

Hazards at the production of titanium alloys in the electric arc furnace

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Abstract: This article describes the metal titanium, its characteristics and properties, and the types of titanium alloys with regard to its microstructure. It also describes the production processes, i.e. the melting and casting processes of titanium alloys. The focus is on the production of titanium alloys by the electric arc process, and possible hazards in the production of titanium in electric arc furnaces are also described. Suitable protective measures to be taken in the event of a particular hazard are also highlighted. Concerning the occurrence of possible accidents in the production of titanium, a calculation is also presented that shows how much needs to be invested in protection against possible accidents while maximising profit. Finally, the application and casting process of titanium alloys in dentistry is presented.

Keywords: TITANIUM, PRODUCTION OF TITANIUM ALLOYS, HAZARDS, ELECTRIC ARC FURNACE, COMPUTER PROCESSING, DENTISTRY

1. Titanium and its alloys

Titanium is a hard, light and polymorphic metal that has numerous modifications of crystal structure. At room temperature, the hexagonal close-packed (hcp) lattice, known as α phase, is stable and at 882 °C transforms into a body-centred cubic (bcc) lattice, known as β phase. The alloying elements have a great influence on this transformation temperature. The elements that lower the temperature of alpha/beta transformation are called alpha stabilisers and include: Al, N, B, O, C. The elements that raise the temperature of the alpha/beta transformation are called beta stabilisers and include: Co, Cr, Cu, Mo, Ta, Nb, Ni, W, V. Therefore, titanium alloys can be divided into alpha and near-alpha alloys, beta alloys, alpha+beta alloys and unalloyed titanium. Due to this allotropic transformation, titanium alloys exhibit a wide variety of properties. Among them, excellent biocompatibility and corrosion resistance are the most important for use in dentistry, as is the modulus of elasticity. Titanium alloys of the β -type meet these requirements [1][2] [3] [4] [5] [6].

2. Methods of titanium alloys production

Titanium components are manufactured by casting, forging and powder metallurgy. The casting process results in homogeneous and pure alloys at a low price [7].

Of the various processes for melting titanium and its alloys, two are most commonly used commercially: arc melting in a vacuum and electron beam melting. However, research is continuing to develop other methods for better melt control and better utilisation of processing residues [8]. Vacuum melting processes are routinely used to manufacture products with the highest quality standards. However, the reactivity of titanium and the special conditions provide many opportunities for product defects to occur. Inclusions and porosity are particularly undesirable as they can serve as a cause of stress and failure due to material fatigue [9].

2.1. Electron beam melting

Electron beam melting (EB) is approved for the production of ingots of reactive metals such as titanium, niobium, tantalum and superalloys weighing up to 2.5 tons that can be accommodated in a single furnace. Electron beam melting is characterised by the following features: flexibility and the ability to control the process temperature, speed and reaction; the use of a wide range of raw materials in terms of material quality, size and shape [10].

Electron beam (EB) furnaces are attractive for remelting scrap into ingots and slabs. The clean, granulated, mixed raw material is introduced into the EB furnace through a vacuum system into the melting hearth, which is cooled with water. The metal is thoroughly degassed; high-density impurities sink and collect, and the liquid metal is continuously poured into a water-cooled mould. Electron beams strike the melting area and pour the metal into the crucible to ensure good melting and healthy ingots, which are slowly pulled out of the furnace [9].

The production of titanium castings in EB melting furnaces is not cost-effective because of the high vacuum required. However, it is economical if large quantities of castings of the same size and mass are involved and if a wide range of alloying agents can be used. Another advantage of EB melting is the ability to superheat the pool immediately before casting. However, controlling alloying elements such as aluminium, tin and chromium is very difficult as these alloying elements have high evaporation pressures [10][11].

