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FAKULTA METALURGIE A MATERIÁLOVÉHO INŽENÝRSTVÍ



Noble and precious metals

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Contents

1. Introduction	7
2. Precious metals.....	7
2.1 Gold.....	7
2.1.1 Gold properties	8
2.1.2 Gold compounds	8
2.1.3 Production technology.....	11
2.1.3.1 Cyanide process of gold extraction	11
2.1.3.1 Production of gold from anode sludge after electrolysis of copper	15
2.1.4 Gold refining	15
2.1.4.1 Electrolytic refining of gold	15
2.1.5 Application of gold.....	16
2.1.6 Gold alloys	16
2.2 Silver	17
2.2.1 Silver properties	18
2.2.2 Silver compounds	18
2.2.3 Production technology.....	19
2.2.3.1 Hydrometallurgic processes of silver extraction	19
2.2.3.2 Pyrometallurgic production of silver from lead ores.....	20
2.2.4 Refining of raw silver.....	21
2.2.4.1 Electrolytic refining of silver	21
2.2.5 Application of silver and silver alloys.....	22
2.3 Platinum and platinum group metals.....	24
2.3.1 Properties of platinum group metals	24
2.3.1.1 Platinum	24
2.3.1.2 Palladium.....	24
2.3.1.3 Iridium.....	24
2.3.1.4 Rhodium	25
2.3.1.5 Osmium	25
2.3.1.6 Ruthenium	25
2.3.2 Production technology of platinum metals.....	25
2.3.2.1 Amalgamation of platinum and metals of the platinum group.....	26
2.3.2.2 Chlorination of platinum ores	26
2.3.2.3 Affination of platinum metals	27
2.3.3 Application of platinum metals	28
2.3.4 Alloys	28
2.3.4.1 Pt alloys	28

2.3.4.2 Pd alloys	29
3. Refractory metals	29
3.1 Tungsten	30
3.1.1 Tungsten properties	30
3.1.2 Tungsten compounds.....	30
3.1.3 Tungsten production technology	30
3.1.3.1 Caking with soda	31
3.1.3.2 Dissociation of wolframite concentrate by solution of sodium hydroxide	31
3.1.3.3 Cleaning of sodium tungstate solutions	31
3.1.3.4 Obtaining of tungsten compounds.....	32
3.1.3.5 Preparation of tungsten oxide.....	32
3.1.3.6 Preparation of metallic tungsten.....	32
3.1.3.7 Preparation of compact tungsten	33
3.1.4 Application of tungsten and tungsten alloys	34
3.2 Molybdenum	34
3.2.1 Molybdenum properties	34
3.2.2 Compounds.....	34
3.2.3 Production technology of molybdenum	35
3.2.3.1 Oxidation roasting of molybdenite concentrate	35
3.2.3.2 Preparation of pure molybdenum oxide	36
3.2.3.3 Production of metallic molybdenum	37
3.2.3.4 Production of compact molybdenum	37
3.2.4 Application of molybdenum and molybdenum alloys	37
3.3 Titanium	38
3.3.1 Titanium properties	38
3.3.2 Compounds.....	38
3.3.3 Production technology of titanium	39
3.3.3.1 Processing of concentrates to titanium dioxide.....	39
3.3.3.2 Production of titanium tetrachloride	40
3.3.3.3 Production of metallic titanium.....	40
3.3.4 Application and alloys.....	41
3.4 Zirconium and zirconium alloys.....	42
3.4.1 Zirconium production.....	42
3.4.1.1 Processing methods of zircon concentrates.....	43
3.4.1.2 Production of zirconium tetrachloride.....	44
3.4.1.3 Separation of hafnium from zirconium (dehafnization).....	44
3.4.1.4 Production of metallic zirconium by metallothermic method.....	44

3.4.2 Zirconium alloys	45
3.4.2.1 Zr – Sn alloys	46
3.4.3 Corrosion of zirconium and its alloys	46
3.4.3.1 Water	46
3.5 Niobium.....	47
3.5.1 Niobium production	47
3.5.1.1 Separation of niobium and tantalum	48
3.5.1.2 Production of metallic niobium.....	48
3.5.2 Niobium processing.....	49
3.5.3 Mechanical properties of niobium.....	49
3.5.4 Niobium corrosion.....	49
3.6 Vanadium	50
3.6.1 Properties of vanadium and vanadium alloys	50
3.6.2 Preparation technology of vanadium.....	50
3.6.2.1 Production of metallic vanadium	51
3.6.3 Vanadium alloys and applications.....	52
4. Radioactive metals	53
4.1 Uranium.....	53
4.1.1 Metallic uranium	53
4.1.1.1 Occurrence and uranium ores.....	53
4.1.1.2 Uranium production	54
4.1.2 Physical and mechanical properties of uranium.....	58
4.1.3 Powder metallurgy of uranium.....	59
4.1.4 Uranium alloys	60
4.1.4.1 Uranium alpha alloys	60
4.1.4.2 Uranium gamma alloys	60
4.1.7 Uranium alloys – ceramic fuels.....	61
4.2 Thorium.....	62
4.2.1 Occurrence, ores and their enrichment.....	63
4.2.2 Thorium production.....	63
4.2.2.1 Preparation of pure thorium compounds	63
4.2.2.2 Preparation of metallic thorium.....	64
4.2.3 Thorium properties	65
4.2.5 Thorium alloys	65

STUDY INSTRUCTIONS

Students of the Noble and Precious Metals course in the 1st semester of the master's studies of the field of Progressive Technical Materials receive a study package including lecture notes and study instructions for the combined studies.

1. Prerequisites

The following courses are required to enrol in this course: Basics of Production of Non-ferrous Metals and Metal Materials II - Non-ferrous Metals and their Alloys.

2. Course aim and learning outputs

After studying this module the students should be able to:

- formulate the basic characteristics of this group of metals and alloys,
- select the optimum material for different types of applications in terms of their mechanical properties and interaction with the environment,
- assess and propose optimum production technologies of individual metals and their alloys,
- assess or predict the impact of individual technological parameters on the production process, its effectiveness and impact on the environment.
- assess the effect of possible impurities on the use characteristics of the metals and their alloys,
- propose effective refining process for metals in this group.

knowledge:

- Assess material requirements for concrete applications and modify them using the alloying process, or alternatively using technical and mechanical processing.

Who this course is intended for

This course is offered in the Master's studies of the field of Progressive Technical Materials in the Material Engineering study program but it can be taken by students from any other field who meet the prerequisites.

The study materials are divided into sections, chapters, that correspond to the logical division of the covered subject and have different lengths. The estimated time to study each chapter can significantly differ and that is why long chapters are further divided into numbered subchapters in accordance with the below described structure.

We recommend the following procedure for studying individual chapters:

Study each chapter thoroughly and answer the questions Any questions regarding the covered subject can be discussed within consultations.

Communication with lecturers:

Students of the combined studies will be assigned programs and semestral projects on lectures of the Noble and Precious Metals course. Communication with the lecturer will be ensured in the form of consultations on arranged dates, alternatively via e-mail. The requirements for passing the course will be discussed in detail during the introductory lecture. Students will be provided sample tasks at the introductory lecture.

1. Introduction



Time to study: 0,5 hours



Lecture

Metals and their alloys that were not used very often in the past find increasing application options in the current technological practice. These trends are given by specific requirements of the practice and by the improvement of the production technology and processing of these metals. The main reason behind this is to fully utilize certain properties of materials, such as noble metals, refractory metals and radioactive metals. These metals, alloys and compounds are the subject of this study material. Many of these metals have a wide range of applications in electrotechnics and microelectronics, others are used in aviation technology or rocketry. This group of materials includes both functional materials, which provide interesting physical properties, favourable electrical conductivity, low or high density, and constructional materials, which offer high oxidation resistance at high temperatures, alternatively high mechanical characteristics at increased temperatures. As far as noble steels are concerned, we will pay attention to Au, Ag and metals of the platinum group. In terms of metals with high melting temperature, so called refractory metals, we will focus on W, Mo, Ti, Zr, Hf, Nb, Ta and V. The last group of metals introduced in this study material is radioactive metals, with attention paid especially to uranium and its possible forms suitable for nuclear energy.

2. Precious metals



Time to study: 10 hours



Aim After studying this section the student should be able to:

- Characterize the group of noble metals, become familiar with properties of these metals.
- Design concrete practical applications of noble metals with regards to the required properties.



Lecture

2.1 Gold

Gold is one of the first metals used by people for working, since it could be found in its pure form. People also knew how to cold-form gold by beating. Later on, gold was melted and separated from silver. Already from the ancient times, gold was the indicator of value and basis of all trade (thanks to its durability and values). First gold coins were minted in the 7th century BC. In case of gold mining, the mined rock was crushed and gold was obtained by gold-washing, as well as gravitation enrichment methods, floatation and amalgamation. The

most used method at present is cyanidation. In 2012 approximately 2700 tons of gold were produced worldwide.

2.1.1 Gold properties

Gold is the only metal with yellow color and beautiful lasting gloss. Its density is 19.32 g.cm^{-3} . The melting temperature is 1063°C . The boiling temperature of this metal is 2966°C ; however, it starts to evaporate significantly already at 1100°C . It has the FCC lattice. Gold is the most malleable and ductile metal. Gold can be formed to a film with thickness of only 0.0001 mm or it can be drawn to a wire with a diameter of 0.005 mm . Its casting properties are excellent – it does not oxidize or absorb gases during the melting process and it can be melted without any protection measures (flux agents, etc.). From the chemical point of view, it is a high-resistance metal, which is related to its very high positive potential. It is completely resistant to most acids, leaches and salts and it is easily extracted from its alloys in the metal form. It is dissolved only in mercury (it forms an amalgam with this metal); in cyanides and also for instance in aqua regia it forms a complex compound ($1 \text{ HNO}_3 : 3 \text{ HCl}$). Purity of gold is measured in carats. Pure gold corresponds to 24 carats, from which it follows that 1 carat is 41.66 ‰ . Most commonly used gold for jewellery purposes has 14 carats, i.e. 583.33 ‰ .

2.1.2 Gold compounds

Gold in its compounds is either trivalent or monovalent. Trivalent gold is the most stable. All gold compounds are easily dissociated thermally or by reducing agents.

These compounds are unstable and easily thermally dissociated, as depicted in Fig. 2.1. Gold(I) oxide is created by the reaction of gold(I) chloride with alkaline carbonate. Gold(I) oxide is a black powder, which is obtained from gold(III) chloride and alkaline carbonate.

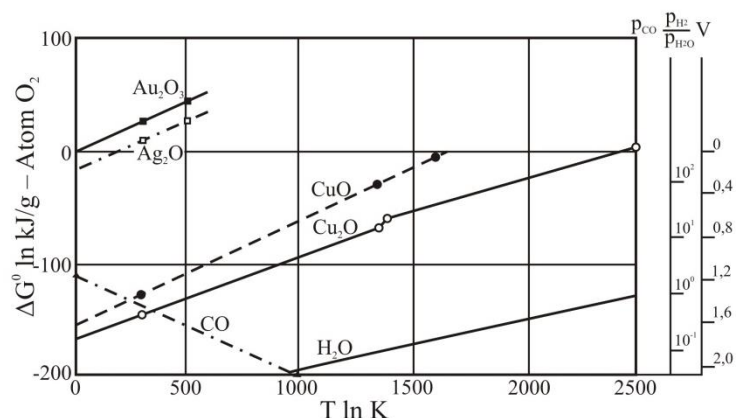


Fig. 2.1 Dependence of Gibbs free energy on temperature for oxides.

Gold halides

Gold(I) chloride AuCl is created from gold(III) chloride at 185°C . It is dissociated by water already at a room temperature. Gold(III) chloride AuCl_3 is prepared in water-free state by chlorine acting on elementary gold precipitated by iron(II) sulfate. Gold(I) bromide AuBr is obtained by slow heating of gold(III) bromide. It is dissociated faster than gold(I) chloride. Gold(I) iodide AuI is created by dissolving gold(III) oxide in hydroiodic acid. It dissociates faster than the previous halides. Gold(III) iodide AuI_3 is prepared by adding neutralized solution $\text{H}[\text{AuCl}_4]$ to aqueous solution of potassium iodide. The dependence of free energy on temperature for selected halides is shown in Fig. 2.2.

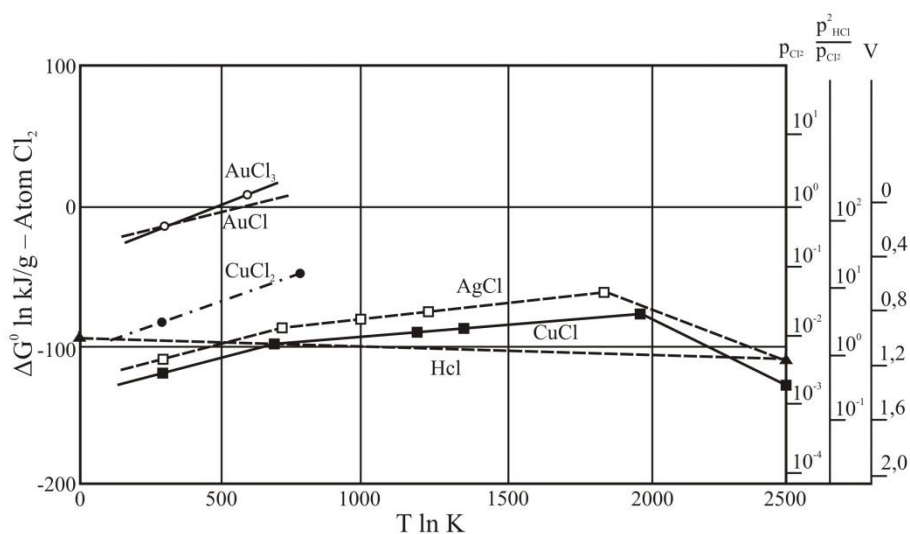
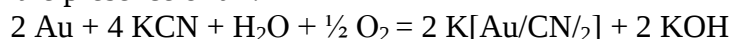


Fig. 2.2 Dependence of Gibbs free energy on temperature for halides.

Gold cyanides

Gold cyanide AuCN is produced by similar transformations as iodides. It is prepared by heating of complex gold cyanide with hydrochloric acid at a temperature of 50°C . It is not dissociated in water, it is poorly soluble. It dissolves well in alkaline cyanides, creating complex salts of type $\text{M}^I[\text{Au}/\text{CN}/_2]$ – aurocyanides.

Potassium aurocyanide $\text{K}[\text{Au}/\text{CN}/_2]$ is obtained by dissolving gold in a potassium cyanide solution in the presence of air:



Potassium aurocyanide dissolves well in water, which is why it is used in hydrometallurgical extraction of gold from gold-bearing raw materials.

Gold(III) cyanide $\text{Au}/\text{CN}/_3$ has low stability and has therefore no practical application. Gold cyanide compounds play an important role in hydrometallurgy and are derived from monovalent gold cyanide.

Gold sulfides

Gold(I) sulfide Au_2S is released by saturation of solution $\text{K}[\text{Au}/\text{CN}/_2]$ by hydrogen sulfide and by adding hydrochloric acid. It is insoluble in water and in diluted acids. It can be dissociated by strong oxidizing agents. It is dissolved in excess aqueous solution of alkaline sulfides and forms double thioaurites with them.

Gold(III) sulfide Au_2S_3 is formed by introducing a current of hydrogen sulfide to the AuCl_3 solution. It dissolves in sodium sulfide at a temperature of $3 - 4^\circ\text{C}$. It is a black amorphous powder that dissociates at a temperature below 200°C . Dependence of ΔG on temperature for creation of sulfides is shown in Fig. 2.3.

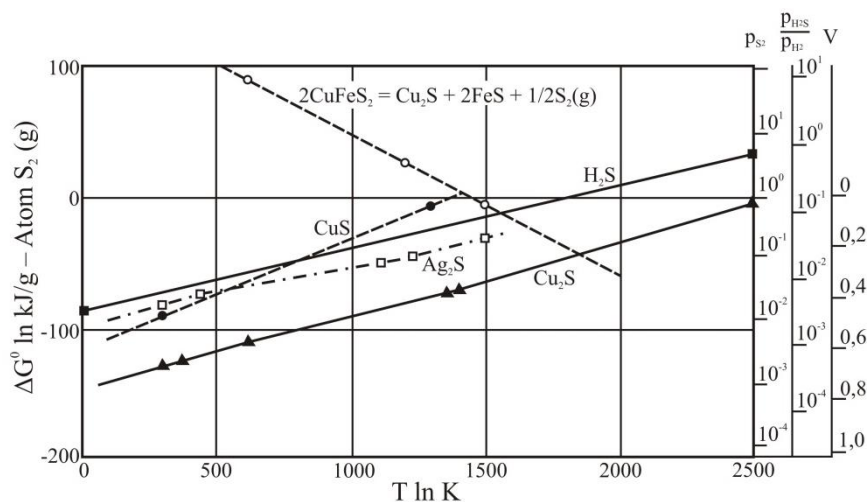


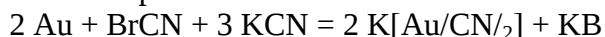
Fig. 2.3 Dependence of Gibbs free energy on temperature for sulfides.

Gold sulfates

This compound is stable only in concentrated solutions of H_2SO_4 . Dilution of the solution immediately causes hydrolysis and creation of gold(III) hydroxide. Similar process applies for gold(III) carbonate. These compounds appear in solutions in the form of complex compounds.

Gold telluride AuTe_2

This compound occurs in nature as the mineral calaverite. It is dissociated when heated in the air. It can amalgamate directly and dissolves in solution of alkaline cyanides, especially if cyanogen bromide is present:



Gold amalgams

Amalgams are systems, in which one component consists of mercury. Under normal conditions, Hg takes a liquid form; however, amalgam containing semi-free mercury constitutes a semi-liquid compound.

In addition to precious metals, other metals also form amalgams with mercury – alkaline metals, alkaline earth metals. Formation reaction of precious metal amalgams, as opposed to other metals, are characterized by very low thermal effects. Such created compounds are dissociated under the melting temperature while releasing the remaining mercury.

Fig. 2.4 shows a binary diagram of Au – Hg. Mercury forms three compounds with Gold: AuHg_2 (δ phase), Au_2Hg (γ phase), Au_3Hg (β phase) and a solid mercury solution with the maximum concentration of 16.7 at. % Hg (α phase).

Solubility of gold in mercury at normal temperature ranges between 0.15 – 0.20 %. In terms of their chemical composition, operation amalgams represent an interval between the pure component (Hg) and amalgam with a 33% content of Au. These heterogeneous semi-liquid compounds can be separated by filtration – in this case Hg represents the filtrate. In addition, a non-negligible amount of gold is also dissolved in this mercury (approximately 0.15 – 0.17 %).

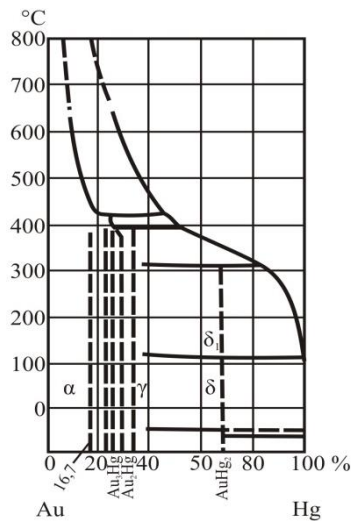


Fig. 2.4 Binary alloy phase diagram Au-Hg

2.1.3 Production technology

Gold in nature occurs in a metallic form. It is a rare metal, since it appears in a mineable scope only at few places of the earth's surface. This metal is mostly mined from primary deposits – mostly from silica dikes in the form of a fine dust, grains, sheets, etc. These dikes penetrate pyrite, chalcopyrite, antimonite and other minerals. It occurs also in the form of chemical compounds with tellurium, such as calaverite AuTe_2 , sylvanite AgAuTe_4 and nagyagite $([\text{Pb}(\text{Pb},\text{Sb})\text{S}_2][\text{Au},\text{Te}])$.

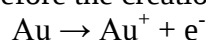
The oldest and easiest way to obtain gold is gold washing. This procedure is based on a different density of pure gold and accompanying minerals.

Another method of gold production is amalgamation – it is based on the ability of gold to create amalgams with mercury. This process was performed on equipment that enabled the best contact of mercury with gold. Excess mercury is then separated by filtration. So-called hard amalgam, which consists of intermetallic compounds of Ag and Au, undergoes distillation and mercury evaporates. Mercury vapours are collected, condensed and used to prepare another amalgam.

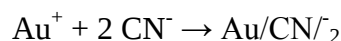
The basic method of gold mining from ores and concentrates is the cyanide procedure. This procedure is based on dissolving gold in a solution of alkaline cyanides, i.e. it is a hydrometallurgical production process. As the two first methods are no longer used, the following text will describe only the cyanide process. The process of obtaining gold from anode sludge during the production of Cu will be also mentioned.

