Al-Ni, La-Al-Cu, La–Al–Cu–Ni a La–Al–Cu–Ni–Co), more accessible and cheaper methods of preparation could be used with a less critical speed cooling, such as casting melt into water-cooled copper forms, while at the same time it was possible to obtain products of bulk volumes, with greater thicknesses, or a greater diameter from a few mm to several cm, such as poles. Development proceeded over the partial substitution of rare-earth metals with alcalic metals (Mg–Y–Cu, Mg–Y–Ni, and others) or zirconium (Zr–Cu–Ni, Zr–Cu–Ni–Al), so now it is possible to prepare BMG with very low critical speeds of cooling, such as 0.10 K/s for alloys Pd40Cu30Ni10P20 with a thickness up to 10 cm.

An important step in the introduction of these materials into different sectors of industry and commerce was the preparation of alloys based on ZrTiCuNiBe (Peker a Johnson). This alloy, known today under its commercial name Vitalloy (vit1), shows a clear glass transition to the glass state, a high stability of its supercooled state, and high stability against crystallization. For this the Vitalloy 1 alloy with composition of Zr41Ti14Cu12,5Ni10Be22,5 the nose for nucleation of crystals within TTT diagram lies in a position corresponding to 10² on the timeline axis, and the critical cooling speed is 1 K/s. Thus, the alloy is cast using a conventional method into copper forms in the shape of bars, with a diameter of 5-10 cm, at the creation of completely glass state. The preparation of BMG based on a quinary system does not require any special preparation or processing method, their GFA and production process is comparable to normal silicate glasses. This development heated up, and 3 years after its discovery, BMG based on Zr was introduced in many industrial and commercial applications.

Currently, most BMG alloys in the required shape is prepared by vacuum pressure casting. In contrast to the traditional crystalline materials, in which we can influence the running of the melt by pre-heating the forms, BMG must cool faster, so the preparation of more complex thin-walled shapes or, on the contrary, of bulky pieces is much more difficult. However, it is possible to prepare relatively well the cases or boxes for certain electronic applications (e.g., mobile phones, etc.).

Relatively new processes involve the rapid heating and preparation of metallic glass at temperatures in the range 500 to 600 °C, at which it has the same flow characteristics as liquid plastic. It is, therefore, sufficiently liquid to be injected into a form, and capable of being tempered into a noncrystalline state. During the normal casting of parts from metallic glasses the alloys are heated over 1,000 °C above the melting temperature of the crystalline phase. After that the molten metal is cast e.g. into the steel forms, and cooled, so as not to crystallize. Of course, the problem is that the steel forms are normally designed for temperatures up to around 600 °C, so due to the higher temperatures of castings these forms are often bursting, and they must be replaced, so the process is more expensive. The heating rate is ensured by ohmic heating through a short-performance shock (approximately 1 megawatts) with a brief jolt of power, so that a small rod of metallic glass is warmed during 1 millisecond. A pulse current heats the whole rod with a 4mm diameter and a length of 2 mm with a speed 10^6 K/s. This way the material heats up thousands of times faster than when using conventional heating methods. After that the material is injected into a form and cooled in a way not to form crystals.

In addition to casting, it is possible to form BMG products using viscous flow in a state of supercooled melts. For the above mentioned BMG based on Zr it is possible to achieve maximum extension up to 300 % at the speed of deformation $5,0x10^{-2} \text{ s}^{-1}$ at 673 K. Even for cylindrical samples with a diameter 5mm there were found values of extension up to 10^6 %! With such an extensive formability it is possible to prepare not only common small machine parts, but using micro-forming we can produce also micro parts. Alloys in a state of supercooled melt behave as the Newtons liquids

(without creep limits), and they can fill cavities or pass through a matrix of 100 mm during their extrusion.

As to their characteristics the metallic glasses are very attractive for industry, and for better application in various engineering structures. It is, therefore, desirable to find the means of connecting BMG with other BMG, or with a crystalline material. As possible ways for the time being we prefer the friction welding, spark erosion, or by using an electron beam, in which the conservation of glass condition after the process is emphasized. With careful inspection of the process parameters it is possible to amorphous maintain an structure in the welds and the strength is comparable to volumetric glazed material.