2.2. Vacuum induction melting

Vacuum induction melting (VIM) can be used in many applications, especially for reactive titanium alloys and complex moulded parts. In vacuum induction melting, the primary conductor is el. current wound and generates secondary currents by electromagnetic induction, which develop heat inside the metal charge. Melting takes place under a vacuum or inert gas atmosphere by electromagnetic induction using coils. It enables rapid homogenisation of the melt by electromagnetic stirring. The advantage of this melting method is that the electromagnetic mixing of the melt ensures the homogeneity of the chemical composition of the alloys. Concerning the material of the crucible, a distinction is made between indirect and direct induction heating. The graphite crucible used for indirect heating should be preheated before the titanium is melted by the induced heat. However, a vacuum should be ensured to avoid contamination by the graphite. For direct melting, crucibles made only of CaO are used because of the strong affinity of titanium for oxygen. However, care should be taken when using CaO as it has high hygroscopy and low handling strength [7] [10].

2.3. Plasma arc melting

Plasma arc melting (PAM) uses the heat of thermal plasma in an argon atmosphere to produce materials. The furnaces operate under slight overpressure to prevent contamination with oxygen and nitrogen and the selective vaporisation of alloying elements. The PAM process uses copper crucibles cooled with water and porosity and flowability are retained [7] [9].

There are also advanced melting processes such as vacuum plasma spraying or selective laser melting that do not require crucibles and produce high-quality castings [7].

2.4. Casting of titanium

Titanium casting can be performed by static, centrifugal, vacuum die and countergravity casting.

Static casting is a simple method of casting titanium that requires no additional equipment. However, the pouring rate and superheating of the melt cannot be controlled, so it is very difficult to ensure the required flowability. In addition, there is an interfacial reaction between the metal and the mould.

Flowability is improved by centrifugal force in this method of casting. Centrifugal force can be applied horizontally or vertically. The vertical method produces porous castings due to turbulent melt flow. The advantage of horizontal casting is that the centrifugal

force does not occur in the mould, but the melt itself pours into the mould under the influence of the centrifugal force.

Vacuum die-casting is a cost-effective alternative to mould casting. Higher productivity rates are achieved with this casting process. However, the porosity caused by the turbulent flow of the melt cannot be avoided due to the application of pressure. An even bigger problem with vacuum-die casting is the lack of suitable materials for making moulds for titanium castings. Therefore, only titanium alloys with a low melting point can be cast in this way.

The CLV process allows for better mould filling, better casting, less mould erosion and fewer oxide inclusions. The disadvantage of this process is that a ceramic crucible and mould are required for casting, so there is the contamination of the titanium castings by the materials of the crucible and mould [10].

3. Hazards in the production of titanium alloys in the electric arc furnaces

Arc melting (AM) is the melting of an alloy by means of an arc generated between an electrode and a water-cooled casting mould, usually of copper, in a vacuum or inert gas atmosphere. The electrode may be consumable, i.e. made of titanium or a titanium alloy, or non-consumable, e.g. made of tungsten. If a consumable titanium electrode is used for melting, the process is called vacuum arc melting (VAM). Arc melting produces ingots of the highest purity. The disadvantage of the process is that the ingots are not homogeneous and have to be remelted several times. Therefore, this melting process is mainly used in laboratories [7] [13].