2.1.3.1 Cyanide process of gold extraction

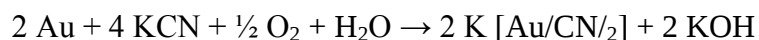
This process is based on dissolution of gold in a solution of alkaline cyanides. The reaction between gold minerals and the solution depends on the chemical stability of minerals. During dissolving, the metal needs to transform from atomic form to ion form. Gold, when dissolved, transforms to the ion form before the creation of the complex:



This is immediately followed by the creation of complex cyanide due to the diffusion of cyanide ions to the metal surface:



The most available oxidation agent in operating conditions is oxygen, which is contained in the cyanide solution. The dissolving equation for gold in cyanide solution can be expressed as follows:



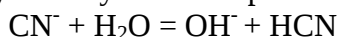
Gold dissolution kinetics

For the sake of simplicity, the kinetics of this process can be summarized as follows:

- Convection - balancing of concentration in the whole reaction volume.
- Diffusion - plays an important role near the surface of the dissolved grain; it determines the penetration speed of $(\text{CN})^-$ and O_2 by a so-called diffusion layer that surrounds the grain.
- Chemical composition of the metal - consists mainly of easily soluble admixtures oxidable in Au.
- Concentration of O_2 - saturation of $(\text{CN})^-$ solutions by O_2 . Leaching at increased air pressure or leaching in oxygen atmosphere - autoclave - can be used.
- Degree of mash dilution - ratio of solid to liquid phase p:k. This ratio influences the solution viscosity and subsequently the speed of O_2 diffusion in mash to gold.
- Dimensions of gold particles - the surface area with which the cyanide solution reacts.

Loss of cyanide during leaching

The consumption of the cyanide solution is one of the main economic and technical production indicators and is determined by chemical and mechanical factors. Loss of cyanide can be prevented by adding a so-called protection base, mostly in the form of NaOH, to the solution during the process. These alkalis protect cyanide salts from hydrolysis. The following reaction occurs during the hydrolysis of cyanide compounds:



This reaction produces a highly volatile compound HCN with a boiling temperature of 26.5 °C. It was determined that 0.01 % content of NaOH in the solution protects cyanide solution against hydrolysis. However, the content of alkali must not exceed a certain limit to prevent creation of thin layers on the surface of the dissolved gold.

Pure gold is most commonly accompanied by Fe minerals (pyrite, pyrrhotine). Pyrrhotine is the most harmful of Fe sulfides, since its oxidation consumes a large amount of oxygen from the solution.

Leaching methods of gold-bearing ores

These methods include percolation - seeping or leaching together with mixing. Seeping is used to leach coarse-grained materials, which enable filtering of the solution through a relatively high ore column. The moisture content is usually 20 %: Leaching with mixing is performed with finely ground material containing approximately 40 – 60 % of moisture. After leaching, the solution needs to be separated from the insoluble residues – leach.

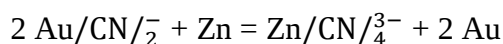
Percolation leaching is a time-consuming process. All operations combined can take up to 100 hours. This process can be applied if fine grinding of the gold-containing material is not required.

Agitation leaching, as opposed to seeping, is significantly faster and yields better results. These processes take approximately 6 – 40 hours. The leaching time can be reduced

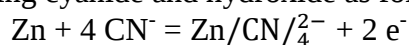
by finer grinding of the ore, thorough separation of coarser fractions, etc. Mash mixing can be done mechanically, pneumatically or by combining these two methods. After the process is finished, the mash is thickened and dehydrated and the gold-containing leach is separated. Thickening consists of mash sedimentation, which is accompanied by partial dehydration. Further dehydration can be performed by vacuum or pressurized filtration using drum filters, disc filters, filter press, etc.

Gold extraction from cyanide solutions

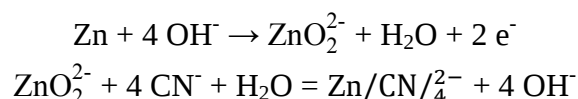
This step can be realized by metallic, as well as non-metallic agents. However, the most widespread technology is gold cementation by metallic zinc. The process of zinc cementation is following:



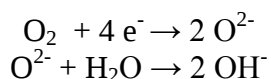
Presence of oxygen in this reaction would result in dissolution of cemented metal. In this process, oxygen is removed using cyanide and hydroxide as follows:



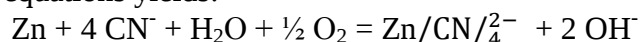
Dissolution of Zn in hydroxide is accompanied by the transition of Zn to a complex cyanide salt ion:



Excess electrons in the dissolved oxygen are consumed by its reduction, while creating hydroxide:



Combination of these equations yields:



Processing of gold precipitate

The precipitate obtained together with the zinc powder by cementation is first dehydrated on filters and then undergoes one of the following operations:

- Direct melting in a crucible with admixtures without previous processing – this method can be applied only for pure and rich precipitates.
- Processing by acid followed by remelting with lead dioxide to raw lead and by cupellation. This method is not used very often.
- Processing using diluted H_2SO_4 followed by melting with admixtures.

The gold precipitate contains a mixture of precious metals, Zn dust, non-ferrous metal oxides, hydroxides, cyanides, etc. The gold and silver content usually ranges between 20 – 50 %.

Precipitate processing by sulfuric acid

The reaction between acid, zinc and carbonate is quite vigorous, whereas the gases released in the process contain highly poisonous substances, such as AsH_3 and HCN . Washing in acid is followed by washing in water. The next steps consists of filtration, drying and melting. Table 2.1 shows the chemical composition of the precipitate before and after processing by acid.

Zinc dissolves well in 16% H₂SO₄, concentration of 10 – 15 % is also used in practice. Approximately 1.25 kg of acid is consumed for one kg of precipitate. The process takes 3 hours. Loss of gold in this process is 0.84 g.t⁻¹.

Table. 2.1 Chemical composition of the precipitate before and after processing by H₂SO₄.

compound	Before processing	After processing
Au	19,3	52,0
Ag	1,88	4,52
Pb	8,79	24,23
Cu	0,47	1,49
Zn	48,17	24,34
Fe	0,1	0,2
Ca	0,05	0,12
Ni	2,63	-
S sulfidic	4,19	2,63
S sulfate	stopy	8,75
SiO₂	0,9	1,36
Organic comp.	2,63	-
other	10,93	0,32

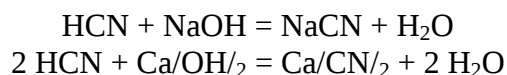
Remelting of processed precipitate

This process takes place in a crucible or flame furnace. The batch consists of the precipitate with admixtures of soda, borax, silica and calcium fluoride. Individual constituents play their specific roles. Soda – low melting temperature of the created slag; borax – good fluidity of the slag; silica – creation of bisilicate slag with low melting temperature. This slag does not react with graphite crucibles. CaF₂ also reduces the melting temperature of the slag. Sodium nitrate can be used as an oxidant.

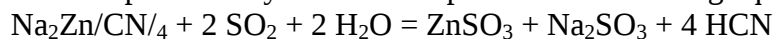
The process temperature ranges between 1100 – 1200°C. Casting is performed as soon as the slag layer is 25 mm thick. Then the metal is granulated and if it is still heavily contaminated, another melting process with admixtures is performed

Cyanide solution regeneration

A whole range of methods have been developed for regeneration of used cyanide solution. The most commonly used method is the solution processing by sulfuric acid, during which the created hydrogen cyanide is captured in the sodium hydroxide solution. This regeneration method yields a precipitate of cyanide, sulfocyanide of silver, copper and ferrocyanides that are insoluble in acidic environment. Almost perfect regeneration can be achieved only if the cyanide group is bound to simple cyanides or to complex zinc cyanides. Created HCN can then react:



The cheapest regeneration method uses sulfur dioxide (e.g. from roasting of sulfide ores). Dissociation of complex zinc cyanides correspond to the following equation:



Regeneration is performed on tower equipment, using a vaporizer to create HCN and an absorber, where HCN is absorbed, e.g. using NaOH. It goes without saying that the apparatus is hermetically sealed.

2.1.3.1 Production of gold from anode sludge after electrolysis of copper

During the production of copper from copper ores, which in most cases contain precious metals, the gold is gradually concentrate in matte, black copper and after electrolysis it moves to the anode sludge. This sludge can be processed by different methods – depending on the chemical composition. The first step of all methods consists of separation of copper by dissolution in diluted H_2SO_4 at a temperature of 70°C with air blowing.

Decoppered sludge is further processed in two stages. In the first stage Se and Te are removed with the aim to increase the concentration of precious metals in the residues. The next stage consists of oxidizing melting of the sludge with the aim to obtain an alloy of Ag + Au (i.e. doré).

Majority of Se and Te is obtained by oxidizing roasting, sulfatizing roasting and soda caking. The prepared Ag + Au alloy then proceeds to electrolytic refining.

2.1.4 Gold refining

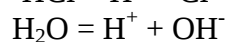
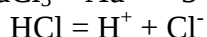
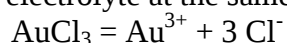
Use of gold in technological practice requires a high-purity metal. Gold is refined either by the electrolytic method or by selective precipitation of individual admixtures. The most important role is played by electrolytic refining.

2.1.4.1 Electrolytic refining of gold

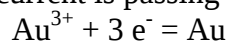
This technology offers a whole range of advantages in comparison with other methods. This method can be used to prepare the purest metal, the process price is economically acceptable and it can yield platinum metals as by-products. It was first used in 1908.

Solution of HCl and AuCl_3 is used as electrolyte. Raw gold is used as anodes in this process. Cathodes are used in the form of a mother sheet after electrolytic refining. After the introduction of direct current, anodes are dissolved and gold is transformed to Au^{3+} . Part of the admixtures enters the solution and part deposits at the bottom of the electrolyzer in the form of anode sludge.

The following ions are contained in electrolyte at the same time:

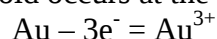


The following processes occur as the current is passing through the electrolyte:



This occurs on the cathode, admixtures and hydrogen are not released at the cathode due to their potentials, which are low in comparison with gold ($\text{Au}/\text{Au}^{3+} = 1.5 \text{ V}$).

Electrochemical oxidation of gold occurs at the anode:



Gold that enters the electrolytic refining contains the following admixtures: Cu, Pb, Ag, Pt, Pd and others. The behaviour of these admixtures depends on their solubility in electrolyte, potentials and other factors.

2.1.5 Application of gold

The largest amount of gold is used for the production of artistic and decoration objects. Due to its low mechanical properties, gold needs to be used in form of alloys, most often with silver. The content of gold in various alloys is stated in thousandths or carates.

Another application of gold consists of gold-plating of objects made of less noble metals – mostly silver or copper. Gold can also be used in stomatology, as well as for special equipment in chemical laboratories. Last but not least, this metal is used to produce special contacts and in semi-conductor and space technology.

2.1.6 Gold alloys

Gold is most frequently alloyed with metals of the same group. In addition, the following metals can also be used: Zn, Cd, Cr, Mn, Ni, Co, etc.

Au – Ag system

An addition of silver decreases the melting temperature of the alloy, whereas the crystallization interval is narrow. Both elements form a binary diagram with perfect solubility of both constituents in solid form. The colour changes and contains a tinge of green. Ag is the most commonly used admixture when the alloy is used for minting, alternatively with copper for jewellery.

Au – Cu system

Binary diagram of the Au – Cu system is shown in Fig. 2.5. Addition of Cu causes a slight change of colour to red; alloys with copper have also higher hardness than pure gold. Binary Au – Cu alloys are usually not used; silver is commonly added to these alloys. As the Ag – Cu system is eutectic, similar crystallization applies also to ternary alloys with higher contents of these metals. Alloys rich in Au usually consist of solid solutions and may contain AuCu compound only in case of higher Cu contents. Alloys of this type are used in goldsmith's trade and previously also in stomatology. An interesting fact is that these alloys were used to make the tips of exclusive fountain pens. Fig. 2.6 shows the ternary Au – Ag – Cu system depicting the approximate colors depending on chemical composition.

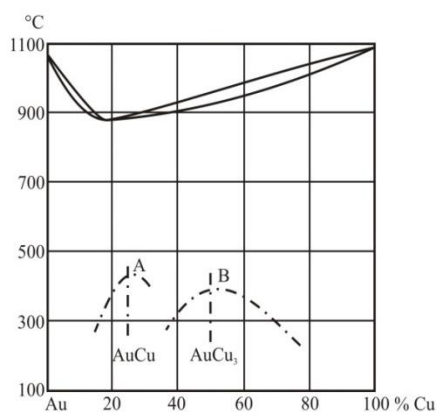


Fig. 2.5 Binary alloy phase diagram Au – Cu.

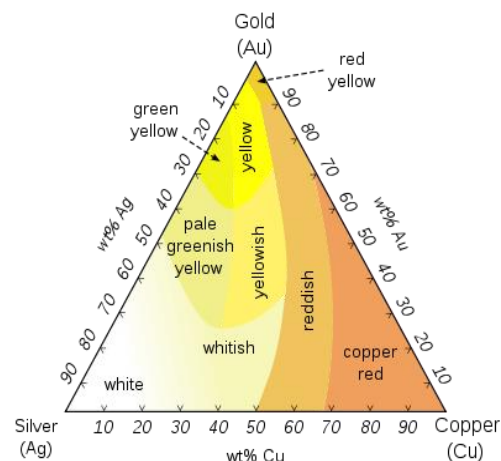


Fig. 2.6 Ternary system Au-Ag-Cu, colors in dependence on chemical composition of the alloy.

Au – Ni system

Alloys of this system have higher hardness and are therefore less malleable than other alloys. Ni causes discoloration of gold to silver – in the past this method was used to produce white gold. These alloys contained 7 – 15 % Ni. This process is no longer used and white gold is produced from the Au – Pd system.

Au – Pd system

Similarly to Au – Ag, this system creates a wide range of solid solutions. The addition of Pd causes a significant increase of the melting temperature of the alloy. Pd also causes discoloration, the alloy is completely silvery white already at 15 % of Pd. Alloys have good malleability and resistance to corrosion. They are applied in stomatology, as well as to produce protection melting insert to small electric furnaces.

Au – Pt system

There is a wide range of crystallization in this system and that is why the composition of the alloy during crystallization is considerably unbalanced. Two solid solutions begin to separate in the solid state, which results in brittleness of medium-composition alloys. Only alloys with up to 20 % of Pt are malleable. For binary diagram of this system see Fig. 2.7.

In terms of application, the alloys can be divided into the following groups:

- alloys for jewellery,
- dental alloys,
- alloys for production of contacts,
- alloys for special purposes.

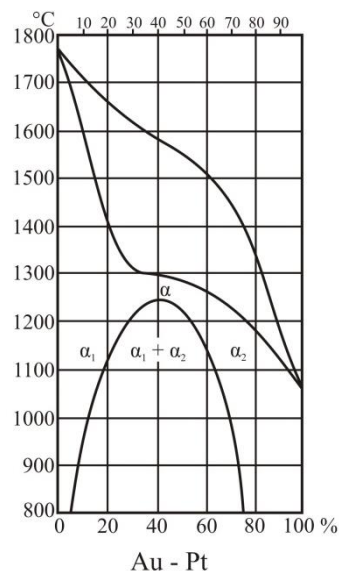


Fig. 2.7 Binary alloy phase diagram Au – Pt.

2.2 Silver

Together with gold, silver is one of the first metals discovered by the people. In nature it occurs in the metallic form in sediments or in minerals. Since silver is relatively rare and is very soft, malleable and air-stable, it was used namely to produce various decorations. Only later it was applied also in minting. Today, most of the silver is obtained as a by-product from the production of lead, copper and zinc.

2.2.1 Silver properties

The melting temperature of silver is 960.5°C, boiling temperature is 2212°C. Its specific weight is 10.5 g.cm⁻³. It has the highest electrical and thermal conductivity of all metals. Silver crystallizes similarly as gold in the FCC lattice. After gold, silver is the most malleable metal. It is possible to create a film with a thickness of 0.002 mm.

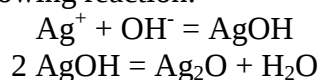
Silver is air-stable and is not damaged in contact with other metals. It is resistant to weaker oxidizing agents, as well as to most saline solutions. It dissolves in nitric acid and in hot sulfuric acid.

2.2.2 Silver compounds

Almost all compounds are derived from monovalent silver. The general formula of these compounds is AgX. Exceptionally, silver may be bivalent and very rarely trivalent.

Silver oxide

Ag₂O is created by the following reaction:



It is formed mostly by the addition of ions OH⁻ to the solution of silver salts. This oxide dissolves in aqueous ammonia solution.

Silver halides

This group includes silver fluoride, which is also its most soluble representative. Least soluble is iodide. Fluoride may be prepared by dissolving Ag₂O in HF. Silver chloride AgCl is released from the solution containing ions Ag⁺ and Cl⁻ in the form of a white precipitate. In nature it occurs as cerargyrite – this ore can be found in larger amounts only in America. AgCl dissolves in concentrated HCl and in ammonia, while creating complex salts.

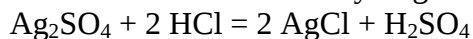
The sensitivity of AgCl to light also has an important practical application. It enables its use in the area of analogue photography. Silver bromide is a similar substance. However, it is more sensitive to light than chloride.

Silver nitrate

Silver nitrate is the most important compound from the technical point of view. It is prepared by dissolution of elementary silver in HNO₃. Silver nitrate dissolves well in water.

Silver sulfate

The melting temperature of Ag₂SO₄ is 660°C. It does not dissolve well in water. Sulfate can be transformed to chloride when melted in hydrogen chloride environment:



Silver sulfide

Ag₂S is released as a black precipitate when hydrogen sulfide is introduced to the solution of silver salts. It is also created by the effect of sulfides or hydrogen sulfide on elementary silver. It is the least soluble silver salt. In nature it occurs as double arsenic and antimony sulfide.

Silver cyanide

AgCN – a white precipitate released from solutions of silver salts after CN⁻ ions are added. It is insoluble in water but dissolves well in alkaline cyanides, creating complex salts.

2.2.3 Production technology

Silver is a relatively common metal and its content in the Earth's crust is in the order of 10^{-5} %. In nature it occurs in pure form, as well as chemically bound. Pure silver almost always contains admixtures of copper and gold.

The most common form of silver in nature is the sulfide form and it usually accompanies sulfides of other metals (Pb, Sb, As, Cu). It often constitutes a significant admixture of galenite.

The most important minerals include:

- **Argentite** – Ag_2S . This is an important ore; its most significant deposits are located in Mexico.
- **Pyrargyrite** – Ag_3SbS_3 .
- **Proustite** – Ag_3AsS_3 .
- **Tetraedrite** – the silver content in this mineral is low (about 1 %); however, it occurs in many copper and lead ores.
- **cerargyrite** – AgCl . After it is transformed to sulfide, this mineral floats well, cyanides and amalgamates well.

Argentite and tetraedrite have good floatation properties. Cyaniding of argentite may be performed directly under specific circumstances, tetraedrite cannot be leached directly. Other sulfides need to be processed before leaching.

Silver is produced by pyrometallurgic and hydrometallurgic processes. Hydrometallurgic processes include amalgamation and cyaniding; pyrometallurgic processes include mainly silver production as the by-product of copper and lead production. Nowadays silver is mostly prepared pyrometallurgically.

2.2.3.1 Hydrometallurgic processes of silver extraction

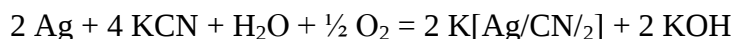
As already stated above, this group of processes includes amalgamation and cyaniding.

Amalgamation

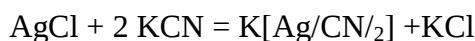
This method, just like in the production of gold, is based on the ability of silver to form amalgams with mercury. Most suitable for amalgamation is AgCl . Sulfidic minerals have poor solubility in mercury and therefore require chlorination. The yield of these process was very low and that is why they needed to be improved - amalgamation was performed simultaneously with grinding, amalgam was heated by water vapours, etc. This method is no longer used today.

Cyaniding

The process is based on dissolving of pure silver and silver minerals in cyanide solutions. Pure silver is dissolved in an alkaline cyanide solution in accordance with the following reaction:



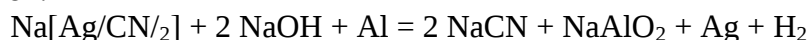
Dissolution of AgCl cerargyrite in alkaline cyanide occurs relatively fast in accordance with the following reaction:



Cyaniding of silver ores is very similar to the process used for gold. However, the cyanide solution concentration is higher in this case. Silver ores need to be ground to finer particles, which is why their leaching is performed simultaneously with mixing. Percolation

leaching was used only exceptionally. During leaching it is necessary to aerate the mash. Leaching takes tens of hours.

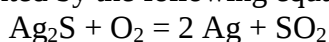
Silver from the cyanide solution is precipitated by zinc dust (aluminium or sodium sulfide can also be used). Silver precipitation by aluminium occurs in accordance with the following reaction:



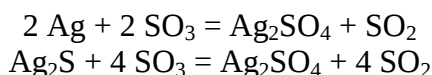
An important advantage of aluminium is the better regeneration of cyanide.