Fig..6.11 Technologies of metallic glass processing: a) melt spinning, b) spinning cup, c) double roll quenching a d) planar flow casting

An additional challenge of the technology development in preparation of the metallic glasses was the requirement to ensure a continuous casting process, so that it was possible to produce wires, tapes, and bars with an amorphous structure. Several different methods were implemented for the continuous process, i.e. the adjusted Bridgman method with the customized speed of pulling from a warm zone (bars), casting wires (with a diameter between 0.5 and 1.5 mm) on the rotating disk, casting belts (with a thickness up to 2 mm) between two cylinders, the zonal melting of strips (with a thickness 10mm, width 12mm, and a length 170 mm).

In Figure 6.11 there are diagrams of preparation metallic glasses from melt mentioned. Their names are written in English, as there are no adequate translations, but in all cases it concerns the preparation of thin stripes by quenching the melt (rapid solidification) to a chilled substrate, whether on a single cylinder or between two rotating cylinders, by injecting melt in the coolant inside the drum, or on the cool flat pad.

Fig. 6.11 Selected technologies for the preparation of metallic glass from melt

The manufacture of metallic glasses Liquidmetal[®] is carried out from highly pure metals using vacuum-injection melting methods, and by casting with injection of molten metal. Thus the oxidation is also limited, and so is the possible contamination from an extraneous substance.

Equipment for the melting and casting is designed for 100 grams charge per one cycle. An alloy Lm001b has density of 6.0 g/cm³, then the current maximum volume of this alloy is 16.7cm³.

Material is loaded into a hermetically sealed chamber, which has been washed with argon (Fig. 6.12). Heating is carried out till the required temperature for casting within the circulating argon atmosphere is reached. At the time, when the required temperature is reached, the copper form and the the quartz tube are connected to the chamber. All gas pipes are closed, the chamber is hermetically

sealed, and then the inlet of pressurized gas is opened, which presses the molten metal into the quartz tube and into the copper mould. During this casting the injection chamber was pre-heated to 650 °C, and the material was supplied until the capacity of form was filled by 90 %. For example, by this method there were prepared rectangular shapes 3×7 mm, with a length up to 125 mm, in the temperature range 490 - 585 °C, and injection pressure of 0.3 - 1.0 bar (1 bar = 1.10^5 PA).



Summary of terms

Amorphous structure, metallic glass, BMG, reduced temperature, rapid solidification, crystallization temperature, TTT diagrams, C curve, deephluboké eutektikum, GFA, GFR, viskozita BMG.



Question to the topic

- 1. Explain the term BMG.
- 2. Can you describe methods of preparing metallic glassesl?
- 3. Can you define the parameters controlling the ability of glassy state transition?
- 4. Can you define the critical rate of cooling?
- 5. Can you define the reduced temperature?
- 6. Explain the theory of deep eutectics?
- 7. What you can determine from TTT diagrams?



What resources can you use to help?

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7. Production technology of metal foams



Time needed to study: 2 hours



Learning objectives:

When you have completed this module, you will be able to:

- Define basic parameters of preparing metal foams
- Describe basic classification of processes
- Explain GASAR method
- Explain differencies between open and close cells
- Distinguish methods of metal foam preparing

Lecture

7.1 Characteristic of processes

Metallic foams are relatively new materials, the origins of their production and applications date back to this century. In the following chapters we will explain the basic processes of their preparation, and factors that affect their properties for various applications.

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.7.1-7.3):

- 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.
- 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%.
- (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.
- * *Metal sponges*: the morphology of cellular metals usually with open and interconnected cavities.



Fig.7.1 Aluminum foam (IFAM).



Fig.7.2 Cellular structure of an FE based material, stretched in one direction (MER Corp.).



Fig.7.3 Bronze sintered powder, i.e. sintered porous material (so-called metal sponge).