The commercial production of titanium began around 1950. Earlier safety problems resulted from a lack of knowledge about the construction of the furnaces and possible explosions. The knowledge at that time was based on steel technology, so hydrogen explosions were a completely new problem. When molten titanium reacts with water, it decomposes, binding oxygen and releasing hydrogen, and an explosion occurs. The next problems that challenged the industry were sponge fires and explosions. The third problem was the operator's entry into the work area, where there is not enough oxygen to breathe, but gases such as argon, nitrogen and other inert gases are prevalent. To solve these problems, safety committees were formed, safety procedures were developed and the safe operation of the plants was ensured. The melting of titanium in a water-cooled furnace with copper crucibles naturally involves risks. Namely, water leakage can occur, which is why everything is done to avoid this. The problem arises when water comes into contact with molten titanium because then the water turns into steam. Titanium has such an affinity for oxygen that it decomposes water, absorbs oxygen and releases hydrogen. Under these circumstances, both steam and hydrogen explosions are possible. The aim is therefore to develop equipment, processes and facilities that function safely. If a problem occurs, equipment and procedures must be developed to ensure the safety of all involved, even under the worst conditions. When water enters the furnace, it causes an explosion, which occurs in two stages. The first is a steam explosion, followed by a hydrogen explosion. In one of the first industrial explosions, it was calculated that the combined explosion was equivalent to a bomb with an explosive force of 100 to 200 TNT, which is obviously not good in a melt. The first industry-wide safety committee was established in the late 1950s and operated until 1965. They produced guidelines for plant operation and design that were accepted by the industry and are still widely used today. The main outcomes were improvements in the design of furnaces, the relocation of melting areas to sheltered areas and the relocation of operators out of the working area. Since then, there have been a significant number of explosions in the industry, but the number of tragic deaths has been reduced to a minimum. The most common accidents that occurred were fires. The most common cause of the fire was poor maintenance and operator inexperience. Examples from 2000 show how expensive such fires can be, when there were five fires that cost the titanium industry around \$ 1 million. Therefore, in the following, we calculate how much needs to be

invested in protecting against potential accidents while maximising profit [14].

First, for the sake of simplicity, we will assume that there is only one possible accident and that N is the value of material damage from that accident, and with $o(x)$ we will denote the danger (in percentages, so $o(x) \in [0,1]$) that the accident will occur in some fixed time interval (e.g. annually). At the same time, x is the amount of money that we invest in protection with which we want to prevent an accident from happening. In doing so, it is logical to assume that it is always necessary to invest the same amount y to halve the risk. Therefore, we assume that if by investing a monetary amount y we reduce the risk from, for example, 20% to 10%, by investing an additional amount y we will reduce the risk from 10% to 5%. This is logical to assume because this is exactly how nature works in various processes. Let us recall, for example, radioactive decay. If, after T years, the amount of radioactive substance decreases, for example, from 2 kg to 1 kg, then after additional T years the amount will decrease from 1 kg to 0.5 kg (T is exactly what physicists call the half-life). If we now remember the famous saying "time = money", the comparison is complete.

So we assume that

$$o(x + y) = \frac{o(x)}{2}.$$

If we apply that formula several times, we get:

$$o(x + ny) = \frac{o(x + (n-1)y)}{2} = \frac{o(x + (n-2)y)}{4} = \dots = \frac{o(x)}{2^n}.$$

If we now put $x = 0$, we get $o(ny) = o(0) \cdot 2^{-n}$, and after the substitution $x = ny$ we can write that formula in the form

$$o(x) = o(0) \cdot 2^{\frac{1}{y}x}.$$

For simplicity of calculation, we will write this formula below in the form of an exponential function with a natural base:

$$o(x) = A \cdot e^{-ax}. \quad (1)$$

Here we have $A = o(0)$ and $a = \ln(2^{1/y})$. Of course, A and a are generally unknown parameters that can only be estimated empirically for the corresponding type of danger. Nevertheless, a quality assessment of these parameters is necessary for the successful application of this model.

If we denote by P the expected profit from business in the observed period, the actual average profit for that period is in fact

$$p(x) = P - x - N \cdot o(x), \quad (2)$$

i.e. the profit from the business should be reduced by the costs of accident protection and potential costs if an accident occurs. Namely, over m periods we expect $m \cdot o(x)$ accidents with total material damage $N \cdot m \cdot o(x)$, i.e. the average expected damage per period is exactly $N \cdot o(x)$.