2.2.3.2 Pyrometallurgic production of silver from lead ores

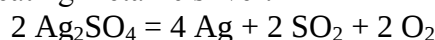
Silver is obtained during the production of lead as a by-product, since lead ores contain a significant amount of silver. That is why lead-processing plants usually process concentrates, whereas the first step is usually agglomeration. During agglomeration of a concentrate with granularity of 0.1, argentite is oxidized at a temperature of 650 °C. Oxidizing roasting can be represented by the following equation:



Oxidation of silver sulfide and formed silver then continues as follows:



Silver sulfate is a stable compound, which begins to disassociate at a temperature of 850 °C and ends at 1080 °C, while creating metallic silver:



Lead is an excellent collector of precious metals, which is why when melted in a shaft furnace, 90 % of silver and 98 – 99 % of gold is transferred to raw lead. Raw lead can therefore contain 10 – 15 g.t⁻¹ Au and 1 – 5 kg.t⁻¹ Ag. Historic methods of precious metal extraction from lead included cupellation and patinization. These methods are no longer used today.

Parkerizing

Parkerizing is the most used method today. This method of silver extraction from lead using zinc was implemented to practice in 1842. It is a highly progressive method of silver extraction with minimum losses of the metal. This process is based on bounded mutual solubility of lead and zinc and total insolubility of zinc and silver alloys at low temperatures in zinc-saturated liquid lead.

It is clear from the binary diagram of the Ag – Zn system (Fig. 2.8) that Zn forms several inter-metallic compounds with silver. The composition of the created alloy depends on the mutual ratio of silver and zinc in the melting and on the temperature. Two inter-metallic compounds are formed during the refining of lead from silver using zinc: Ag₂Zn₃ with a melting temperature of 665°C and Ag₂Zn₅ with a melting temperature of 636°C. The Ag₂Zn₃ compound dissolves in lead at a higher temperature; however, its solubility significantly reduces with decreasing temperature and at 330°C it is practically insoluble in lead. Its density is lower than lead and it creates a hard layer concentrating all silver contained in the raw lead. This layer is removed mechanically together with a significant amount of lead. However, not all lead is a mechanical admixture; part of it forms a ternary alloy with zinc and silver with the content of Pb of approximately 2 – 5 %. The ternary system of Ag – Zn – Pb is shown in Fig. 2.9.

The alloy layer forms a so-called "parkerizing foam", which is removed and the refined lead is impoverished for silver. The process is repeated up to four times based on the content of silver in the raw lead. Finally, almost all silver is transferred to the foam.

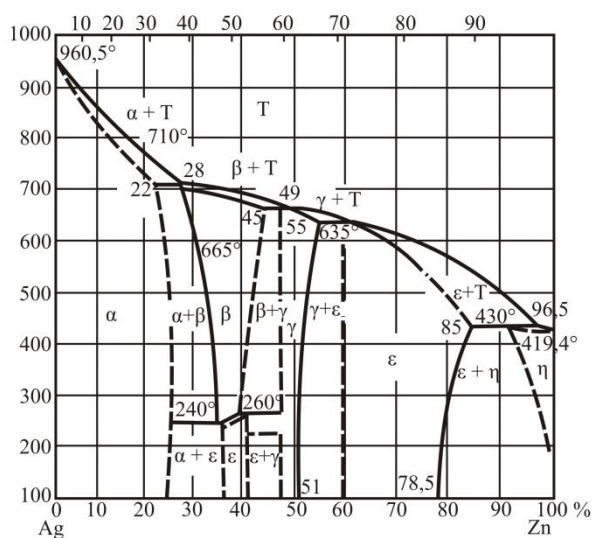


Fig. 2.8 Binary alloy phase diagram Ag-Zn.

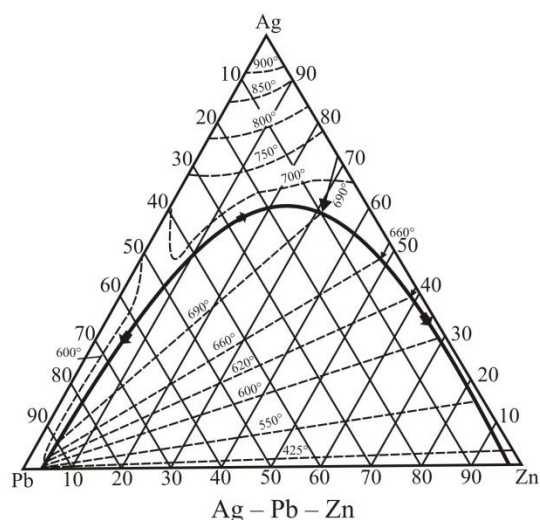


Fig. 2.9 Ternary alloy phase diagram Ag-Pb-Zn.

The first foam is referred to as the gold foam since it contains not only silver, but also platinum metals and gold. This first foam contains a relatively low amount of silver. Most silver is concentrated in the second foam, which is then processed to silver. The following foams contain a lower amount of silver and are returned to following parkerizing processes.

The silver foam contains a relatively large amount of Pb, which is first removed by pressing or by segregating. Segregated foam undergoes distillation to remove zinc. Zinc is then re-used for refining of lead.

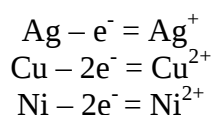
2.2.4 Refining of raw silver

Raw silver contains many metal admixtures – Cu, Pb, Bi, Au, etc. That is why refining is required. Admixtures can be removed by oxidation by air oxygen and certain compounds (silver sulfate). Oxidation by oxygen is performed in a small cupellation furnace, where the raw silver is melted in the supplied compressed air. The surface of the melted silver is covered by special compounds (e.g. bone-ash), which absorb the created oxide and are separated from the melt together with the surface. The melting process continues until the achieved silver purity is at least 998/1000. This method is quite time-consuming.

2.2.4.1 Electrolytic refining of silver

Electrolytic refining is performed if the silver contains 10 – 350 parts of gold. This process is based on the solubility of silver and insolubility of gold in HNO_3 and AgNO_3 solution. The anode is cast from silver with admixtures of gold and possibly other non-ferrous metals; cathode is made of pure silver, alternatively from a material insoluble in HNO_3 .

The electrolyte consists of a dilution solution of silver nitrate (1 – 2 % AgNO_3) with the addition of nitric acid at a concentration of 1 – 1.5 %. The following occurs at the anode during electrolytic refining. Ag, Cu, Zn, Ni, Fe and part of Pd are dissolved and transferred to ions:



Silver is further released at the cathode and Ni, Fe and Zn remain in the solution. Cu and Pd usually cause certain problems due to their increasing concentration in the solution. That is why a cleaning of the solution should be included.

Au, Se and Te do not dissolve; after the anode material is dissolved, these materials are released in their elementary form in the form of dust that gathers at the bottom of the apparatus as the anode sludge.

Bi, Sb and Pb are dissolved and enter the electrolyte. Pb is then precipitated to PbO_2 , bismuth hydroxide and antimony. These products also do not dissolve and are transferred to the anode sludge.

The cathode releases silver if the copper concentration in the solution does not exceed 150 g.l^{-1} . The obtained cathode silver has a coarse-grained crystalline structure and is relatively brittle, which is why it needs to be periodically removed from the cathode. At the same time, the cathode and anode areas may be separated. Purity of the cathode silver is 999.8 – 999.9/1000. Other products of the electrolysis are: anode sludge (approximately 28 % of the anode weight), anode residues (approximately 15 %), spent electrolyte containing 20 g.l^{-1} Ag and gases.

Cathode silver is then remelted in an electric furnace at a temperature of 1000°C . Se and Te are oxidized during this process by leaving the melting rest for approximately 20 minutes and then adding wood coal in order to absorb excessive oxygen. After this operation the silver is cast.

Spent electrolyte is processed by electrolysis with insoluble anodes (extraction electrolysis) It is performed until the silver is completely extracted (yielding silver with a purity of 800/1000). This silver is used to produce anodes. Copper is removed from the solution by cementation using Fe shavings. The next operation consists of processing of the anode sludge.

2.2.5 Application of silver and silver alloys

Metallic silver is used namely for decorative and utility objects and it also plays an important role in the chemical industry (reaction vessels, crucibles) and electrotechnics (contacts, circuit breakers). In the past this metal was used in coin minting.

Ag – Cu system.

These are the oldest alloys ever. Cu significantly improves the mechanical properties, which is why these alloys are used for minting of coins and for technical purposes. Cu reduces the thermal and electrical conductivity.

Both metals create a simple binary diagram with limited solubility in the solid state (see Fig. 2.10). At a normal temperature, the solubility of Cu drops to 0.2 %, which enables hardening of alloys with suitable concentration of Cu.

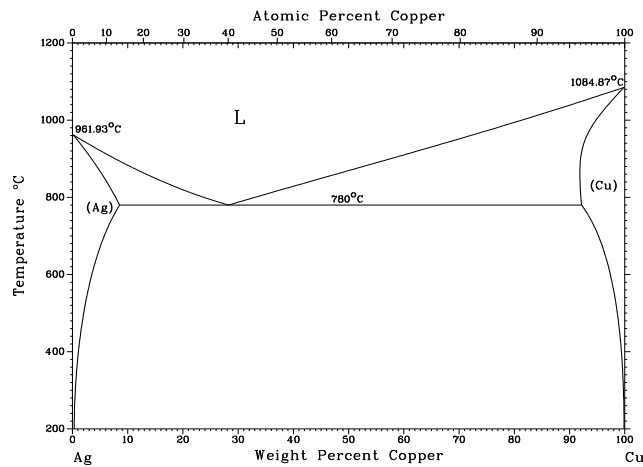


Fig. 2.10 Binary system Ag - Cu.

The Ag + 10 % Cu alloy - used in coin minting.

- in Czech Republic the content is determined to 959 ‰, 935‰, 900‰, 835‰, 800‰.

The Ag + Cu alloy – contact material – Ag95-Cu, Ag90-Cu, Ag80-Cu.

Ag - Zn system

An addition of Zn (approximately 1 %) improves the foundry properties and bonding of dissolved oxygen, which prevents sputtering of the metal during casting. Zinc is often included in silver solders.

Ag - Ni system

Alloys of this system are used as contact materials. Fig. 2.11 documents the dependency of the erosion on the number of contact closures for selected materials Fig. 2.12 represents the dependency of the electric conductivity of the binary alloys on the chemical composition.

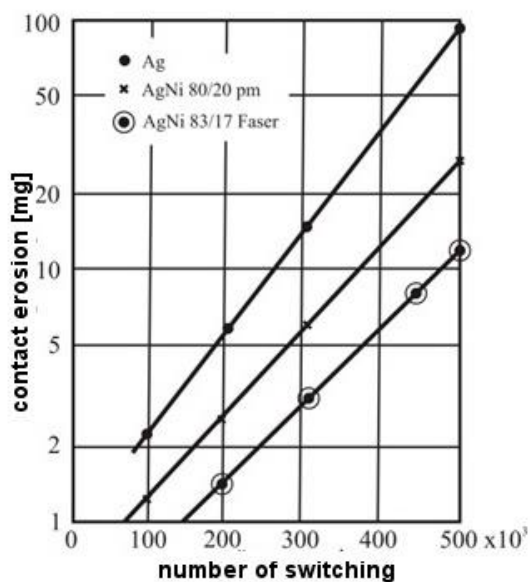


Fig. 2.11 Dependence of the amount of burn-off on the number of contact closure for selected materials.

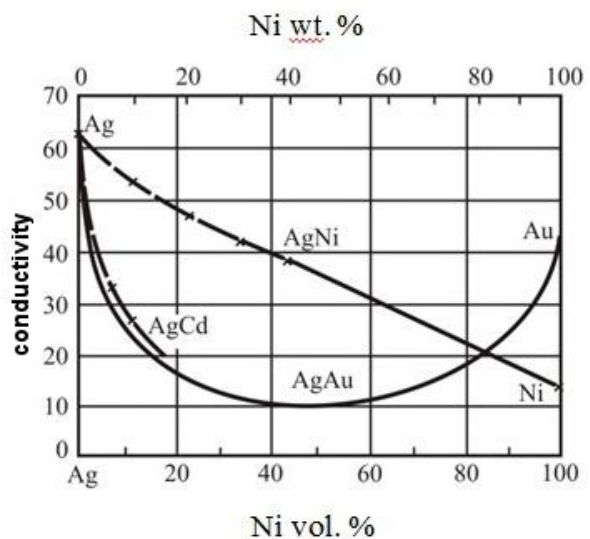


Fig. 2.12 The dependence of the electrical conductivity of binary alloy according to the chemical composition.

Ag – Cu - Zn alloys

This group includes a large number of alloys used as solders. They are characterized by a relatively low melting temperature, provide strong and tough connection and are chemically more resistant than brass solders. Silver solders are used, if the part cannot be heated during hard soldering to the temperature required by brass solders.

Ag pseudo alloys

These alloys are used for significantly stressed contacts. They are produced by powder metallurgy.

Containing Ag + Mo, W, Ag – ensures conductivity; Mo, W ensure resistance against oxidation, attrition and high melting temperature.

Ag + CdO, Ag + PbO, Ag + graphite.

2.3 Platinum and platinum group metals

The platinum group includes platinum, ruthenium, rhodium, palladium, osmium and iridium. All these metals share high resistance to acids and most of them have excellent catalytic effects and hardness. With the exception of Pd, their solubility is poor and they look similar to silver in dry air.

2.3.1 Properties of platinum group metals

2.3.1.1 Platinum

This metal is not very hard, yet very ductile and easily hot-forged and welded. Platinum has a density of 21.45 g.cm^{-3} , melting temperature of 1769°C and it crystallizes in the KPC lattice. Platinum can absorb a significant amount of hydrogen, namely in the form of a sponge – it can absorb hydrogen in the volume of 100x its own volume. It can also absorb helium and oxygen. Platinum is also characterized by catalytic effects. In terms of electro-chemistry, it is a highly noble steel with low affinity to oxygen that dissolves in aqua regia while producing H_2PtCl_6 .

2.3.1.2 Palladium

This metal looks like silver and platinum. In pure form it occurs in the form of scarce grains in platinum ores. It is a malleable and weldable metal. The density of palladium is 12.02 g.cm^{-3} , which is the lowest density of all metals in the platinum group. Its melting temperature is 1552°C , crystallizes in the KPC lattice. As far as mechanical properties are concerned, this metal is harder and less malleable than platinum.

Similarly to platinum, it is capable of absorbing metals, namely hydrogen. It can absorb 350 – 850x its volume. It becomes significantly brittle after the hydrogen absorption. Hydrogen is released when slightly heated in vacuum.

2.3.1.3 Iridium

This metal only occurs in the pure form, sometimes also in an alloy with platinum or osmium. An interesting fact is that osmium and iridium alloys are contained in all platinum ores. Iridium has a density of 22.4 g.cm^{-3} , the melting temperature is 2410°C and it crystallizes in the KPC lattice. It is a silvery white, very hard metal. Its catalytic effects rank between platinum and palladium. It offers excellent properties for application in the technological practice, such as chemical stability and high hardness. The most important alloys include oxides, halides and sulfides.

2.3.1.4 Rhodium

White, malleable metal. It occurs in platinum ores and certain gold-bearing sands. The melting temperature of this metal is 1960 °C, the density is 12.44 g.cm⁻³, crystallizes in the KPC lattice. Melted Rh can dissolve up to 7 % of C, which is released during cooling in the form of graphite. Just like other metals in this group, rhodium has excellent catalytic effects. It can be used also in electro-technics as a contact material, as no oxide layers are created on it (it maintains a very low resistance).

2.3.1.5 Osmium

This metal occurs in platinum ores in the form of an alloy with iridium. This alloy is insoluble in aqua regia. The content of Os ranges between 17 – 80 %. This metal has a density of 22.5 g.cm⁻³, melting temperature of 3033°C, and the HTU lattice. Osmium is a blue-grey, very hard and brittle metal. It was discovered in vapours of highly irritable osmic oxide, which is produced during melting of residues of platinum minerals insoluble in aqua regia. It has the best catalytic effects of the whole group of metals.

2.3.1.6 Ruthenium

This metal is the rarest metal from this group. It rarely occurs as the mineral laurite RuS₂. The density of ruthenium is 12.4 g.cm⁻³, its melting temperature is 2250°C and it has the HTU lattice. It is a matte grey, very hard and brittle metal. It evaporates during arc melting, as well as during high-temperature annealing (in the form of ruthenium dioxide). It can absorb a relatively large amounts of oxygen or hydrogen. Just like other metals in this group, it is characterized by catalytic effects.

2.3.2 Production technology of platinum metals.

Platinum occurs quite sporadically in the Earth's crust. Its content is the orders of 10⁻⁵ %. It often occurs in the form of an alloy with iron and chemical compounds with other metals of the platinum group. The most important minerals include:

- **Poxylene** – ferroplatinum, this mineral contains about 5 – 10 % of Fe and the highest amount of platinum, i.e. 88 %.
- Minerals associated with pyrrhotite, pentlandite and chalkopyrite – **Sperilite** PtAs₂, **Cuprite** PtS, **Breggite** /Pt, Pd, Ni/S and **stibiopaladinite** Pd₃Sb.
- **Cuproplatinum** – alloy with copper (5 – 13 % of Cu).
- **Nickelplatinum** – approximately 3 % of Ni.
- **Nevyanskite and sysertskite** – natural alloys of osmium and iridium.

Platinum grains are often covered by a thin layer of Fe oxides and are therefore magnetic. Pure platinum in Cu – Ni ores occurs mostly in the form of breggite, cuperite or sperilite. The most important sites of raw platinum metals are located in Russia, South Africa, US, Canada and some other areas.

Raw materials used to produce platinum metals can be divided into the following groups.

- Platinum ores.
- Non-ferrous metal ores containing platinum metals.
- Wastes.

Due to the amount of target metals in the input raw materials, the platinum ores are first concentrated. This is done by gravitation, floatation, amalgamation, chlorination and other methods.

2.3.2.1 Amalgamation of platinum and metals of the platinum group

The platinum surface is usually strongly passivated, more so in comparison with other noble metals such as Au and Ag. These metals can be amalgamated very easily (due to the excellent mercury wetting power); however, the thin oxide layer needs to be removed. Platinum does not dissolve well in mercury at a normal temperature (approximately 0.02 %); however, its solubility increases with the increasing temperature. It reaches a value of 1.2 % at a temperature of 172 °C and 1.7 % at 200 °C. The maximum solubility of platinum in mercury is 23 % (as shown in Fig. 2.13). Platinum forms three intermetallic compounds with mercury – PtHg, Pt₂Hg and Pt₃Hg.

Three amalgamation methods can be used on the industrial scale:

1. amalgamation by zinc amalgam in acidic environment,
2. electro-amalgamation,
3. amalgamation in chlorine water using zinc amalgam followed by regeneration of the solution by electrolysis.

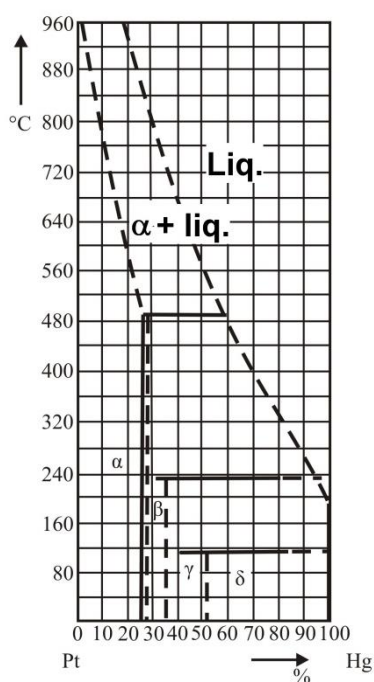


Fig. 2.13 Binary system Pt-Hg.

In the first method the platinum ore is processed by mixing with a zinc amalgam in diluted solution of H₂SO₄. Zinc enters the solution, while hydrogen is released from the platinum surface. Acid removes the passivation layer on the platinum surface, as well as oxides of other non-ferrous metals. Hydrogen released at the surface activates the platinum, removes adsorbed oxygen, as well as the thin layer of oxides. In the second phase, platinum particles come in contact with mercury. Mercury is slowly diffused to platinum. Copper sulfate is often added to the amalgam and is then reduced by zinc. Copper grains cover the platinum. This makes the platinum easier to amalgamate.

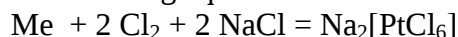
The obtained amalgam is pressed and then leached in a 10% solution of sulfuric acid in order to remove zinc and iron. The solution is decanted and then filtered. The precipitate with approximately 3 % of platinum is roasted in a muffle furnace and processed by HCl. This increases the platinum content to 70 %.

2.3.2.2 Chlorination of platinum ores

This method is based on the reaction of platinum metal minerals with chlorine, while creating complex, easily soluble salts of platinum, palladium and other metals. This method is

used to process platinum ores in South Africa. Ores contain approximately the same amount of platinum and palladium in sulfide form.

Ground ore is first floated and then obtained concentrate undergoes chlorinating roasting. The concentrate contains approximately $250 - 340 \text{ g.t}^{-1}$ of the target metals. The process takes place at a temperature of $550 - 600^\circ\text{C}$ in a compound with NaCl for 4 hours. The process can be described by the following equation:



where Me represents Pt, Pd, Ir.