7.2 Stability of metallic foams

Foams are, due to their large surfaces, unstable systems; the energy of such systems does not reach their minimum value. Foams may be in a metastable state, constantly disintegrating at a specific rate. Aqueous and other foams are stabilized using detergents (surface-active agents), which generate a compact mono-layer on the foam film. These layers reduce the surface tension, increase surface viscosity, and create electrostatic forces, so that the foam film does not collapse. Metallic foam shall be stabilized by various other means, as it does not contain detergents, and electrostatic forces are shaded in the metal. The pure metals melt, as well as water, cannot form lather, but with ingredients acting as stabilizers, foam can be created. According to the latest knowledge of leaded and aluminium foams it can be said that the more stable foam required, the higher the content of oxides within the powder input material must be.

7. 3 Preparation of metallic foams from melt

Some of the currently used technologies of casting preparations are based on the speciallyprepared molten metals with adjusted viscosity. Then, such melts may form lather by using gas, or adding foaming agent of the released gas in the form of bubbles, during decomposition of such an agent inside the melt.

Metal melts or alloys may be foamed by the emerging bubbles of gas in the melt, but only under certain conditions. Gas bubbles emerging in the metal melt are trying quickly to reach the surface, due to the influence of large buoyant forces within the melt of a large density. Their rising may be decelerated (restricted) by increasing the viscosity of the molten metal, either by adding fine ceramic powders, alloying elements (forming stabilizing particles in the melt), or by other means.

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.9.4 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.

7.4 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.



Fig.9.4 Processes of metallic foams preparation



Metal foam definition, stability of foam, foaming agent, factors of process, close cells, open cells.



Question to the topic

- 1. Vysvětlete rozdíl mezi pěnami s otevřenými a uzavřenými buňkami.
- 2. Definujte základní parametry procesu.
- 3. Popište proces GASAR.
- 4. Jaký je rozdíl mezi zpožděným a okamžitým procesem?
- 5. Navrhněte metodu pro výrobu filtrů.
- 6. Navrhněte metodu pro výrobu součástí pro deformační zóny?



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8. Plasma technology in preparing of metallic alloys



Time needed to study:1 hours

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Learning objectives:

When you have completed this module, you will be able to:

- Define basic properties of plasma
- Explain the differences of low- and high-temperature plasma
- Explain Advantages and disadvantagies of plasma technology
- List application areas of plasma metallurgy



Lecture

8.1 Basics of process

Plasma metallurgy is one of the promising methods of refining and synthesizing the number of materials, in particular highly-meltable and reactive metals, their alloys or compounds. The use of plasma heating is invoked by the necessity to obtain mono crystals of highly-meltable metals, which are of large sizes, with a heightened degree of purity and structural perfection. Using the arc plasmatrons the ionized gas-plasma-heats to the temperature from 10,000 to 30,000 K. A simple design of plasmatrons, a broad range of their performance characteristics, the possibility of high a concentration of thermal energy, allow their broad application in technology, in particular in the metallurgical industry. The method of tungsten mono crystals preparation and other highly-meltable metals and their alloys with a low level of ingredients, especially carbon, using plasma heating, has the following special features:

- Using a high-temperature adjustable source of heating ensures the melting of a sufficiently high volume of metal, and if necessary, also the considerable melt overheating.
- By using a controlled atmosphere of an inert gas (Ar-He, Ar-H₂, Ar-N₂...) we protect the molten metal from pollution, and additionally refine a metal using physically chemical reactions with admixtures contained in the melt and molten metal.
- Ensuring the continuous or semi-continuous process of crystals growth.
- The possibility to control the parameters of mono-crystals growth in a wide range, the stability of performance for the heating source.

8.2 Advantages and disadvantages of plasma metallurgy

Advantages:

- 1) The lower contamination of melted material by atmosphere from the source of heating.
- 2) The establishment of low temperature plasma and any gas mixture, a controllable atmosphere, oxidation, reduction or inert.
- 3) Melting in an inert atmosphere will reduce the evaporation of metals.
- 4) The possibility of degassing metals.
- 5) Achieving high and easily controllable temperatures.
- 6) High energy concentration, high heat transfer to the heated material \rightarrow a high speed of melting.
- 7) The high usability of alloying ingredients.
- 8) The reaction of plasma with metal \rightarrow the preparation of special alloys.