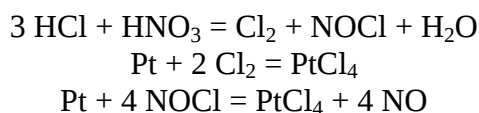
After chlorination the material is processed by HCl solution. Pt, Pd and Ir enter the solution in the form of complex alkaline chlorides accompanied by copper and nickel (in the form of simple chlorides). For further processing of the solution see.

2.3.2.3 Affination of platinum metals

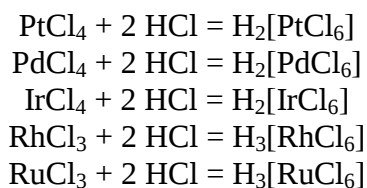
The term affination refers to mutual separation of individual metals of the platinum group. Affination processes of platinum metals are done using concentrates prepared by the gravitation treatment, precipitates after chlorination of platinum concentrates, alloys from amalgamation, anode sludge from Ni and Cu electrolysis, residues after electrolytic production of gold, wastes of selected products, etc.

There are more processing variants for individual materials due to their varying composition. After the gravitation treatment, platinum contains 80 % of Pt, 3 – 6 % of Ir, below 1 % of Rh. It also contains Pd and a significant amount of Fe, up to 18 %. Pt concentrates from processing of anode sludge from the production of Cu and Ni contain usually about 30 – 50 % of Pt metals with high content of Pd.

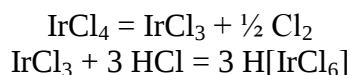
The first step of affination of gravitation concentrates consists of dissolution of the material in aqua regia while stirring the material. The reaction of metals with the acid can be represented as follows:

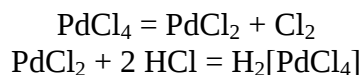


Chlorides of platinum metals created by the reaction with aqua regia further react with HCL and create complex acids:

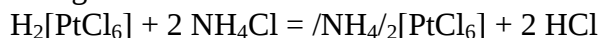


Osmium is oxidized and creates osmium tetroxide, which remains in the insoluble residues. HNO_3 is completely removed from solutions containing complex acids of platinum metals with the addition of HCl. This is followed by precipitation of platinum by ammonium chloride in the form of ammonium hexachloroplatinate. Pd and Ir are precipitated together with platinum; however, the valence of these elements needs to be lowered. Reduction of Pd and Ir can be carried out using various reducing agents. Most commonly the solution is heated, evaporated and then sulfuric acid, oxalic acid or alcohol are added. At a temperature of 140°C , after the addition of H_2SO_4 for pH adjustment, the reaction occurs in accordance with the following equation:

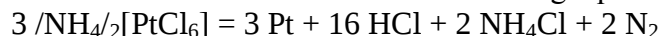




After reduction of palladium and iridium, platinum is precipitated by ammonia chloride in accordance with the following reaction:



The precipitate of ammonium hexachloroplatinate is filtered, washed by HCl in order to remove ammonium chloride, dried and annealed at a temperature of 600 °C and then at temperature of 1100 – 1200°C, it is dissociated in accordance with the following equation:



The produced platinum sponge is melted in an induction furnace. The yielded platinum is referred to as the first grade platinum and it contains 99.8 % Pt, up to 0.1 % Ir and other metals. Chemically pure platinum is obtained by repeated dissolution and precipitation. Other metals in this group can be prepared by a whole range of other complex processes.

2.3.3 Application of platinum metals

Pure platinum has whole range of applications in the production of resistance thermocouples, as well as in the field of electro technics as contact materials. This field utilizes the fact that this metal is not covered by a thin layer of oxides, which ensures low resistance of the contact. Platinum can also be used in chemical industry, including high-pressure applications, thanks to its excellent corrosion resistance.

Palladium is often used as a substitution of platinum due to its lower price and lower density. This metal can also be used as contact material. Other application options include catalyzer. It can also be used as hydrogen absorber.

Rhodium can be used in the field of coating of other metal materials thanks to its high gloss.

Iridium application consists of platinum alloying to increase the strength characteristics. In addition, it is used in chemical industry as the material for crucibles for high temperatures.

Osmium is used almost exclusively to prepare alloys (with approximately 80% content of Os and further containing Ru and other metals of this group) with high hardness.

Ruthenium is used as the alloying element to palladium and platinum to increase their mechanical properties. At the same time, this metal may be used as catalyzer.

2.3.4 Alloys

2.3.4.1 Pt alloys

Thermocouple:

0-1500°C – Pt-Pt90Rh10

1400-1700°C – Pt70Rh30-Pt94Rh6

Resistance:

Pt + 10-20%Rh

Pt + 40%Rh – temperatures 1550 – 1800°C

For production of contacts:

The surface is not coated by a layer of oxides, they are used for small current loads; for higher loads Pt + Ir (10-25%) are used.

Production of glass fibres or artificial fibres:

(jets Pt+10Rh)

Jewellery:

Pure Pt

Pt + 5%Ir, Pt + 4.5%Pd

2.3.4.2 Pd alloys

For production of contacts:

Pd + 10-30% Ag

Pd + 40% Cu

Pd + 4.5% Ru

Pd + Ni, Co - exceptionally

Solders

These alloys contain a relatively low content of Pd, yet they significantly affect the solder properties – the solders are referred to as palladium solders. Alloys with Ag, Cu, sometimes Ni and Mn.

At the end of each chapter you will find a list of literature used to prepare this study material. The list of publications may also include literature for further individual study.



Summary of terms in this chapter (subchapter)

- Cyanide process
- Amalgamation
- Affination
- Parkerizing



Questions to the covered material

- Briefly describe the production technology of gold by the cyanide process.
- Why is the so-called protective base used in the cyanide process?
- What other gold production technologies can you name?
- Describe the technology of silver production as a by-product of the production of heavy non-ferrous metals.
- Name the basic Ag alloys.
- Briefly describe the technology of platinum preparation.

3. Refractory metals



Time to study: 10 hours



Aim After studying this section the student should be able to:

- Characterize the technologies of refractory metal preparation.
- Select suitable material for application in technological practice.



3.1 Tungsten

3.1.1 Tungsten properties

Tungsten has the highest melting temperature of all metals – 3422 °C; at the same time it has the lowest pressure of vapours. The boiling temperature of tungsten is also very high – 5660 °C. This metal is highly resistant to corrosion and offers high strength properties. The density of tungsten is 19.1 g.cm⁻³, and it crystallizes in the KSC lattice. The thermal conductivity of this metal is approximately half the thermal conductivity of Cu but is higher than conductivity of Ni or Fe

Powder tungsten is grey, metallic tungsten is white and glossy. It oxidizes when heated. It is acid-stable. The compact metal reacts with aqua regia and nitric acid only on the surface; it slowly dissolves in the HNO₃ + HF compound. It is also affected by molten salts and other alkaline melts.

3.1.2 Tungsten compounds

Tungsten creates a whole range of compounds. The most important compounds include tungstates, tungstic acid and tungsten trioxide.

Tungsten trioxide WO₃

Yellow tungsten trioxide is produced during oxidation of the metal of tungsten compounds by air oxygen. This oxide has a melting temperature of 1473 °C and evaporates at 1750 °C. It is insoluble in water; it dissolves in alkaline hydrate oxides while creating tungstates and tungstic acid salts. This oxide can be prepared from acid by annealing; however, it cannot be transformed to acid by water.

Tungstic acid H₂WO₄

It is released from hot tungstate solutions after strong acids are added. It has a yellow color and is insoluble in most acids and in water.

Sodium tungstate Na₂WO₄

This compound is created by melting tungsten compounds contained in ores together with sodium. This compound plays an important role in the preparation of tungsten compounds and of metallic tungsten. It dissolves well in water.

3.1.3 Tungsten production technology

This metal does not occur in nature in pure form. It usually occurs in the form of oxide bound to Fe, Mn and Ca oxides, less frequently to Pb and Cu oxides. There are about 15 tungsten minerals; however, the most important minerals for industry are wolframite and scheelite.

Wolframite (Fe, Mn)WO₄ is an isomorphic compound of Fe and Mn tungstates. Individual pure minerals, i.e. ferberite and hübnerite, occur only scarcely. Its density is 7.1 – 7.9 g.cm⁻³ and it is weakly magnetic.

Scheelite CaWO₄ has a density of 5.9 – 6.1 g.cm⁻³, and is not magnetic.

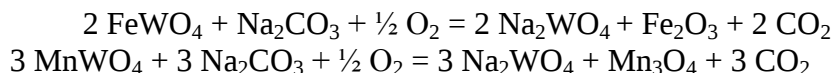
Tungsten ores are usually poor and contain no more than 0.5 – 2 % of WO_3 . That is why these ores need to be processed. The processing of tungsten ores includes gravitation, floatation, electromagnetic and electrostatic methods. These processing methods yield a concentrate containing 60 – 70 % of WO_3 . Mostly wolframite and scheelite concentrates are prepared.

Processing of tungsten concentrates consists of three stages: a) concentrate dissociation, b) obtaining technical tungstic acid, c) cleaning of the technical tungstic acid and obtaining clean products with the required physical properties. The industrial methods of tungsten concentrate dissociation can be divided into alkaline and acidic.

Wolframite concentrates are dissociated by caking with soda, leaching by NaOH aqueous solution or acid leaching. Scheelite concentrates are also caked with soda or leached in sodium aqueous solution. Another option is pressurized acid leaching. The following sections briefly describe two commonly used methods.

3.1.3.1 Caking with soda

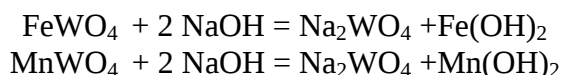
This is the most widespread method. The process takes place at a temperature of 800 – 900°C, whereas the wolframite reacts with soda in the presence of air in accordance with the following reactions:



Caking of wolframite with soda yields a product that contains sodium tungstate, ferric oxide, manganese oxide and other compounds. The dissociation yield usually ranges between 98 – 99.5 %. In practice, this process can be realized continually.

3.1.3.2 Dissociation of wolframite concentrate by solution of sodium hydroxide

This method is also used very frequently. It is based on the reaction of wolframite with concentrate solution of NaOH , while creating sodium tungstate. This process can be described by the following reaction:

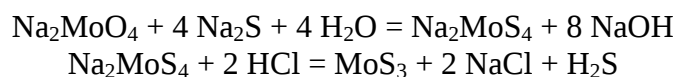


This method has a whole range of advantages in comparison with baking: it does not require furnace, as the reaction takes place at a low temperature. The disadvantage of this method consists in the requirement of fine grinding of the material.

3.1.3.3 Cleaning of sodium tungstate solutions

The solution of sodium tungstate is prepared by one of the described methods and it usually contains a certain amount of soluble salts, which could contaminate the tungstic acid obtained in the following operation. The solution needs to be cleaned of silicon, phosphorus, arsenic and molybdenum. Similar methods are used to clean the solution of sodium molybdate.

Removal of molybdenum is based on a reaction, during which molybdenum precipitates in the form of MoS_2 . This method is based on the difference of solubility of molybdenum sulfosalts and of tungsten, which are created during the passing of hydrogen sulfide, when alkaline sulfides are added to the solution containing tungstate and sodium molybdate. After the solution is acidified, sulfosalts are dissociated, while creating precipitates of molybdenum and tungsten sulfides. When slightly alkaline sulfide is continued to be added, only molybdenum sulfosalts are created and after acidification, molybdenum is precipitated in the form of MoS_2 . This method can be described by three reactions:



HCl acid is added to the solution (in the presence of congo red indicator), while the solution is being heated. This is followed by perfect precipitation of MoS₂, which brings about 1 – 2 % of tungsten to the precipitate.

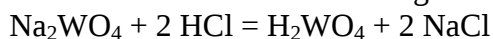
3.1.3.4 Obtaining of tungsten compounds

Cleaned solutions of sodium tungstate can be used to obtain tungsten compounds as described below.

1. Direct precipitation of technical tungstic acid.
2. Precipitation of calcium tungstate, which is further processed by acid to technical tungstic acid.
3. Crystallization of sodium tungstate or paratungstate.

Precipitation of technical tungstic acid.

The precipitation is preformed directly by processing the sodium tungstate solution using HCl, HNO₃ or H₂SO₄ in accordance with the following reaction:



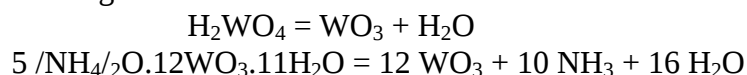
24 – 25 % of HCl with a small addition of HNO₃ (0.5 – 2 %) is used most frequently. Precipitation is carried out in a ceramic or steel vessel. HCl is heated to 80 °C and a heated solution sodium tungstate is then slowly added. The tungstic acid precipitate formed during this process is washed by water and then by hot water acidified by HCl. This is followed by filtration, centrifuge and drying. The process effectiveness is usually 98 – 99 %.

Cleaning of technical tungstic acid

The prepared technical H₂WO₄ contains approximately 3 % of admixtures. These include namely Na, Ca, Fe salts, H₂MoO₄ and other compounds. Cleaning of H₂WO₄ is usually performed using the ammoniac method. It dissolves well in ammonia, while creating a solution of ammonium tungstate and most of the admixtures remain in the precipitate. Precipitate is separated and tungsten is precipitated from the ammoniac solution in the form tungstic acid or ammonium paratungstate.

3.1.3.5 Preparation of tungsten oxide

Annealing of tungstic acid or ammonium paratungstate yields tungsten oxide in accordance with the following reaction:



The first reaction occurs at 500 °C, the second one above 250 °C. Tungsten oxide intended for preparation of metallic tungsten must have the given chemical composition and defined size of particles. In practice, these compounds are calcined in an electric muffle furnace at temperatures of 600 – 800 °C depending on the required particle size of the produced oxide. The vapor tension of tungsten oxide is significantly high already at temperatures over 800 °C, which leads to its losses.

3.1.3.6 Preparation of metallic tungsten

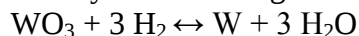
The production of a compact metal uses metallic powder as the basis. The powder is obtained by reduction of tungsten compounds, e.g. by hydrogen, at relatively low temperature of 800 – 1200 °C. The requirements on properties of the powder are highest if the powder is

intended for preparation of malleable tungsten. The production of tungsten carbides may use less pure powders.

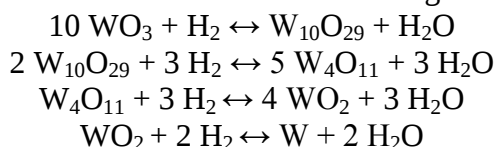
Tungsten compounds may be reduced by hydrogen, carbon, aluminium, silicon and sodium. The reduction of WO_3 by carbon and hydrogen has the highest practical importance. The purest metallic tungsten is prepared by reduction by hydrogen.

WO_3 reduction by hydrogen

This process may be described by the following summary equation:



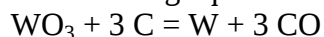
Research has shown that the reduction consists of several stages:



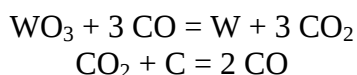
In practice, this process is performed in a tube furnace. Continual or discontinuous method may be used. The used hydrogen must be completely free of all admixtures, such as oxygen and carbon dioxide. The reduction consists of two stages; the first one occurs at 700 °C, while tungsten dioxide is produced. Tungsten dioxide is then reduced at a higher temperature. This process is suitable for obtaining powder with the desired granulometry. Sublimation of WO_3 begins at 850°C, W_4O_{11} at 900°C and WO_2 at 1050°C. Particles of metallic tungsten increase in size during the sublimation of oxides. Higher temperature leads to creation of coarser particles.

Reduction of WO_3 by carbon

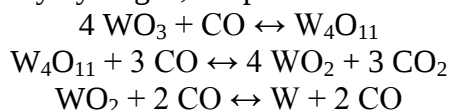
This process is used if both tungsten powder and tungsten carbide need to be produced. Tungsten carbides W_2C and WC are produced at a temperature exceeding 900 °C. The process can be represented by the following equation:



The reduction is not performed directly by carbon but using CO, which is produced by the Boudouard reaction:



Similarly as in WO_3 reduction by hydrogen, the process consists of several stages.



In practice, the reduction is performed by carbon materials, such as coke, soot with a small content of ash. Tube rotation or crucible furnace is used.

3.1.3.7 Preparation of compact tungsten

High melting temperature of this metal represents a certain difficulty for melting and casting. The basic preparation method for compact metal is powder metallurgy. This method consists of the following basic processes:

1. Powder pressing.
2. Caking of mouldings.
3. Mechanical processing.

The aim of pressing is to transform the shapeless powder to an object with a certain shape. Pressing may be performed in steel matrices. The mouldings are caked in two stages. The first stage, which occurs at a temperature of 1150 – 1300°C, is referred to as low-temperature caking. The second stage, with a temperature of 3000 °C, is called high-temperature caking. In this way it is possible to obtain metal with satisfactory porosity and structure, which is suitable especially for the following plastic deformation. Caking is usually carried out in a hydrogen atmosphere. The obtained semi-finished products may be hot-forged or hot-rolled.

3.1.4 Application of tungsten and tungsten alloys

The first significant application of this metal was the production light bulb fibres. Another important field of application consists of alloying of HSS (High Speed Steel). These alloying elements result in high hardness of the material and short-time resistance up to a temperature of approximately 600 °C. This hardness is caused by the presence of very hard carbide phases.

In addition, this metal may be used for production of thermocouples and heating resistors. Tungsten may be applied also in the preparation of alloys for contacts (10 – 40 % Cu, 20 – 40 % Ag). Tungsten is often contained in special fire-resistant and corrosion-resistant steels. Here it is combined with chromium, nickel and cobalt.

Another important application consists of the production of sintered carbides.

3.2 Molybdenum

3.2.1 Molybdenum properties

Compact molybdenum has a silver-grey color and is glossy. In powder form its color is darker grey. It is a relatively hard metal; it can be polished and at higher temperatures also forged. The melting temperature of molybdenum is 2610 °C, its density is 10.2 g.cm⁻³. It crystallizes in the KSC system.

Mechanical properties of this metal depend namely on the preceding thermal and mechanical processing. At a normal temperature, it is air-stable; when annealed, it is quickly covered by a layer of MoO₃. Its absorption of hydrogen is low and it releases hydrogen already at 300 °C. It forms carbides with carbon.

This metal practically does not react with diluted acids or with concentrated HCl. It does, however, react with concentrated HNO₃, hot H₂SO₄ and more strongly with aqua regia. Molybdenum is practically insoluble in alkaline hydroxides. It forms compounds on multiple oxidation levels. In addition to MoS₂, it occurs in hexavalent form in compounds that are important for the technological practice.

3.2.2 Compounds

Molybdenum forms a whole range of compounds. The most important compounds include oxides, molybdic acid, molybdates and sulfides.

Oxides

The most stable oxide is MoO₃, which is produced by molybdenum oxidation by air oxygen. It is a very fine white powder with a melting temperature of 791°C, which sublimates at temperatures right below the melting temperature. Annealed MoO₃ is soluble in water. It is dissolved in HF, in concentrated H₂SO₄, alkaline hydroxides and aqueous ammonium solution while creating molybdates.

Other oxides include MoO₂ and Mo₂O₅.

Molybdenic acid

After standing for a longer period of time, molybdenic solutions release molybdenic acid, a yellow crystalline precipitate with low solubility in water. Its chemical composition is $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$. When slightly heated, it is transformed to the water-free form of H_2MoO_4 .

Ammonium molybdate

Ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$ can be prepared by dissolution of MoO_3 in ammonia. Ammonium paramolybdate 3 $(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ crystallizes from ammonium solutions. It is air-stable and starts to dissociate at 151 °C. Reducing agents (SO_2 , H_2S , etc.) affect molybdenic acid or acidified molybdenum solution and create dark, intensive coloring of the solution – so-called molybdenum blue.

Sulfides

Molybdenum creates two sulfides. MoS_3 is released by the effect of H_2S on acidified molybdenum solutions. It creates a brownish precipitate, easily soluble e.g. in aqua regia. MoS_2 occurs in nature in the form of the mineral molybdenite. It can also be prepared artificially. In air it quickly reacts with oxygen, while producing MoO_3 .

3.2.3 Production technology of molybdenum

Molybdenum is not a very common element, its mean content in the Earth's crust is in orders of $1 \cdot 10^{-3} \%$. There is a large number of minerals, the most important of which are molybdenite, povelite, molybdate and wulfenite.

Molybdenite MoS_2 - the most important mineral, most widespread in the industrial scale. This mineral is used to prepare the largest amount of molybdenum. It is a soft mineral with metallic gloss and a density of $4.7 - 4.8 \text{ g.cm}^{-3}$. It occurs for instance in silica dikes together with scheelite, wolframite, cassiterite, pyrite, etc. Molybdenite usually contains 4 – 200 g.t^{-1} of rhenium.

Povelite CaMoO_4 – secondary mineral created by oxidation of molybdenite. It is white to grey with a dark green shade. Its density is 4.45 – 4.52. It is isomorphic with scheelite, which is why it often contains tungsten.

Molybdenum ores are poor, which is why they need to be treated and concentrated before processing. This is done almost exclusively using the floatation method. Molybdenite is one of the easily floatable minerals.

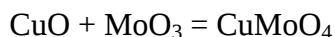
Molybdenite concentrates constitute the basic raw material for production of ferromolybdenum and compounds that are used for the production of molybdenum oxide and sodium paramolybdate. Pure compounds are prepared either pyrometallurgically or hydrometallurgically – processing of the calcinated ore in solution of ammonia, soda, sodium hydroxide.

3.2.3.1 Oxidation roasting of molybdenite concentrate

Further processing of concentrates would not be possible without oxidation roasting. The aim of this processing is complete or partial removal of sulfur and transformation of sulfides to oxides. The basic reaction may be represented as follows:



Molybdenite is oxidized by air at a temperature of 450 – 500°C. All sulfides of other accompanying elements are transformed to oxides or sulfates. Certain sulfates, such iron sulfate, are again dissociated to oxides at increased temperature. The produced molybdenum oxide then reacts with oxides of accompanying elements, while producing molybdates. We may use the following example:



Roasting is performed usually in level furnaces, rotary retort furnaces or in swirl layer.

3.2.3.2 Preparation of pure molybdenum oxide

This compound represents the basic raw material for the production of metallic molybdenum. It is obtained from the calcinated ore after oxidizing roasting by distilling off of MoO_3 or using the hydrometallurgic method, which first yields ammonium paramolybdate (potassium molybdate, sodium molybdate).

Distillation process

Heating of MoO_3 to a temperature exceeding 600°C increases its vapor tension and it is intensively evaporated at a temperature of 795°C . The temperature used in the industry ranges between $900 - 1000^\circ\text{C}$ and the evaporation speed may be further controlled by using vacuum. Admixtures, with the exception of lead molybdate, do not distill at the given temperature. In the presence of lead molybdate distillation is performed at a temperature below 1000°C . The obtained molybdenum oxide is highly dispersive; its purity is 99.95 %. The equipment scheme is shown in Fig. 3.1.

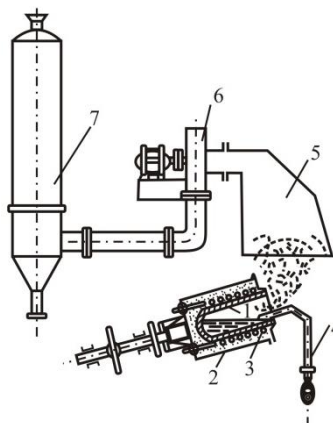
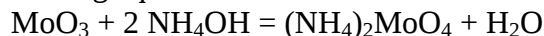


Fig. 3.1 Apparatus for distillation of MoO_3 .
1 – silica crucible, 2 – device casing, 3 – heating (electric), 4 – compressed air inlet, 5 – cover, 6 – fan, 7 – filter.

Hydrometallurgic processes of obtaining molybdenum oxide

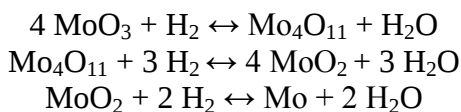
The most widespread method is the ammonium process. The calcinated ore is leached in ammonia, whereas molybdenum enters the solution in the form ammonium molybdate. The obtained solution is cleaned of admixtures and molybdenum precipitates from it in the form of ammonium paramolybdate or molybdic acid. The transition of molybdenum to the solution can be expressed by the following equation:



Solutions obtained by leaching of the calcinated ore in ammonium solution contain Cu, Fe and other admixtures. Solutions need to be purified in order to prepare pure Mo compounds. The solution free of Cu and Fe is used to produce pure Mo compound in two ways – neutralization or evaporation. Neutralization using HCl acid yields a precipitate. This precipitate is washed by water and dried at 100°C . It is then annealed at $400 - 450^\circ\text{C}$. This produces MoO_3 with purity of 99.9 %.

3.2.3.3 Production of metallic molybdenum

Pure molybdenum compounds may be reduced using C, Na, K, Al, etc. All these methods cause contamination of the produced molybdenum. The purest molybdenum is produced by reduction of MoO₃ by hydrogen. The process consists of three stages and can be represented as follows:



The reduction is performed in a horizontal furnace made of fire-proof steel, with a nickel boat filled with molybdenum oxide (alternatively by ammonium paramolybdate). The boat moves in the opposite direction of the supplied hydrogen. The hydrogen excess is three times the stoichiometric amount. The reduced molybdenum powder should be pure and at the same time it should have uniform granulometry.

3.2.3.4 Production of compact molybdenum

High melting temperature of molybdenum represents an obstacle during melting and casting of this iron. There are two technologies for the preparation of malleable material – powder metallurgy and melting and casting.

Powder metallurgy

This method is based on the following processes: a) pressing of molybdenum powder, b) baking of mouldings, c) mechanical processing. The powder density of the input molybdenum powder is 2.2 – 2.8 g.cm⁻³, the used pressure is 300 MPa. Mouldings prepared by this method have a porosity of about 40 %. The material volume is reduced 3 – 4x.

Pressed Mo briquettes are sintered in two phases. The first stage, which occurs at a temperature of 1200 °C, is referred to as low-temperature caking. The second stage, referred to as high-temperature caking, occurs at temperatures of 2200 – 2400°C. This method yields metal with minimum porosity. Molybdenum briquettes are brittle and break down during cold deformation. However, after heating, the mouldings may be rolled or forged.

Melting and casting

This technology is performed in an electric arc furnace. Copper, water-cooled ladle is used as the fire-proof material.

3.2.4 Application of molybdenum and molybdenum alloys

Molybdenum in form of a wire or sheet may be used as a heating element in laboratory and industrial furnaces. In this case, the operating temperature may be increased up to 1700°C. Mo may be used to prepare tools for processing and hot-working of metals.

Other possible applications include production of special steels, namely for fire arms, armour plates, etc. A small addition of molybdenum increases the strength and toughness of steel. It is used together with vanadium, chromium, nickel and cobalt for production of high-speed steels. Furthermore, it may be used for preparation of magnetic steels and alloys resistant to corrosion in acidic environment. In these fields it is used mostly in the form of ferromolybdenum.

An important field of application that needs to be mentioned is the chemical industry, where molybdenum is used due to its high corrosion resistance for the production of armatures, mixers, etc.

3.3 Titanium

3.3.1 Titanium properties

Titanium belongs to the group of refractory metals. The most important characteristics of this metal include its low density, very good strength properties, relatively easy workability and excellent corrosion resistance. It constitutes a very good alloying element; most metals form solid solutions with titanium. It has a melting temperature of 1670°C , density of $4.54\text{ g}\cdot\text{cm}^{-3}$. Titanium is a polymorphic metal. In a temperature range of $25 - 882^{\circ}\text{C}$, it has the HTU structure; above a temperature of 882°C , it has the KSC structure.

In compact state it resembles steel. It is air-stable at low temperatures. At increased temperatures it reacts with oxygen. Its solubility in acids is worse than that of iron. In HCl it dissolves only after heating; hot HNO_3 also attacks this metal. Titanium dissolves best in HF. The addition of interstitial impurities (oxygen, carbon, nitrogen) significantly increases its hardness and reduces ductility, see Fig. 3.2.

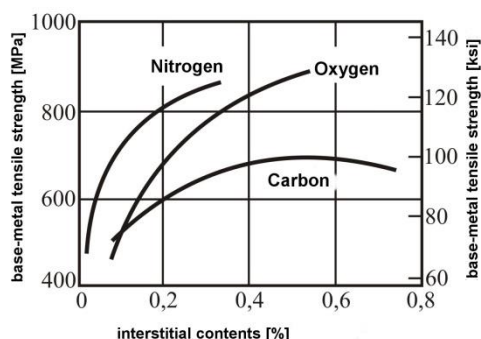


Fig. 3.2 Influence on N, C, O on mechanical properties of titanium

3.3.2 Compounds

Titanium in compounds occurs mostly in the tetravalent form. The most important alloys include oxides, sulfates, compounds with halides, carbides and nitrides.

Oxides

Titanium dioxide – TiO_2 occurs in nature as the mineral rutile. TiO_2 begins to melt at 1800°C , at higher temperatures it transforms to Ti_2O_3 . TiO_2 dissolves slowly only in hot H_2SO_4 . This oxide may be obtained by heating a mixture of titanium of titanium dioxide.

Halide compounds

Titanium tetrachloride – TiCl_4 may be prepared by the reaction of chlorine with heated titanium, TiC , alloy of $\text{Ti} - \text{Al}$ or a mixture of titanium dioxide with coal (coke). Its melting temperature is 136.5°C , and it solidifies at -23°C . It is an important compound used in the preparation process of metallic titanium.

Titanium tetraiodide – TiI_4 may be prepared by reaction of TiCl_4 with HI . It has a melting temperature of 150°C and a boiling temperature of 365°C . This compound plays an important role in titanium refining.

Titanium sulfates

Evaporation of titanic acid or reaction of titanium dioxide with concentrated sulfuric acid produces titanium(IV) oxysulfate TiOSO_4 . It is a white powder soluble in water.

Titanium carbide

TiC is prepared by heating of fine titanium powder with soot in hydrogen atmosphere at a temperature of 2000 °C. It is more resistant to acids than titanium. It is also an extremely hard material. Its melting temperature is 3450 °C.

3.3.3 Production technology of titanium

In nature titanium occurs mostly in the form of TiO₂. The mean content of this element in the Earth's crust is 0.61 %. There are about 70 titanium minerals containing TiO₂ or different titanium salts. The main mineral is **rutile** – TiO₂.

Another important mineral is **ilmenite** – FeTiO₃. It is often found at large sites in the form of ores that do not need to be concentrated, together with hematite or magnetite.

The processing of titanium ores includes gravitation, floatation, electromagnetic and electrostatic methods.

The processing of titanium concentrates yields titanium dioxide, titanium tetrachloride and ferrotitanium. The basic material for the production of titanium is an ilmenite concentrate. This concentrate may be processed using four methods:

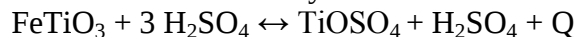
1. **Concentrated H₂SO₄.**
2. Reduction of oxides of iron in ilmenite.
3. Melting with sodium sulfate and coal.
4. Chlorination

3.3.3.1 Processing of concentrates to titanium dioxide

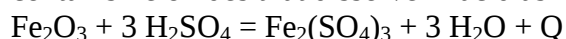
Digestion with sulfuric acid

This process consists of four stages: a) digestion of the concentrate with acid, b) cleaning of the solution, c) precipitation of titanium by hydrolysis, d) annealing of obtained metatitanic acid and creation of TiO₂.

The digestion of ilmenite concentrate may be described in the following way:



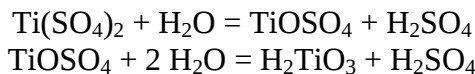
Ilmenite concentrate also contains Fe oxides that dissolve in acid as follows:



The concentrate digestion may be performed in a solid, semi-liquid or liquid state. Digestion in solid state is most common. The concentrate is digested in a steel tank with conic bottom, with supply of air and water vapor, as well as with mixing and heating equipment. The walls are covered by acid-resisting lining.

Sulfuric acid is diluted to 90 %, which releases sufficient amount of heat to increase the solution temperature to 160 – 170°C. After cooling, the solution is heated by water vapor to a temperature of 120 °C and the digestion occurs after 5 – 10 minutes. Then water is added and titanium enters the solution. This is followed by cleaning of the solution of iron.

Trivalent iron poses the largest problems. Trivalent iron is removed by its reduction to bivalent form and crystallization of the obtained iron(II) sulfate FeSO₄·7H₂O at 0°C. The solution volume after removal of iron(II) sulfate is reduced for approximately 20 %. Titanium is then precipitated from the solution. Hydrolysis of titanium dioxide occurs in accordance with the following reaction:



Finally, the precipitation yields metatitanic acid, which is further used for the production of titanium dioxide.

This process may be realized by hydrolysis with the addition of crystallization nuclei. During this process, pre-prepared crystals of metatitanic acid are added to the solution, pH is modified and further crystals of metatitanic acid begin to form. The solution is left to boil, which transfers 96 % of TiO_2 to the precipitate.

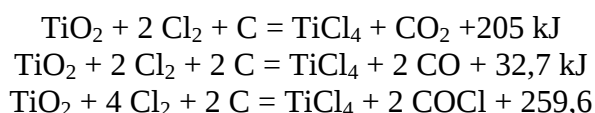
The produced precipitate contains TiO_2 , SO_3 and water. It releases water during annealing at a temperature of 200 – 300°C, and SO_3 at a temperature of 500 – 800°C. After this, polymorphous modification of TiO_2 – anatase appears and is then transformed to rutile at a temperature of 910°C. The created TiO_2 is cooled and ground.

3.3.3.2 Production of titanium tetrachloride

Chlorination of titanium dioxide, titanium cuts and other titanium raw materials may be done using various techniques. The chlorination process is following:



This reaction occurs slowly at a temperature of 800 – 1000°C. When chlorinating a mixture of TiO_2 and coal (coke), the reaction begins already at 400°C and has a sufficient speed at 600 – 800°C to be used in operating conditions. In such case, chlorination may be represented as follows:



It has been discovered that up to a temperature of 600 °C, namely the first reaction occurs. Chlorination of chips is much faster than chlorination of rutile. Chlorination may be performed by various methods.

3.3.3.3 Production of metallic titanium

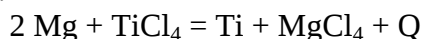
Complications connected with the production of metallic titanium are caused by its high reactivity and chemical stability of its compounds. Titanium reacts with carbon, nitrogen, oxygen and whole range of other elements. Metallic titanium can be obtained by reduction oxides and namely of titanium tetrachloride using alkaline metals. During reduction, the metal is obtained in the form of powder or sponge with varying purity. It is further processed into a compact form using powder metallurgy or melting processes.

The most important preparation method of metallic titanium include:

1. **Reduction of titanium tetrachloride by magnesium (sodium).**
2. Reduction of titanium dioxide by calcium or calcium hydride.
3. Electrolysis.
4. Thermal dissociation of iodide.

Reduction of titanium tetrachloride by magnesium

Titanium tetrachloride is the starting compound for the production of metallic titanium. It can be easily cleaned of admixtures using distillation or rectification. Reduction by magnesium is the most widespread method – it is called the Kroll process. The reaction may be represented as follows:



The reaction has a sufficient speed at 800 – 900°C; it is performed in a closed steel apparatus in an inert gas. Titan is created during the reduction on walls of the crucible and is slowly accumulated in the upwards direction and towards the centre of the vessel. This produced titanium is referred to as titanium sponge. Liquid magnesium chloride is gathered at the

bottom of the crucible and needs to be drained several times, in order to ensure continuous contact of magnesium with the supplied titanium tetrachloride.

After the process is finished, the titanium sponge is left to cool in a protective atmosphere. Such produced magnesium chloride may be used in electrolysis to obtain Cl.

The produced titanium sponge, however, is still not suitable for further processing. The performed reduction caused an entry of magnesium chloride and magnesium. These may be removed by two separation methods. Vacuum distillation, which occurs at 900 °C, or leaching by diluted hydrochloric acid or aqua regia, during which, however, the sponge is filled with hydrogen and oxygen, which is definitely not desirable.

Thermal dissociation of titanium tetraiodide

This method is used to prepare high-quality titanium. An important part of the process is the fact that Ti iodides are highly volatile and can be therefore used to refine titanium, provided that admixtures do not form volatile iodides. Volatile iodide is formed in a single place of the apparatus (at a temperature of 175 - 200°C), which is then thermally dissociated (at a temperature of 1300 – 1400°C) on a hot fibre. Possible input material includes for instance a Ti sponge produced by the Kroll process. The equipment scheme is shown in Fig. 3.3. The reaction may be represented as follows:

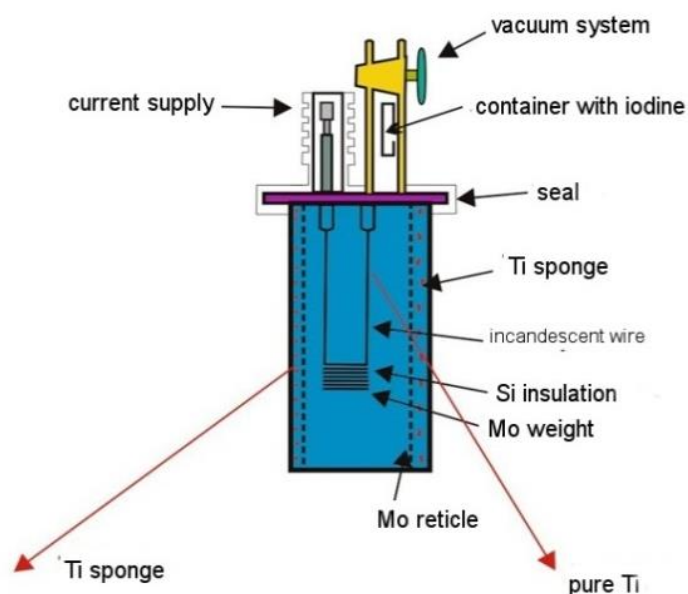


Fig. 3.3 Device for iodine refining of titanium

Production of compact titanium

Melting of titanium poses a certain challenge. It is necessary to prevent reactions with common gases, and to ensure suitable material of the furnace (vessel), in which it will be melted. Many materials have been tested and it has been shown that the most suitable material is graphite, namely thanks to its price. However, even graphite dissolves in titanium and thus increases its strength and reduces its ductility.

At present, titanium is usually melted from an electric arc furnace to a copper, water-cooled mould. Titanium recycling and production of castings is done in an induction furnace with a graphite crucible.

3.3.4 Application and alloys

Thanks to its low density and very good strength, titanium is applied (mostly in the form of compounds) in the demanding field of aircraft and spacecraft production. Due to its

very favourable chemical and corrosion properties, this metal may be used in chemistry, engineering or food industry. Furthermore, this metal is used in engineering for the production of turbine blades and equipment for contact with sea water.

In metallurgy it can be used as deoxidizing agent and as an alloying element of Mn, Cr and Cr – Mo steels. Last but not least, it is used to produce titanium white.

Titanium alloys can be divided into the following three groups:

- α alloys,
- $\alpha + \beta$ alloys,
- β alloys.

Titanium alloys are discussed in more detail in the Progressive Materials course, as they constitute a relatively extensive area. A rough overview of Ti alloys is shown in Fig. 3.4.

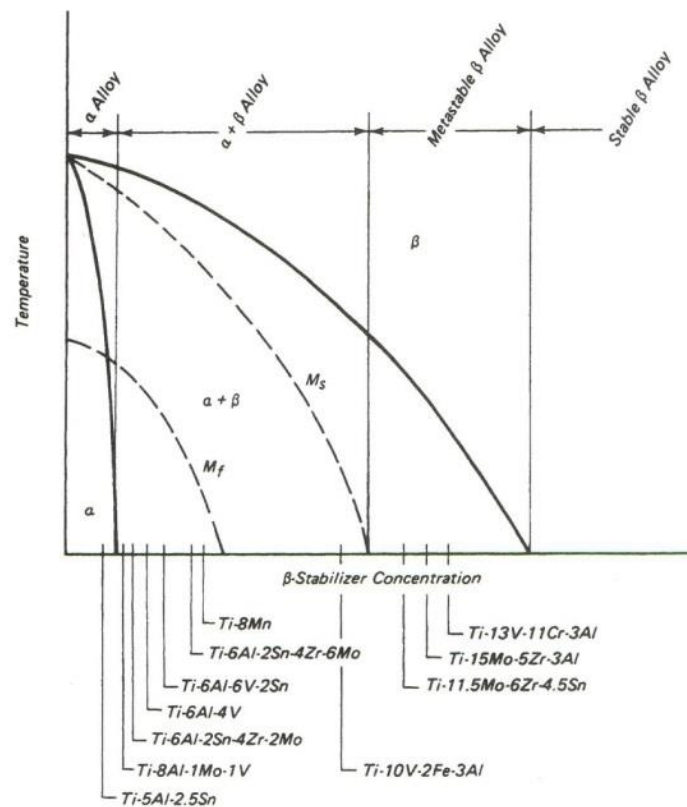


Fig. 3.4 Ti alloys overview.

3.4 Zirconium and zirconium alloys

Previously zirconium did not have any significant application; today this metal plays a crucial role for nuclear technology. Non-alloyed zirconium is used as gas absorber, deoxidizing agent and alloy for many other metals and alloys. The main application area of zirconium alloys is represented by coating materials.

3.4.1 Zirconium production

There are two main approaches to the preparation of zirconium:

- Reduction of zirconium tetrachloride (Kroll process) producing a metallic sponge,
- electrolysis of $K_2(ZrF_6)$ in an environment of halogen compounds of alkali metals, which create powder metal.

High-purity zirconium is required for its application in nuclear technology. This concerns namely very low contents of hafnium, which has a very negative impact on nuclear properties of zirconium due to its high absorption cross section for thermal neutrons. Since the

atomic structure of Zr and Hf is very similar, resulting in very similar properties of these elements, their perfect separation is technologically challenging.