Disadvantages:

- 1) Lower metal degassing in comparison with the vacuum furnaces.
- 2) The use of highly pure argon to melt reactive metals.

Application:

- 1. The preparation of highly pure metals. Fe, Ni, Co, Cu, Ti, Nb
- 2. The preparation of special alloys and standards: shape memory materials based on NiTi (ternary alloying with Fe, Cu); alloys Fe31.5Ni, Fe31.5Ni1Si, alloys Hasteloy, Inconel
- 3. The preparation of materials with increased content of gasses: Fe-V-N, Fe-V-Al-N, Fe-V-Al-Si-N, (6-8 % N)
- 4. Chemical reaction in low temperature plasma: the reduction of oxides in Ar + H2; nitriding in Ar + N2
- 5. Spraying metallic and ceramic coats: NiCr, NiAl, + welding powders W, Cr, B + Si; Al2O3 + 3% TiO2, ZrSiO4, CaZrO3, MgZrO3.
- 6. Porcessing of low quality, poor raw materials and waste
- 7. Widespread use of alternative electroenergy sources



Summary of terms

Plasma, ionised gas, plasma gun, low-temperature plasma

Question to the topic

- 1. Can you define the difference between the low-temperature and high-temperature plasma?
- 2. Define the principle of plasma metallurgy.
- 3. Which temperatures can be reached at plasma melting process?
- 4. Which materials are prepared using this technology?



What resources can you use to help?

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9. CVD technology



Time needed to study: 1 hours



Learning objectives:

When you have completed this module, you will be able to:

- Define the principle of CVD method
- Describe main process parameters
- Name CVD precursors

Lecture

9.1 Characteristics of processes

Chemical vapour deposition method CVD (Fig. 9.1) takes place at high temperatures (700-1,500 $^{\circ}$ C); this method was used in the past for the deposition of sintered carbides and can be performed in three options:

- thermally induced,
- plasma activated,
- photon enhanced (e.g., by laser)

With this technology development these basic methods began to subdivide.

CVD is a chemical process used to prepare thin films. This substrate is exposed to the effects of one or more volatile precursors, which are reacting to one another on its surface, or decompose during the formation of a required material, the entire process is carried out at a high temperature. In this process, volatile by-products often emit, which are removed from the reaction area by a flow of gas or a vacuum. This method is widely used in the semiconductor industry. It is used for the preparation of semicrystallic, amorphous, and epitaxial silica, carbon dioxide, carbon fibres, and nanotubes, <u>silicon nitride</u>, etc. Using CVD synthetic diamonds are also used.



Fig. 9.1 Principle of CVD process and deposition mechanisms

9.2 CVD methods

There is a relatively large quantity of this method modification used to prepare thin films, such as:

- APCVD Atmospheric Pressure CVD the process takes place at atmospheric pressure
- ALCVD Atomic Layer CVD in this process two precursor are brought into the reaction chamber (i.e. Al(CH₃)₃) a H₂O). One of the precursors is absorbed on the surface of the substrate, but a complete decomposition does not take place without the presence of the second precursor. ALCVD allows good control of quality and of the emerging film.
- AACVD Aerosol Assisted CVD in this process a precursor is transported to the substrate in the form of an aerosol, generated by ultrasound. This technique is usable even for non-volatile precursors.
- MOCVD Metal Organic CVD- as precursors organometallic substances are used, e.g. tantalic ethoxide Ta(OC₂H₅)₅ for the preparation of tantalic oxide Ta₂O₅
- PECVD Plasma Enhanced CVD this method uses plasma for the initiation of chemical reactions. PECVD enables reaching a deposition at low temperatures.

Fig.9.2 Different CVD reactors:

a) horizontal, b) vertical, c) polozploštělý, d) soudkovitý a e) s vícenásobnými membránami



Summary of terms

CVD, precursor, reactant, gaseous by-product, thin films, reactor, vaporization.



- 1. Do you know the principle of CVD method?
- 2. Specify the temepratures at which CVD method is performed?
- 3. Specify the main parameters of the process.
- 4. Can you describe the steps of CVD process?
- 5. Which parameter is limiting during film deposition?
- 6. Which precorsors in CVD method do you know?