The Earth's crust contains about 0.028% of zirconium, which is more than Ni, Cu, Pb or Zn. There exists a whole range of minerals, the most important of which are listed below.

Zircon ZrSiO_4 – most widespread mineral of yellowish color. It does not disintegrate in acids but it does during melting in alkaline compounds.

Baddeleyite – monoclinic form of ZrO_2 of yellowish-brown color, it disintegrates in compounds of sulphuric and hydrofluoric acids.

Most of zircon is mined from sea sands. It is accompanied by other minerals, such as rutile, ilmenite, monasite. The composition of zircon and baddeleyite concentrates is similar to monomineral materials. Zircon concentrate contains 65 % and baddeleyite concentrate over 90 % of $\text{ZrO}_2 + \text{HfO}_2$. The hafnium content reaches up to 0.8 – 2.5 % from the sum of Zr + Hf. Sea sands are usually processed using the gravitation method. The final cleaning is done by magnetic or electrostatic separation.

3.4.1.1 Processing methods of zircon concentrates

Zircon is one of the minerals that are difficult to disintegrate and that is why various pyro-methods are used for processing:

- melting with sodium hydroxide creating water-soluble sodium metazirconate.
- caking with oxides and carbonates of alkali metals.
- Chlorination of zircon and carbon compounds creating zirconium tetrachloride,
- melting with potassium fluoride or potassium fluorosilicate creating potassium fluorozirconate,

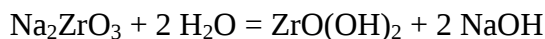
thermal disintegration of zircon.

Melting of zircon concentrate with NaOH

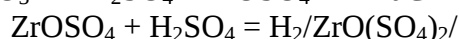
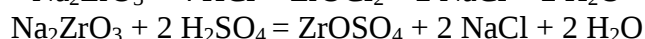
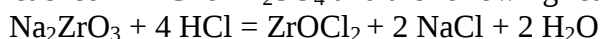
This universal process can be used to obtain not only metallic zirconium (hafnium) but also their compounds, including ZrO_2 . Leaching of sinter that consists of silicate and sodium zirconate yields zirconium (hafnium) solutions and these are separated by extraction. The following reaction occurs during caking:



The process begins at a temperature of 250 – 300°C and usually occurs at temperatures below 700°C. At least 130 % of the excessive agent is used. After the melt solidifies, it is leached in water in an iron vessel or it is leached simultaneously with grinding. During the solution process, sodium silicate enters the solution and zirconate is hydrolyzed:



As the solution alkalinity decreases, it is necessary to keep the content of NaOH at 3 – 5 % in order to prevent hydrolysis of Na_2SiO_3 connected with its transformation to a precipitate. The precipitate, which consists of 80 – 84 % ZrO_2 (other contained impurities include SiO_2 , Na_2O), is leached in HCl or H_2SO_4 and the following reactions occur:

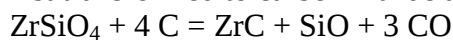


HCl is used for high-purity Zr compounds. Part of silicic acid is released during the solution, whereas the precipitation of voluminous silicic acid is sped up by a coagulant. After filtering, pure Zr compounds can be obtained from the filtrate. However, these compounds still contain

Hf. Hf is separated from Zr by a whole range of methods – most importantly extraction in organic liquids.

3.4.1.2 Production of zirconium tetrachloride

These processes are commonly used in the preparation of zirconium to prepare the input material, i.e. zirconium tetrachloride, for production of zirconium using the Kroll process. These methods are used to process the zircon concentrate, zirconium oxide; alternatively zircon might be first transformed to carbon nitride and then chlorinated.



3.4.1.3 Separation of hafnium from zirconium (dehafnization)

Hafnium as an admixture in zirconium is very undesirable in nuclear technology due to its high absorption cross section for thermal neutrons. That is why separation of hafnium from zirconium needs to be included in the preparation process of zirconium compounds for production of metallic zirconium. The separation is usually performed by a hydrometallurgical process. Despite the similarity of chemical behaviour of both metals, certain properties differ significantly and can be therefore used to separate these metals. Used methods include:

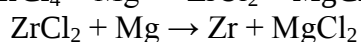
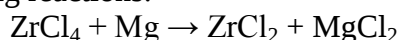
- fractional precipitation – this process is based on solubility of the same salts that are produced by adding a suitable agent to a solution with precious metal ions,
- fractional crystallization,
- ion exchange,
- extraction in organic solutions – this method has the widest application.

3.4.1.4 Production of metallic zirconium by metallothermic method

Metallic zirconium is produced predominantly by metallothermic reduction (see fig. 3.5) of Zr compounds – the most important is reduction of ZrCl_4 using Mg. Another method is electrolytic production from molten alkali halides and K_2ZrF_6 .

Reduction of ZrCl_4 by magnesium

This reaction constitutes the basis of the Kroll process. The reduction occurs in steps in accordance with the following reactions:



These reactions apply only if the input substances are in gaseous state. Mutual reaction of Mg with ZrCl_4 starts at 410 – 470°C; ZrCl_4 is reduced only to lower chlorides at temperatures below 650°C.

Reduction of ZrCl_4 by magnesium is a complex heterogeneous process consisting of several liquid and several solid phases, where the most important processes include wetting, evaporation, heat and matter exchange.

After the process is completed, the basic mass of the obtained metal consists of a porous block located at the bottom of the reactor and may have the following composition: Zr 58 wt. %, Mg 32 %, MgCl_2 10 %. The next step is vacuum distillation of Mg and MgCl_2 at a temperature of 1000°C. The last step consists of arc melting of the produced material.

The production technology of Zr using reduction of ZrCl_4 by magnesium consists of the following operations:

1. preparation of input substances,
2. reduction,

3. vacuum separation,
4. modification of the sponge block (grinding).

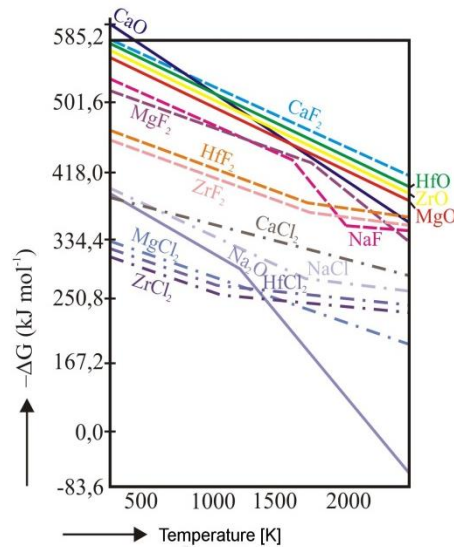


Fig. 3.5 Dependence of Gibbs free energy on temperature for selected chemicals.

3.4.2 Zirconium alloys

Zr alloying requires a complex approach, just like for other metals. For instance, if the goal of the alloying process is to increase the corrosion resistance, it is necessary to consider the mechanical properties of the concrete alloy, as well as its absorption cross section for thermal neutrons. The most important requirements placed on Zr alloys for nuclear reactors are:

1. The alloying elements must have a low absorption cross section for thermal neutrons.
2. The alloying element must ensure sufficient corrosion resistance of products intended for the reactor's active zone for the whole duration of their function.
3. The alloying element must ensure mechanical reliability of fuel elements in all possible operating modes of the reactor, including emergency situations.
4. The alloying element must not produce long-time radionuclides with strong α radiation, as this would extend the shutdown period during repairs and would increase the costs for processing irradiated fuel elements.

The main alloying elements used in Zircalloys is tin and even though it compensates the negative effect of nitrogen, it increases corrosion. No other group IV element besides tin can be used. Titanium has a highly negative effect on the corrosion behaviour, Hf has a high cross section for thermal neutrons, Pb is volatile and negatively affects the corrosion properties, Si and Ge have significantly different diameters and are practically insoluble in α Zr and in β Zr.

The only group V.A element that comes into question is Nb. Vanadium increases the corrosion of pure Zr even in small amounts and can only be used in polycomponent alloys for superheated vapour. Tantalum has a 100x higher absorption cross section for thermal neutrons.

Potential elements in group VI.A are Cr and Mo. These elements are suitable for alloys operating in superheated vapour at temperatures ranging from 400 – 500 °C.

The only interesting element in group VIII is Fe, since Ni significantly increases the hydrogenization of Zr during corrosion and Co has high absorption cross section for thermal

neutrons and a strong γ emitter ^{60}Co with long half-life is created in the reactor. The main alloys for iron are alloys for superheated vapour with a temperature of 400 – 500 °C. It is clear from what has been stated above that the only element from groups V, VI A and VIII suitable for alloying zirconium used in water and water vapour at a temperature range of 300 – 350 °C is Nb.

3.4.2.1 Zr – Sn alloys

In addition to niobium, Sn can also improve mechanical properties and corrosion resistance. Studies of Zr – Sn alloys arrived at the conclusion that Sn is highly soluble in α zirconium (max. 9 % at 980°C; at 300 – 350°C the solubility is negligible). Independently from these studies, corrosion tests proved that tin mitigates the effect of many harmful admixtures. All alloys were prepared from the same input material. It shows that up to a content of 0.5 %, tin slows down the corrosion process by eliminating harmful admixtures. The corrosion speed increases if the tin content exceeds 0.5 %. Reduction of the corrosion resistance of unalloyed Zr is caused by the presence of a very small amount of nitrogen (0.006 % N_2). Acceptable nitrogen contents in relation to the tin content in the alloy is shown in table 3.1.

Tab. 3.1 Permitted levels of nitrogen in the alloys Zr – Sn.

Sn content [hm. %]	max. nitrogen content [hm. %]
0,5	0,02
1,0	0,03
2,0	0,06
2,5	0,07
3,0	0,08

3.4.3 Corrosion of zirconium and its alloys

3.4.3.1 Water

Thanks to their properties, zirconium materials are suitable especially for water-cooled reactors. The coolant – water, vapour or their mixture – transfers water molecules to the oxide layer. These molecules are absorbed by the layer, whereas part of electrons is also absorbed while producing oxygen and hydrogen ions. Oxygen ions penetrate through the oxide layer and create ZrO_2 molecules in contact with metal. This increases the coating thickness. The created oxide layer consists of monoclinic ZrO_2 , it has sufficient density and adheres well to the metal surface.

The kinetics of zirconium and zirconium alloys oxidation is not governed by one specific law. The initial oxidation period is usually characterized by a parabolic dependence that expresses the inverse proportionality of the growth speed to its thickness. The parabolic dependence changes to cubic at the layer thickness of approximately 1 μm . If the layer is 2 – 3 μm thick, the growth kinetics of the oxide layer changes to linear dependence. Micropores of various diameters and longitudinal or transverse cracks are uncovered in the layer.

Until the break of growth speed the layer has good adhesion properties, black color and smooth, glossy surface. Its corrosion stability is also high. Oxide contained in the layer is substoichiometric, its formula is ZrO_{2-x} , where $x \leq 0.05$. At the break, when the layer thickness reaches 2 – 3 μm , the layer color turns grey and if the thickness increases to 50 – 60 μm , the color changes to white.. This layer is stochiometric and is a sign of corrosion failure. This type is referred to as "breakaway". Failure occurs even at lower thickness of the layer if tension or impurities are present. This phenomenon is represented in Fig. 3.6.

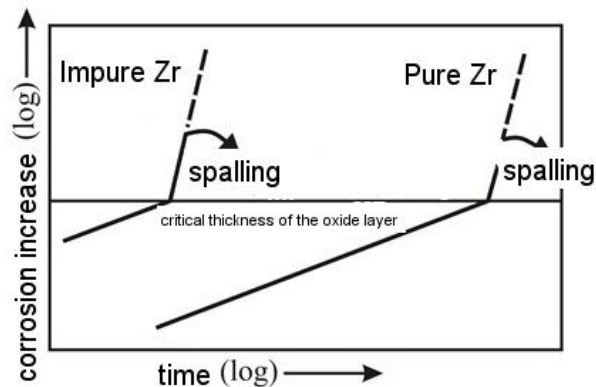


Fig. 3.6 Corrosion of pure and impure Zr, breakaway effect.

The oxidation of zirconium and its alloys is an exceptionally complex process due to the dependence of the kinetics and oxidation character on various factors:

1. chemical composition of zirconium alloy in terms of admixtures and alloying elements,
 2. structural composition of the alloy, which is given by a whole range of operations during the melting processing into a finished product (casting, forging, pressing – including thermal processing),
 3. quality of the product surface,
 4. coolant composition (water purity in terms of admixtures, oxygen and hydrogen content); coolant characteristics – input and output temperature of the coolant in the active zone, real temperature of the fuel element surface, boiling character, speed, flow,
 5. integral batch of fast neutrons at the given moment of corrosion, duration of the product's stay in the coolant at presence and absence of a neutron field,
- mechanical composition of the zirconium product – tension, cyclic stress, friction, shocks, contact with other materials (stainless steel).

3.5 Niobium

This metal has a whole range of interesting properties for use in high-temperature reactors. Its mechanical properties at higher temperatures are significantly better than for classic coating materials. It has a relatively good malleability. The melting temperature of niobium is high (2415°C) at relatively low density (8.57 g/cm³). The cross section for thermal neutrons is also satisfactory (1.15×10^{-28} m²). It has good corrosion resistance in molten metals (Na, Li, Hg, Sn, Zn, Bi) and it practically does not react with U and Pu.

Its disadvantages include poor resistance to oxidation at temperatures exceeding 200°C and heavy dependence of its malleability on the content of gaseous and non-metallic impurities.

3.5.1 Niobium production

This metal occurs in nature together with tantalum. Tantalum and niobium also share similar properties. The production technology of both these metals is identical, whereas the chemical compounds of both elements are separated during the last phase before production of metallic Nb. Perfect separation of these elements is necessary for use in nuclear technology due to the negative nuclear properties of Ta ($\sigma_a = 21.4 \times 10^{-28}$ m²).

Niobium is not a very common metal, its average content in the Earth's crust is approximately $1 \times 10^{-3} \%$. There are more than 130 minerals in total; however, only several of them are used in the industry. The most important minerals include: **Columbite and tantalite** – $(\text{Fe, Mn})(\text{Nb, Ta})_2\text{O}_6$, that represent an isomorphic compound of tantalate and iron niobate; **Loparite** – a compound of titanate and sodium niobate, calcium and REM $(\text{Na, Ca, Ce})_2(\text{Ti, Nb})_2\text{O}_6$. Ta and Nb ores are usually poor and contain 0.03 – 0.2 % of Me_2O_5 oxides; that is why they need to be concentrated. The basic used methods are gravitation methods.

3.5.1.1 Separation of niobium and tantalum

The similarity of these metals poses an obstacle for their separation. The original separation method used different solubility and crystallic structure of $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ and K_2TaF_7 . Potassium fluorotantale has lower solubility than the similar niobium compound and it can therefore be filtered from the solution after cooling. Solution containing K_2NbOF_5 evaporates and $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ is released from the solution. These crystals are cleaned by further crystallization. Other applicable methods include:

- use of ion exchangers,
- fractional distillation of Nb and Ta chlorides,
- extraction by liquids (cyclohexanone, MIBK, etc.).

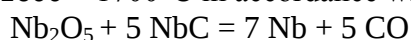
The process of liquid extraction found wide application in practice. This process is characterized by three stages:

1. extraction of niobium and tantalum in organic solvents and their separation from admixtures contained in the solution,
2. re-extraction of niobium from the organic solvent using water,
3. re-extraction of tantalum from the organic solvent by water solution of ammonium fluoride.

3.5.1.2 Production of metallic niobium

Metallic niobium is produced either by reduction of Nb_2O_5 by sodium or by niobium carbide. Due to high thermodynamic stability of Nb_2O_5 it can be reduced only by Na, other metals (Mg, Ca, Al) cannot be used. The disadvantage of this method consists in the difficulty of separating oxides and the reduced metal, which results in insufficient purity of the produced metal.

The carbidothermal process of niobium preparation is based on reduction of Nb_2O_5 using NbC at a temperature of 1600 – 1700°C in accordance with the following equation:



The process is performed in a graphite tube furnace in hydrogen or argon atmosphere. The advantage of this method is the use of cheap reduction material (soot) and the high achieved reduction degree.

Reduction of NbCl_5 chlorides is also possible. It is performed in a steel bomb using Na with an addition of CaCl_2 , which reduces the reaction speed and the amount of released heat. The electrolytic production method is applied particularly for tantalum but it can also be used for niobium. Electrolysis is performed from molten alkali fluorides or chlorides with admixture of K_2NbF_7 or K_2NbF_5 . These methods are used to prepare powder niobium and the following processes are used to achieve compact metal:

1. powder metallurgy,
2. arc melting in vacuum or inert atmosphere,,
3. electron melting.

3.5.2 Niobium processing

Powder niobium is processed similarly as Mo and W. The process is divided into the following two operations: powder pressing and caking. The pressing depends on the grain size and pressure ranges between 250 and 750 MPa. Caking is realized in vacuum (simultaneously with cleaning due to volatilization of certain admixtures). The caking temperature is 1400 – 1500°C and lasts for 2 hours. The final caking is done at 2300°C.

Niobium melting is performed in an electric arc furnace with a consumable electrode in a copper water-cooled crystallizer. The electrode is produced by caking powder niobium. Electron melting has a wide range of advantages: the metal can be overheated and maintained in melted state in high vacuum, the metal can be used in any form (powder, sponge, etc.), it is possible to prepare super alloys. The use of high vacuum also leads to evaporation of certain admixtures, which results in refining of the metal.

Niobium produced by powder metallurgy or electron melting in particular has good malleability. It can be easily processed with all chipless processing methods, such as pressing, drawing, rolling, etc. Cast niobium might contain inclusions. Common impurities, such as carbon or nitrogen, reduce the niobium workability and increase its hardness.

3.5.3 Mechanical properties of niobium

Mechanical properties of niobium are highly influenced by the content of impurities. It is strongly affected by elements that create interstitial solid solutions with niobium. These include namely carbon, oxygen and nitrogen that might cause brittleness even at normal temperature. The effect of oxygen is represented in Fig. 3.7. The deformation ability of niobium is very negatively affected already at 0.03 % of carbon, 0.3 % of oxygen and 0.1 % of nitrogen. Suitable alloying elements can be used to improve the mechanical properties of niobium. Systems relevant for nuclear technology are binary systems Nb – V, Nb – Zr, Nb – Mo, Nb – Ti and ternary systems Nb – Ti – Cr, Nb – Ti – Mo.

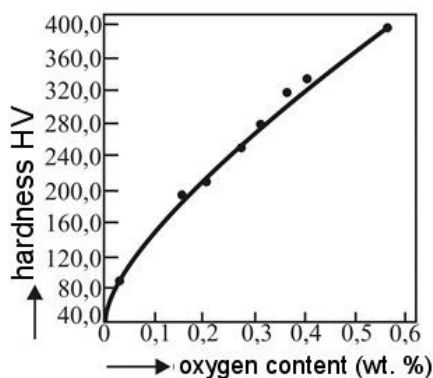


Fig. 3.7 Influence of oxygen on hardness of unalloyed Nb.

3.5.4 Niobium corrosion

In terms of corrosion, niobium is not very resistant in contact with air at higher temperatures. Starting at 200 °C, a thin layer of oxides is created on the surface and it is stable up to 400 °C. At a temperature exceeding 400 °C, the created Nb₂O₅ is porous and does not protect the metal against oxidation. In addition to oxidation, oxygen is also diffused in the metal, causing embrittlement of niobium. Niobium forms NbN and Nb₂N nitrides together with nitrogen. Absorption of nitrogen causes significant embrittlement of niobium already at 400 °C. Created nitrides are very stable and can be removed only by annealing in vacuum at

temperatures of 2000 °C. Hydrogen is also absorbed by niobium, which results in embrittlement.

However, it is possible to significantly improve the resistance to oxidation by adding V, Ti, Cr, Mo or W. Further improvement is also achieved by ternary systems. These alloys still need to be protected by silicide coatings for long-term use in oxidation environments at increased temperatures. Niobium alloys with zirconium or vanadium are suitable to water vapour environment, where mostly zirconium alloys with relatively low strength values are used. Ternary alloys Nb – Ti – Cr can also be used.

The behaviour of niobium in molten metals is very interesting. Especially important is the good corrosion resistance of niobium in liquid sodium or in the sodium – potassium system. However, the corrosion resistance is conditioned by low oxygen content (up to 5 ppm).

3.6 Vanadium

3.6.1 Properties of vanadium and vanadium alloys

Vanadium is a steel-grey, hard metal that can be ground and polished. Physical and namely mechanical properties are greatly affected by impurities constituting interstitial solid solutions. These include namely oxygen, nitrogen, hydrogen and carbon. These elements cause brittleness of vanadium. In order to ensure vanadium is malleable, the maximum content of oxygen and nitrogen combined must not exceed 0.2 wt. %. Carbon does not significantly affect the hardness up to a content of 0.25. Mechanical properties of vanadium may be modified by alloying. The disadvantage of most of the alloying elements is the fact that the resulting alloys are usually brittle. Malleable alloys are V – Ti and V – Zr.

Vanadium has a relatively low density of 6.1 g.cm^{-3} and a high melting temperature 1910°C. It has a KPC lattice. In compact state, vanadium does not react with air, water and alkaline hydroxides at a normal temperature. It is resistant to acids with oxidizing effects – with the exception of HF. It dissolves in aqua regia and HNO_3 . It easily creates basic and acidic radicals that can form the central atom in polyacid together with elements of groups IV V. VI. A VIII. of the period table. Its most important compounds include oxides, chloride, sulfates and sulfides.

3.6.2 Preparation technology of vanadium

The content of vanadium in the Earth's crust (0.2 %) is higher than the content of copper, zinc and lead. However, the disadvantage is that it rarely occurs in rich finding sites. Usually it is accompanied by other minerals and it often creates complex minerals, most importantly:

Roscoelite $\text{KV}_2/\text{AlSi}_3\text{O}_{10}/(\text{OH})_2$ – a mica containing approximately 32.4 % of V_2O_3 . It occurs in certain poor dikes, namely in the US.

Patronite V_2S_5 – contains 19 – 25 % of V_2O_5 , can be found namely in Peru.

Vanadite – $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ – contains 19.4 % of V_2O_5 , located in the oxidizing zone of lead-zinc ores.

Carnotite $\text{K}_2\text{O}.2\text{UO}_3.\text{V}_2\text{O}_5.3\text{H}_2\text{O}$ – contains 19.8 % of V_2O_5 . Largest sites of these minerals are located in the US.

Due to the fact that it accompanies iron ores in hundredths, it can also be produced from slag, to which it passes during the iron industry and metallurgic processes. Various production processes are used due to the different character of vanadium ores and materials.

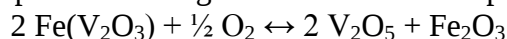
Alkaline methods

The methods for processing of ores or concentrates are based on their melting with NaCl or Na₂CO₃, during which vanadium is transformed to sodium vanadate, which is soluble in water. After leaching in water, it precipitates from the aqueous solution by slight acidification by H₂SO₄ in the form of V₂O₅ and with purity of 85 – 92 %. The rest are alkalis.

Acidic methods

This group of methods is based on leaching by H₂SO₄ and transferring vanadium to the solution in the form of sulfates. Vanadium is precipitated from the solution in the form of V₂O₅ by neutralization of the solution using alkalis or Fe vanadate using iron(II) oxide or FeSO₄.

Chloridation roasting in the presence of NaCl. Vanadium, which is present in the trivalent form in ores and slag from blast furnaces, is transformed to the pentavalent form during roasting. Roasting is performed on ground material at temperatures of 800 – 900°C.



In the next phase, V₂O₅ is transformed to sodium vandate, which dissolves in water at about 80°C. H₂SO₄ is added to the solution and the solution pH is maintained between 1 – 3. Sodium hexavandate, which can be used to prepare V₂O₅ after it is dried, is then released from the solution.

After carnotite ores are processed, acidic and alkaline leaching methods may be used. Acidic methods provide higher yield of vanadium; however, they may be used only if the content of carbonates in the ore is not too high. These methods also place higher requirements on the equipment due to the aggressive environment.

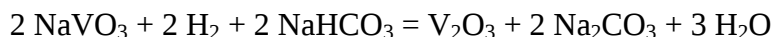
Processing of carnotite ores by carbonate leaching offers certain advantages:

- the solution is not so aggressive and the equipment may be made of a cheaper material,
- the method is especially suitable for ores with high content of CaCO₃,
- Na₂CO₃ are easily regenerated by bubbling through.

Its disadvantages include lower leaching speed and the fact that sulfide minerals react with carbonate and therefore increase its consumption. Acidic sodium carbonate is added to soda after the reaction to reduce the alkalinity of the solution.

Simultaneous leaching of vanadium and uranium complicates their selective separation from the solution. Nowadays, namely ion exchangers and extractions are used in organic solutions.

Another interesting method is leaching of vanadium in the solution in the form of V₂O₃ by hydrogen reduction.



The reduction is usually performed at a temperature of 150 °C and pressure of 1.4 MPA in the presence of Ni as a catalyzer. Nickel is separated from V₂O₃ by magnetic separation.

3.6.2.1 Production of metallic vanadium

One of the most used methods is the reduction of V₂O₅ using calcium. It is performed in accordance with the following reaction:



The reaction is strongly exothermic and is moderated by CaCl₂, which at the same time transforms CaO to liquid slag. The process itself is realized in a steel bomb in a magnetized

crucible. The prepared vanadium is melted by the released heat and creates semi-melted grains. The purity of the prepared metal is 99.9 %.

The purest vanadium may be prepared by thermal dissociation of VI_2 . The equipment and principles are similar as for Ti and Zr. The reaction temperature for creation of VI_2 is 900°C and the dissociation temperature is 1400°C .

Other preparation methods include reduction of VCl_3 by magnesium. The reduction is performed in a steel vertical retort (see fig 3.8). The equipment casing is cooled by water in the upper part. Input VCl_3 is added to the reactor from a reservoir located in the upper part. Magnesium is put to the retort and it is heated to a temperature of $750 - 800^\circ\text{C}$ in an argon atmosphere. Then, VCl_3 is supplied in such an amount so as to maintain constant reaction temperature. After the process is finished, the crucible is quickly put to the furnace, where vanadium is separated from other reaction products and is cooled at the same time. The obtained metal in the form of a sponge is malleable.

Vanadium obtained by one of the above described methods may be further processed by melting or by powder metallurgy. The selection of crucible material for processing of vanadium by melting poses a certain difficulty. Common materials cause contamination of vanadium and thus increase its hardness and reduce its malleability. It seems that the most suitable method is melting in vacuum or arc melting under the protective atmosphere in a copper, water-cooled mould. Powder vanadium is usually pressed at a pressure of $250 - 300$ MPa and sintered at temperatures of $1400 - 1510^\circ\text{C}$. This method yields malleable metal.

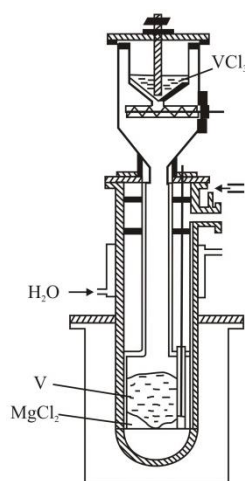


Fig 3.8 Scheme of equipment for the production of vanadium by reduction of VCl_3 by magnesium.

3.6.3 Vanadium alloys and applications

Vanadium is applied namely in the production of alloys and compounds. It plays an important role in steel production, where it is added in the form of ferrovanadium to construction, tool and fire-resistant steels. In construction steels it creates finer grains ($0.15 - 0.25$ %), in tool and high-speed steels it creates very hard carbide phases ($1 - 2.5$ %). Other important application areas include namely powder metallurgy and chemistry, where it is used as catalyzer in the form of V_2O_5 .

This metal can also be used in nuclear technology due to its favourable properties. Important properties of this metal include high melting temperature and good resistance in the environment of various molten metals. Other important properties include namely low sensitivity of mechanical and physical properties to radiation, good mechanical properties at

increased temperature and good thermal conductivity. The combination of these vanadium properties creates good conditions for its use as a coating material.



Summary of terms in this chapter (subchapter)

- Decomposition of concentrate
- Iodine refining
- Extraction



Questions to the covered material

- Specify means of decomposition W - concentrates.
- Describe the process of reduction of pure W and Mo oxides to elemental metals.
- Specify the possibility of preparing compact W, Mo.
- Describe the effect of interstitial impurities on the mechanical properties of titanium.
- Describe the Kroll method, explain the principle, indicate to what metals is applicable.
- Justify the need for cleaning of chlorides in the technology of preparing pure titanium.

4. Radioactive metals



Time to study: 10 hours



Aim After studying this section the student should be able to:

- Characterize the technologies of radioactive metals.
- Select suitable material for application in technological practice.



Lecture

4.1 Uranium

4.1.1 Metallic uranium

4.1.1.1 Occurrence and uranium ores

Uranium occurs in the Earth's crust in the total amount of approximately 2×10^{-4} wt. %. This corresponds approximately to the content of Sn and Pb and it is about 100x the content of Ag. Relatively large amount of uranium is also contained in sea water, approximately 1×10^{-7} wt. %. Uranium is geologically widespread. This is due to its chemical and physical properties, namely its valence, reactivity, solubility of many of its hexavalent compounds and relatively high frequency. These properties, however, also explain why the concentration of uranium in ores is so low. The largest part of uranium is located in sites with uranium concentration of approximately 0.01 wt. %.

Uranium is contained in more than 100 minerals, whereas only about 10 of them have any economic importance

4.1.1.2 Uranium production

Processing of uranium ores

Most of the locations of uranium provides only ores with low content of uranium that need to be enriched before they can be processed to metallic uranium. Uranium ores can be enriched by classic methods, such as separation by heavy liquids, gravitation or flotation. Minerals such as uraninite, carnotite and torbernite are enriched by gravitation or by heavy liquids. The flotation method is used for example for uranothorite.

Radiometric enrichment of uranium ores can be used as an example. This process can be realized on radiometric separators. This type of separator is schematically represented in Fig. 4.1.

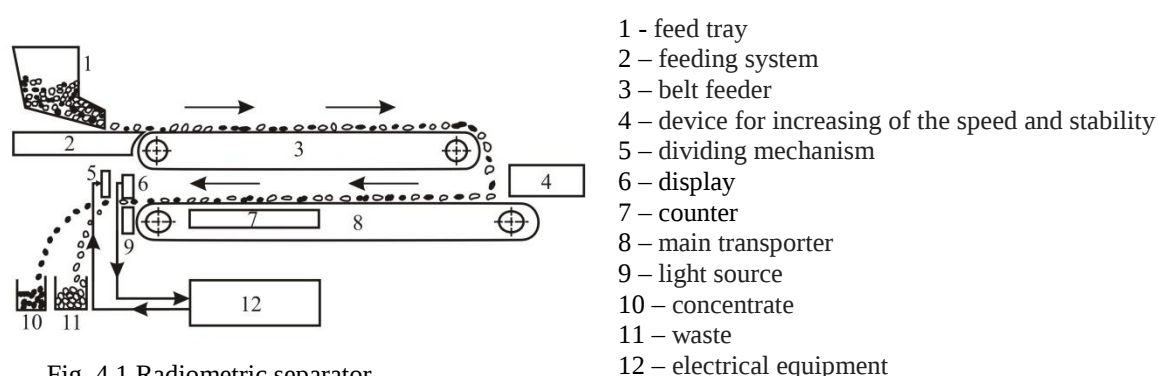


Fig. 4.1 Radiometric separator.

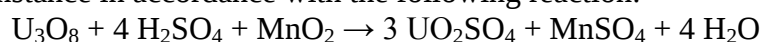
Leaching of uranium ores

The most common method of uranium ore processing consists of hydrometallurgical treatment using acid or carbonate leaching.

Acid leaching

Acid leaching of uranium ores is the most important method of converting the ores to a solution. It is used to process ores containing the following oxides: Th, Ti, Ta, Nb and REM. If the ore contains tetravalent uranium, the acid leaching is done using an oxidant (MnO_2 , HNO_3 , Fe^{3+} , VO^{2+} , etc.). Before the leaching itself, the ore is annealed in order to ensure dissolution of organic substances, oxidization of sulphides, dissolution of carbonates and removal of arsenic and sulphur. Salts are added to ores before leaching; uranium oxides and salts create uranates.

Such modified ore is then processed in acid, usually H_2SO_4 . Dissolution of uranium can be done for instance in accordance with the following reaction:



Uranium is obtained from this uranium solution, which also contains a whole range of additional metals (Fe, Mn, Ni, Al, Cu,...), by precipitation, sorption or extraction. Uranium precipitates from acid solutions in the form of hydroxides through neutralization of the solutions using bases, ammonia or calcium oxides or magnesium oxide. Sometimes uranium precipitates in the form of phosphate after the reduction of uranium to quadrivalent form using iron or aluminium.

Sorption methods consists of capturing uranium using the ionic exchange process. This process is based on differing ability of ions to undergo ionic exchange with ionic exchangers (artificial resin). Sorption by anion-exchange resins (anex), where complete uranium anion $[\text{UO}_2(\text{SO}_4)_3]^{4-}$ is absorbed, is also a common method. Extraction methods are

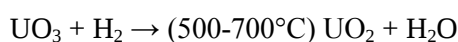
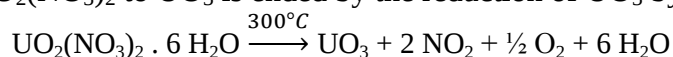
used to obtain uranium from low-concentration solutions. Extraction agents include TBF (tributyl phosphate), MIBK (methyl isobutyl ketone) and a whole range of other organic dissolvents. Optimum extraction environment for H₂SO₄ leaching includes phosphoric acid esters and alkylamines.

Preparation of uranium compounds

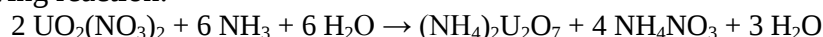
The most important starting materials for the uranium industry include UO₂, UF₄ and UF₆. Fluorides UF₄ and UF₆ are required for the production of metallic uranium and for isotope enrichment of natural uranium with isotope ²³⁵U.

Production of UO₂

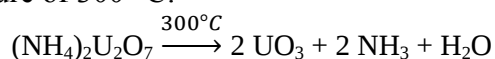
Uranium dioxide can be produced by thermal decay of UO₂(NO₃)₂ or (NH₄)₂U₂O₇. Thermal decay of UO₂(NO₃)₂ to UO₃ is ended by the reduction of UO₃ by hydrogen.



Precipitation of diuranate by ammonia takes places within the pH range of 7-8 in accordance with the following reaction:

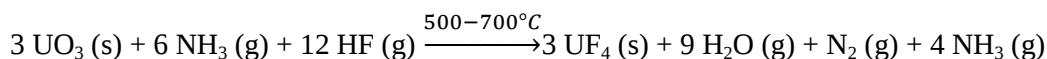
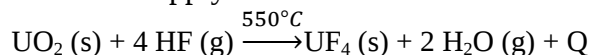


Decay occurs at a temperature of 300 °C:



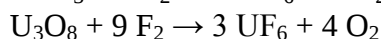
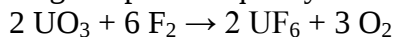
Production of UF₄

The following reactions can apply here:

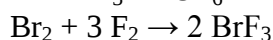
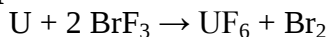


Production of UF₆

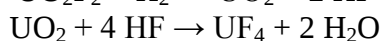
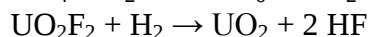
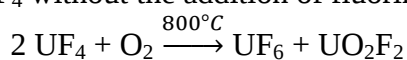
The main used process is fluorination of UF₄ by elementary fluorine, which consumes the least fluorine and ensures the highest product quality. Other options include:



Methods of direct fluorination of metallic uranium using ClF₃, BrF₃, BrF₅ have also been elaborated. The reaction can be represented as follows:



The production of UF₆ from UF₄ without the addition of fluorine is also interesting:



Enrichment of uranium

A whole range of processes have been developed for uranium enrichment. Some of these technologies are commonly used in practice (diffusion, centrifuge), others are in the stage of pilot operation, etc.

Gas diffusion

This process is based on different diffusion speeds of the isotope compound of UF_6 through porous membranes. Gaseous UF_6 is compressed by compressors and the concentration is slightly shifted towards the lighter isotope on the low-pressure side of the membrane due to a little higher diffusion speed of lighter uranium molecules. The scope of the separation effect can be theoretically determined using molecular ratios of isotopes ^{238}U and ^{235}U . The maximum theoretical value of the elementary separation coefficient is 1.0043. In practice its value is usually 1.004.

In theory the diffusion enrichment process can be described based on a different weight and consequently also different speed of the compound passing through the membrane. The following relations apply here.

$$E = \frac{M \cdot v^2}{2}$$
$$M_1 \cdot v_1^2 = M_2 \cdot v_2^2$$
$$\frac{v_1}{v_2} = \frac{M_2}{M_1} = \alpha \text{ (separační součinitel)}$$

The following relation applies for the enrichment of uranium isotopes in form of UF_6 :

$$\alpha = \sqrt{\frac{M_{^{238}\text{UF}_6}}{M_{^{235}\text{UF}_6}}} = 1,0043$$

Since the separation coefficient is so low, large volume flows need to be processed in order to ensure the economy of the process. Since only negligible enrichment is achieved in one separation step, it is necessary to repeat a large number of these diffusion processes, whereas UF_6 is compressed again by compressors in each separation step and the compression heat needs to be removed. The production of uranium enriched to 3 % ^{235}U , which is used in nuclear reactors, can be used as a typical examples – about 1000 – 1500 separation steps are needed in this process. The diffusion equipment includes a large number of separation elements of relatively large sizes connected in a series. Repeated compression of the operating gas and dissipation of the compression heat result in high energy demands reaching up to 2300 – 2500 kWh/kg JSP.

Gas centrifuges

Gaseous UF_6 is supplied to the operating area by a high-speed rotor. Centrifuge forces cause lighter isotopes to concentrate in the area around the spinning, while heavier isotopes are cumulated near the rotor wall and can be separated by fraction. This separation of isotopes is significantly supported by thermally induced counter current.

The size of the separation factor depends on the difference of molecular weight, the squared volume speed and the rotor length. It has been observed that separation factors 1.2 – 1.5 are usually achieved. Due to this relatively high separation factor it is necessary to repeat each separation step 10 – 15 times in order to achieve 3 % uranium enrichment by isotope ^{235}U . Since the mass flow volume of one centrifuge is relatively low, it is necessary to operate a large number of parallel-connected centrifuges in order to ensure an economic and efficient flow. Unlike diffusion cascades, centrifuge cascades are characterized by a small number of

stages but a large number of small, parallel-connected separation elements. The rotor location practically excludes all friction and the energy consumption is therefore several orders of magnitude lower than for diffusion equipment.

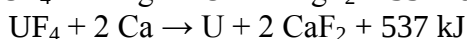
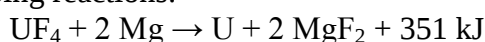
Dynamic gas processes

Separation of uranium isotopes is based on the dependence of the centrifugal force in a fast curved current on the weight. The separation effect ranges between the values achieved in centrifuges and in diffusions; the number of separation stages connected in a series also decreases proportionally. Similarly to the diffusion technology, the process gas (in this case a compound of $H_2 + UF_6$, in order to achieve a high flow speed) is compressed by compressors and the energy consumption is therefore quite high. Separation factors achieved in practice range between 1.015 – 1.025, energy consumption is approximately 3300 kWh/kg JSP.

Preparation of metallic uranium

Uranium in metal form is usually prepared through reduction of UF_4 or UO_2 using suitable reducing agents. Used reducing agents include mainly metals such as Ca, Li, Na, Ba, Mg. Currently the most significant metal for this purpose is magnesium. Metallic uranium is prepared from a melting of $NaCl + CaCl + KUF_5$ by electrolysis.

Reduction of UF_4 in a fine powder form is carried out in a steel bomb (reaction vessel) using high-purity Mg or Ca. Ongoing reactions:



When magnesium is used as the reducing agent, the reaction takes place in a reaction vessel with lining made of dolomite or burnt lime. Finely ground reaction components, which are ground to prevent oxidation before the reaction, are filled to the reaction vessel, sealed by a graphite lid and fire-proof lining. After closing the reaction vessel is put to a furnace at a temperature of approximately 600 °C. The reaction heat is not high enough to completely melt the magnesium structure (the melting temperature is 1263 °C). In order to completely melt the bomb contents it is necessary to supply thermal energy from the outside or through an exothermal reaction inside the reaction vessel:



$KClO_3$ is added in the amount of approximately 1/7 of UF_4 . The melting product consists of a yellowcake containing slag, as well as hydrogen. After the end of the process the reaction vessel is removed from the furnace and is opened only after cooling. The equipment scheme is shown in Fig. 4.2.

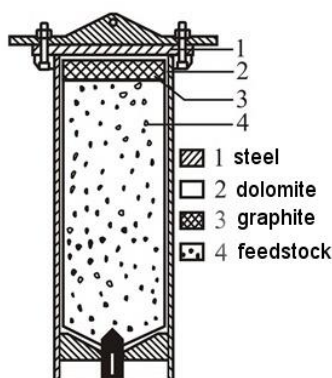


Fig. 4.2 Reaction vessel for reduction of UF_4 by Mg.

Due to the large amount of heat (released during the reaction) the content of the reaction vessel, which is lined with sintered CaF_2 and is equipped with additional electric heating, melts completely during reduction by calcium. The whole apparatus can be evacuated. After drying it is filled with the reaction mix, closed and put into the furnace. Once the reaction occurs, the molten uranium drains to a mould under the reaction vessel. After the reaction is completed, the reaction vessel is closed, evacuated and filled with argon. Smelted yellowcake contains slag residues – CaF_2 and oxides.