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10. PVD technology



Time needed to study: 1 hours



Learning objectives:

When you have completed this module, you will be able to:

- define the principle of PVD method
- describe the parameters of the proces
- explain the differences between CVD and PVD technologies

Lecture

10.1 Characteristics of process

In the previous chapter we have discussed the CVD method, which can be used to prepare thin layers and coatings. Another method is the physical vapour deposition PVD, process during which the material vaporizes from its solid or liquid phase in the form of atoms or molecules. These are transported in the gaseous phase in a vacuum environment or a low-pressure gas (or plasma) to a substrate, where they condense. Typically, the process is used to prepare very thin layers with a thickness ranging from a few nanometres to several micrometers. By this method you can also prepare multi-layer coatings, coatings with gradient composition, or individual structures. Substrates may vary both in size (e.g. up to 25x30 cm), and in shape (flat or complex). The typical speed of deposition ranges from 1 to 10 nanometres per second. By this process we apply elemental metals and alloys, as well as compounds, which are formed in a reactive deposition, such as nitride TiN, which forms during the reaction of an applied material with the surrounding gaseous environment, or carbide TiC, originating from the response of mutually applied materials. PVD methods include vacuum evaporation, sputtering, and ion-plating.



Fig.10.1 Schema of PVD reactor with substrate and cathod target (Modified from [1])

The PVD method is characterised by its low working temperatures (150 to 500 $^{\circ}$ C). This method is mainly used for coating instruments from a high-speed steel. Thanks to the low temperature the heat does not affect these instruments. Today, this method is used for the preparation of about 80 % of all coatings.

During the process this cathode is slowly distorted by molecular bombardment. A typical medium is argon, as it generates sufficient impetus to release atoms from the targets. In a vacuum,

these loose atoms are settling onto the surface of a material and create a required coating. A critical parameter of the PVD process is a specific speed of gaseous mass flow into the vacuum chamber. Vacuum pumping stations require a control valve or a flow limiting device, in order to control the pumping sequence, as soon as PVD gas is introduced. This method is highly sensitive to pressure, and it may lead to an insufficient gas inlet and low quality of the product.

10.2 Methods of PVD technology

PVD processing techniques include:

- 1) vacuum evaporation,
- 2) sputter deposition in a plasma environment,
- 3) sputter deposition in a vacuum,
- 4) ion plating in a plasma environment with a thermal evaporation source,
- 5) ion plating with a sputtering source,
- 6) ion plating with an arc vaporization source
- 7) Ion Beam Assisted Deposition (IBAD) with a thermal evaporation source and ion bombardment from an ion gun.

Contamination encountered in PVD processes can be categorized as:

- Substrate surface related-e.g. oxide layers on metals, embedded particulates
- Ambient (external) process related-e.g. chemical residues, water stains
- *Ambient (external) environment-related*—e.g. settled airborne particulates, adsorbed water vapor and hydrocarbons
- *Deposition environment related*—e.g. residual gases in vacuum/plasma environment, water desorbed from vacuum surfaces, particulates and vapors in the deposition system
- *Deposition process related*—e.g. contaminant vapors and particulates from vaporization sources, fixtures and tooling
- *Postdeposition contamination*—e.g. oxides formed on the free surfaces of the deposited film, adsorbed hydrocarbons



Summary of terms

Thin films, sputtering, ion plating, critical parameters.



Question to the topic

- 1. Can you specify the basic differencies between CVD and PVD methods?
- 2. Can you define the principle of PVD method?
- 3. Can you specify the process temperatures in PVD reactor?
- 4. Do you know which coatings (films) are produced using PVD method?



What resources can you use to help?

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- [2] MATTOX, D. M. Handbook of physical vapor deposition (PVD) processing. Noyes Publications, USA, 1998, 945 p. ISBN: 0-8155-1422-0
- [3] DAVIS, R. Metal Handbook. DESK Edition, ASM International, 1998, 1521 p. ISBN 0-87170-654-7
- [4] *PVD Processes*. Online http://www.oerlikon.com/balzers/en/know-how/coating-technologies/pvd-process/ [citation 07-02-2013]