The disadvantage of reduction by magnesium when compared to reduction by calcium is the relatively low reaction heat; however, it also has certain advantages. This technique spread in North America. Reduction by magnesium has the following advantages: it is cheaper, less magnesium is required to prepare the same amount of UF_4 when compared with Ca (up to 40 % less), it has a higher purity and the melting temperature of MgF_2 is lower than the melting temperature of CaF_2 . Disadvantages of reduction by magnesium include the higher reaction temperature (higher than the evaporation temperature of Mg), which requires the reduction to be performed in closed vessels.

Uranium prepared using this technique needs to be remelted and refined from the slag, gas and other impurities.

Uranium melting and casting

Due to high reactivity of this metal with the atmosphere and a whole range of other materials (crucibles, etc.), the melting process is relatively demanding. The effect of atmosphere can be limited or almost eliminated by melting in vacuum, in the atmosphere of a suitable inert gas or using covering molten salts. Crucibles are selected based on the allowed amounts admixtures in the uranium.

Uranium dioxide and fluorite spar do not react with uranium up to a temperature of 1700 °C. However, these materials cannot be used for melting crucibles. CaF_2 is too soft at high temperatures, UO_2 has unsatisfactory thermal conductivity. Relatively good results have been achieved using BeO , ZrO_2 , ThO_2 and graphite. When graphite is used, uranium carbide is created, the reaction is slow approximately below 1600°C and the carbon that enters uranium in the amount of several hundreds ppm is not too harmful when the uranium is subsequently used in reactor technology.

Graphite represents a suitable material for the mould. Copper water-cooled moulds are also acceptable and their use enables reaching a more fine-grained structure. Moulds based on ceramic materials need to be heated to approximately 700 °C before casting to remove all humidity. The uranium casting temperature depends on the cast size and ranges between 1320 – 1340°C.

4.1.2 Physical and mechanical properties of uranium

Pure uranium has the form of a silver-white metal. However, it quickly oxidizes in contact with air, creating a golden-yellow film. As the oxidation process progresses, the color of this film is getting darker and the metal turns black after 3 – 4 days. The created oxidation layer does not protect the metal from further oxidation

Natural uranium contains three isotopes: ^{238}U (99.274 %), ^{235}U (0.720 %), ^{234}U (0.006 %). All three isotopes are alpha emitters with the following half-lives: ^{238}U (4.23×10^9 a), ^{235}U (8.5×10^8 a), ^{234}U (2.7×10^5 a). Such long half-lives result in relatively low radioactivity of uranium. However, it is still necessary to implement appropriate safety measures. Uranium occurs in three allotropic modifications. Some properties of uranium are shown in fig. 4.3, 4.4, 4.5.

4.1.3 Powder metallurgy of uranium

The most important techniques of powder metallurgy include cold pressing, hot pressing and extrusion pressing, additionally also HIP (Hot Isostatic Pressing) and CIP (Cold Isostatic Pressing). The following methods come into question for the production of powder uranium: Hydrogenation of uranium at 225°C (maximum reaction speed) and following decay of hydrides at 400°C and a pressure of 1×10^{-3} Pa, as well as reduction of UO_2 by calcium or magnesium, reduction of UCl_4 vapours using sodium or electrolysis of molten salts (UF_4 or KUF_5).

Cold pressing followed by sintering results in solidification of powder uranium and creation of the required shape. The pressing power depends on the size and shape of particles and on the moulding size. The moulding density ranges between $10\text{--}11.5 \text{ g.cm}^{-3}$ at the pressing power of 500 MPa. The sintering of uranium mouldings is best performed in vacuum, which ensures low partial pressures of oxygen and nitrogen. When compared to other materials, uranium sintering is more difficult - it starts only after approximately 85% of the melting temperature is reached.

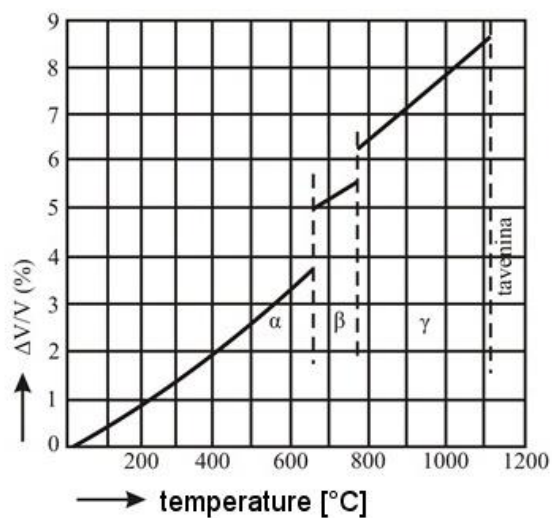


Fig. 4.3 The increase of volume of uranium

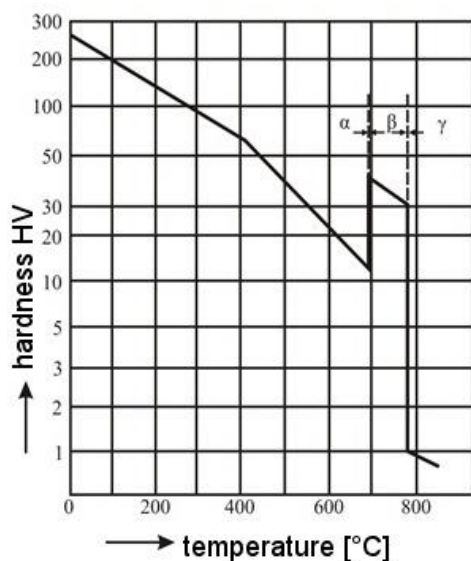


Fig. 4.4 Dependence of hardness on temperature

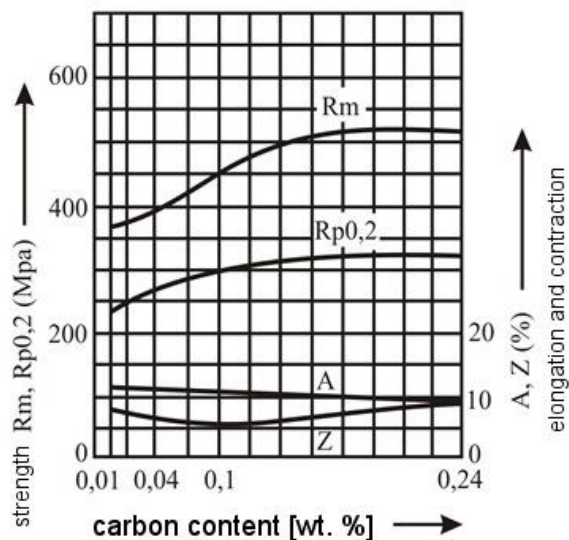


Fig. 4.5 The change of mechanical properties of uranium, depending on the carbon content.

Hot pressing can yield almost theoretical density of uranium. In order to sufficiently utilize the material plasticity, pressing is carried out in the upper section of thermal stability of the α phase. Again, protective atmospheres or vacuum are used for these processes.

4.1.4 Uranium alloys

4.1.4.1 Uranium alpha alloys

This type of alloys has been developed with the aim to decrease the volume growth – swelling. It is assumed that homogeneous dispersion solidification by fine particles can lead to the creation of additional centres for capturing fission gas products. These dispersion particles can be obtained by adding a small amount of elements with low solubility in alpha uranium, such as Si, Fe, Al. These alloys, possibly also Cr, are thermally processed by hardening from beta phase (temperatures of 720 – 730°C) into water or oil and annealing for several hours at upper temperatures of the alpha phase (500 – 600°C). This thermal processing leads to:

- finer grains and lower risk of striation,
- creation of a fine second phase precipitate,
- removal of the forming texture in the alpha phase.

The increased swelling resistance is contributed to the presence of a fine precipitate. Alloy elements dissolve completely (Fe-Si) or partially (Al) by heating up to the beta-uranium zone. Quenching creates an over-saturated solid solution, from which fine particles (UAl_2 , U_6Fe etc.) of a size of approximately $100 \times 10^{-10} m$ are released during the following tempering (500 – 600°C). Volume density of particles is approximately $10^{13} - 10^{15}$ in $1 cm^3$, which corresponds to the density of bubble nuclei of fissile gas in irradiated uranium. It is assumed that this fine precipitate has a beneficial effect on fine nucleation of bubbles or prevents their movement and accumulation by preventing the movement of dislocations and grain boundaries.

4.1.4.2 Uranium gamma alloys

Nb, Mo, Ti and Zr cause stabilization of the gamma phase uranium. Metastable gamma phase uranium created in U-Mo and U-Nb systems is the most passive phase for the transformation, which is why these alloys are only usable in the metastable state. They will be discussed in more details in the chapter dedicated to Ti and Zr.

Uranium gamma alloys are typically represented by the uranium alloy with 10 – 14 wt. % of Mo, whereas the weight content of Mo above 5 % already allows maintaining the metastable gamma phase uranium up to normal temperatures (assuming that the cooling speed of the alloy is not too slow). Isotropic gamma phase uranium is not subject to radiation growth and that is why there is no risk of striation or radiation creep. The main reason of size changes in these alloys is gas swelling. All uranium gamma alloys with solid gamma solution containing Mo, Nb, Ti and Zr usually undergo homogenizing annealing after their production. The annealing process lasts 24 hours and is done at a temperature of approximately 900 °C. Another group of γ uranium alloys consists of alloys obtained by regeneration of uranium irradiated in fast reactors. When this uranium is processed by melting under oxidation slag, volatile elements and REM are removed almost completely, whereas elements Mo, Ru, Rh, Pa, Nb, Te, i.e. the fission products, remain in the uranium and zirconium is separated only partially. Elements that remain in uranium are called "fissium" and uranium alloys with these elements are called uranium fissium alloys.

4.1.7 Uranium alloys – ceramic fuels

With the development of high-power energy reactors, ever increasing requirements are placed on fissile materials, such as high operating temperature, high irradiation, dimensional stability and the maximum possible safety. Uranium or its alloys were not able to meet these requirements. This is due to the fact that metallic uranium undergoes phase transformations at temperatures exceeding 600 °C leading to significant deterioration of its mechanical properties and volume changes caused by recrystallization. It is therefore clear that alloys can be used for fuel elements only at temperatures not exceeding 600 °C. This shortcoming can be removed using the following processes:

- thermal treatment and alloying,
- application of ceramic fuels.

Ceramic fuels have a whole range of advantages when compared to metal fuels, such as:

- significant thermal and radiation resistance,
- high melting temperatures,
- phase stability in a wide interval of temperatures (provided that suitable processing is used),
- weak dependence of the material strength on temperature,
- relatively small expansion,
- dimensional stability under the conditions of the required reactor output,
- higher irradiation depth of the fissile component in comparison with metallic uranium.

Disadvantages of ceramic fuels include mainly:

- high brittleness and low resistance to temperature shocks,
- necessity to use special coating materials that are significantly more expensive than Al or Mg alloys,
- lower thermal conductivity (especially at higher temperatures) in comparison with metallic uranium,
- hard formability of ceramics.

Production of uranium dioxide UO_2

In practice, uranium dioxide can be produced using three methods.

1. Thermal decay of uranyl nitrate followed by reduction by hydrogen, split ammonia or carbon monoxide:
2. Precipitation by ammonia from water solutions of uranyl nitrate while producing ammonium diuranate, which is thermally decayed. This process produces U_3O_8 which is then reduced to UO_2 as in the first example.
3. Precipitation by hydrogen peroxide from water solutions of uranyl nitrate while producing hydrated uranium peroxide, which is again thermally decayed and reduced to UO_2 .

Properties of uranium dioxide UO_2

The listed values characterize uranium dioxide as hard and brittle ceramic material. Elasticity constants decrease with increasing temperature, porosity and the O:U ratio. The bending strength decreases with increasing grain size and porosity. Increasing temperature causes an increase of the bending strength for fine porosity and small grains; for gross porosity and large grain size increasing temperature causes a decrease of the bending strength.

The transition temperature of malleable – brittle fracture is 1250°C for UO₂. Hardness increases with the O:U ratio.

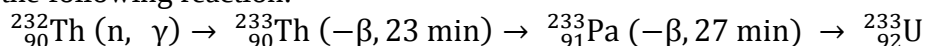
Mechanical properties of UO₂ therefore heavily depend on structural factors and these factors change depending on preparation methods and processing temperatures. Another important factor influencing the properties of UO₂ is the so-called oxygen index. It is the numerical deviation from the oxygen index that should equal 2. Precise designation of oxides is usually UO_{2+x}. Changes of the oxygen index influence the thermal conductivity of fuel, melting temperature of fuel, transition temperature of brittle - malleable fracture, swelling, creep, etc. During creep tests samples of sintered UO_{2,06} and UO_{2,16} deformed already at 800°C, whereas the corresponding temperature for UO₂ is 1600°C.

Preparation of compact UO₂

Uranium dioxide is used in two forms for fuel elements. The first form consists of compact bodies, tablets prepared by pressing and sintering or hot-pressing. The second used form is powder condensed by vibration or rotation forging. Pressing and sintering are the most elaborated preparation procedures of compact UO₂. Pressing is done at a pressure ranging from 4 – 7×10² MPa with the use of plasticizers and binding materials. The sintering process is carried out at temperatures ranging between 1600 – 1750°C for 1 – 4 hours. The process also includes pre-annealing at 600 – 800°C if binding agents are used. Pores are reduced during sintering through diffusion of vacancies along grain boundaries, whereas the speed of the process is determined by the concentration gradient of these vacancies. Sintering is also affected by UO₂ stoichiometry and is accelerated by even slight increase of oxygen in sulphur dioxide to the density of UO_{2,02}, whereas any further increase of the oxygen content does not significantly affect the sintering process. This effect is usually explained by the increase of the O²⁻ diffusion coefficient when compared to U self-diffusion. The sintering process is also affected by the atmosphere. High density UO₂ is obtained in hydrogen; worse results are achieved in N₂ and Ar. UO₂ with high density can be achieved in vacuum. The sintering method itself has been designed so that it can be applied even without sintering additives and yields high density values.

4.2 Thorium

Unlike uranium, thorium does not belong to fissile materials. However, during its irradiation by slow neutrons, nuclear reactions occur and lead to the creation of fissile isotope ²³³U with long half-life. Thorium is therefore referred to as a fertile material – isotope ²³³U is created by the following reaction:



Due to the fact that thorium reserves significantly exceed uranium reserves, it is reasonable to expect that thorium will be used much more in the future. However, a significant disadvantage of thorium in this breeding process is the high required enrichment of fuel by isotope ²³⁵U or ²³⁹Pu. Another difficulties are summarized by the following list:

- low speed of fuel creation in thorium fuel cycle ${}^{232}\text{Th} \rightarrow {}^{232}\text{U}$,
- increased radioactivity of ²³³U in comparison with ²³⁵U and ²³⁹Pu, which is caused by accumulation of isotope ²³²U and its daughter isotopes,
- fuel poisoning by ²³²Pa, which has a large cross section for neutron capture.

4.2.1 Occurrence, ores and their enrichment

In terms of occurrence in nature, thorium holds 35th place among other elements. As far as geochemical properties are concerned, this metal has a lot in common with rare-earth metals (REM), Zr and U, whereas their beds are usually complex. This metal occurs in rocks in scattered state in the form of the following minerals: monazite, ortite, zircon, xenotime, thorianite, etc. There are about 120 known minerals containing thorium.

4.2.2 Thorium production

Monazite concentrates are processed in order to obtain compounds of thorium, REM, uranium and phosphorus. The production technology includes the following processes:

1. Decay of a concentrate to thorium and REM compounds that are soluble in inorganic acids.
2. Conversion of thorium and REM into a solution.
3. Separation of thorium and REM from phosphorus.
4. Split of thorium and REM.

A whole range of methods have been elaborated for the first operation:

- processing by concentrated sulphur acid – so-called sulphate method,
- processing by a concentrated solution of sodium hydroxide – basic method,
- melting with sodium hydroxide,
- caking with soda ash,
- melting with fluorosilicates,
- chlorination,
- phosphate reduction at high temperatures.

The biggest challenge in the thorium production is its separation from REM, since their properties are very similar. These metals are separated based on small differences in chemical properties of certain compounds. However, these methods cannot yield the purity required for nuclear technology. That is why extraction and sorption methods are used in the next step.

4.2.2.1 Preparation of pure thorium compounds

Due to the fact that the prepared concentrates contain not only thorium but also a substantial amount of REM and other admixtures, it is necessary to include a cleaning process. Cleaning methods of thorium compounds after monazite processing can be divided into two groups:

1. Methods of selective precipitation and solution.
2. Methods of selective extraction by organic solvents (significant application in practice).

Methods of selective precipitation and solution

This group of methods includes the following procedures.

Fractional crystallization

This procedure uses different basicity of thorium and REM. Ammonia solution is added in small amounts to a hot solution of these metals in order to achieve even concentration of hydrogen ions. This process yields $\text{Th}(\text{OH})_4$, containing only about 1 - 2 % of REM.

Selective precipitation of thorium compounds

Compounds with lower solubility than corresponding REM salts can be processed for instance using the different solubility of thorium sulphates and REM. $\text{Th}(\text{SO}_4)_2 \cdot 9 \text{H}_2\text{O}$ changes its solubility from 40 g.l^{-1} at 45°C to 8 g.l^{-1} at 0°C . This value is significantly lower than the solubility of all REM sulphates, whereas the solubility of REM sulphates increases with decreasing temperature.

Selective dissolution:

This method is based on the creation of complex thorium compounds with oxalates and carbonates of alkali metals and ammonia. Solubility of thorium oxalate in water and acid solutions is lower than the solubility of REM oxalates. Precipitation of REM oxalates at different pH can be used to separate a certain part of REM from thorium.

4.2.2.2 Preparation of metallic thorium

The reduction of compounds to metal is performed by applying metallothermic methods or electrolysis of molten salts. In both cases the obtained thorium has a solid form, i.e. powder or sponge. This thorium is then processed to a compact material by arc melting or through powder metallurgy.

Metallothermic methods

ThO₂ reduction by calcium

This is probably the most frequently used method. The reduction is carried out in an inert atmosphere in the equipment depicted in Fig. 4.6. A crucible lined a molybdenum sheet or CaO is filled, put into the furnace and closed. After air is drained from the device, it is filled with argon and the furnace is slowly heated to $1000 - 1100^\circ\text{C}$. After a certain period of time at the temperature, the reaction vessel is removed from the furnace and cooled. Ground reduction products are processed by water and diluted HCl in order to remove slags and calcium residues. Thorium powder is then concentrated, cleared of iron admixtures and surface oxides using HNO_3 , washed by water and dried in vacuum.

80% of REM and other admixtures are transferred to the reduced metal thorium. That is why the content of these admixtures in the input thorium oxide must not exceed the allowed amount for use of thorium in nuclear technology.

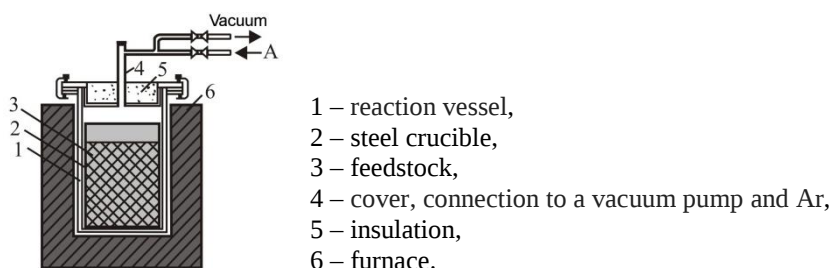


Fig. 4.6 Aparatus for reduction of ThO_2 by Ca.

Iodide refinement

This technology is used to completely clean thorium of non-metallic admixtures, such as oxygen, carbon, nitrogen and hydrogen. Admixtures consisting of volatile iodides cannot be removed. The process of iodide dissociation is analogical to the process described for other metals (Ti, Zr). The decay is represented by the following reaction.

4.2.3 Thorium properties

Thorium is a soft metal with the appearance of steel. However, its hardness is similar to silver. In term of physical properties, this metal has a whole range of advantages in comparison with uranium – namely high thermal conductivity and low thermal expansion coefficient. Its specific weight is significantly lower. Its main advantages include the cubic crystallic structure, thanks to which cyclic thermal stress or radioactive radiation do not cause any significant dimensional and shape changes that are characteristic for uranium. Its melting temperature is approximately 1750 °C. Thorium has a strong affinity to carbon, nitrogen and hydrogen. These elements strongly affect its properties.

4.2.5 Thorium alloys

Pure thorium does provide sufficient strength properties at increased temperatures and that is why it is alloyed with other suitable elements. The selection of suitable alloys needs to take into consideration its absorption cross section for thermal neutrons.

This metal has a strong tendency to create intermetallic phases and only certain metals are dissolved in larger amounts. The most important fissile materials are Th – U alloys. Thorium alloys are produced by melting in a crucible or an arc furnace, alternatively by powder metallurgy. The most important alloying elements include U, Pu, Al, C, Be, V, Si, Mo, Ni, Sn, Zr.



Summary of terms in this chapter (subchapter)

- Uranium production
- Thorium production
- Oxidic uranium preparation
- Metallothermic processes of production



Questions to the covered material

- Production of UO₂ and its importance for nuclear power.
- List and characterize the basic types of uranium alloys.
- Briefly describe the technology of uranium metal.



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