If we substitute (1) in (2) we get

$$p(x) = P - x - N \cdot A \cdot e^{-ax},$$

and we expect the maximum profit at the zero point of the first derivative:

$$p'(x) = -1 + N \cdot A \cdot a \cdot e^{-ax}.$$

We can see that it is really a maximum from the fact that the second derivative is negative:

$$p''(x) = -N \cdot A \cdot a^2 \cdot e^{-ax} < 0.$$

By solving the equation $p'(x) = 0$ we get

$$x = \frac{\ln(N \cdot A \cdot a)}{a}, \quad (3)$$

i.e. formula (3) determines how much money should be invested in accident protection to maximise profit (over a long period). Here, N is something that we can estimate more easily because it is the value of the material damage that the accident would cause, while the parameters of the model A and a are more difficult to estimate. We can only estimate them based on experience, i.e. by studying data on previous accidents and previous investments in protection.

If we are threatened with several possible accidents, the situation is even more complicated. Let us assume that we have d possible accidents with potential material damages N_1, N_2, \dots, N_d and with x_1, x_2, \dots, x_d denote the monetary amounts that we will invest in protection against each accident. If these investments are independent, i.e. if protection from one accident does not contribute to protection from another, then formula (3) can be applied to each accident, i.e. for each $i \in \{1, 2, \dots, d\}$ it holds

$$x_i = \frac{\ln(N_i \cdot A_i \cdot a_i)}{a_i},$$

i.e. for each potential accident, its model parameters A_i and a_i should be determined empirically.

The situation is most complex if protection against one accident also contributes to protection against another accident, but we will not deal with that in this paper.

3.1. Hazards of the explosions

To understand the danger of a steam explosion, one must know the cooling technology in the electric arc furnace and its development. Older electric arc furnaces were fitted with refractory linings so that the furnace could withstand extremely high temperatures. Although the linings did not melt, they tended to disintegrate when the furnaces were operated at higher capacities with much higher temperatures and pressures. The solution was to protect the arc furnace covers and other components with a system of tubular plates through which high-pressure water was pumped to ensure cooling. Although water under pressure is an effective coolant, it becomes a problem when cracks occur, which is relatively common in highly loaded furnaces. Most cracks are small cracks caused by thermal fatigue, which is characteristic of heavily welded structures. Cracks can also occur when an irregular arc strike or mechanical penetration causes holes during operation, allowing water to enter the furnace even faster under very high pressure and in possibly large quantities. Water poured into the furnace does not cause an explosion by itself when it stands on the molten mass. The problem occurs if the surface wobbles or tilts when the melt is poured. This can cause the sloshing molten metal to envelop the water and immediately turn it into steam. The steam then expands to 1,700 times its original volume, causing a violent explosion that can lift off the roof of the furnace and release steam, melt and debris over long distances from the furnace, putting people and equipment at risk. The most important approach to preventing explosions in piping systems is to install an electronic monitoring system that measures the water content of the exhaust gas and detects irregularities [15].

3.2. Hazards at the entry in the limited area and inert gases

Problems in the industry are often caused by misjudgement. For example, by entering a confined space where there is not enough oxygen. A confined space is defined as an area that is restricted or has limited entrances and exits, but is large enough for workers to enter to perform their work. The main gases used in titanium production are argon, helium, nitrogen, chlorine and titanium tetrachloride. Every worker must be trained before being assigned to work that requires entering an enclosed space. Training is required if the work changes to an enclosed space and this poses a risk to the worker. Before entering the confined space, the nature of

the work must be explained and access worked out in detail, and everyone must know how and in what way to behave in the event of a hazard. Care must be taken to ensure that all devices, such as supply and ventilation connections or similar, are switched off or mechanically locked. All mechanical devices that may endanger the safety of workers shall be locked and marked. The atmosphere shall be tested for the presence of oxygen and the lower flammability limit. The internal atmosphere shall be tested for toxic substances if they are suspected. The oxygen content shall be greater than 19.5% and less than 23.5%. Testing for the presence of residual toxic substances must be carried out if such substances are suspected. After carrying out the previous procedures when entering an enclosed space, the following guidelines must be followed. Ensure that the gas level is monitored while the worker is in the room. A person is required to constantly monitor the development of the situation and to wear appropriate protective equipment to be protected in the event of a hazard. The worker must wear a protective belt for the whole body when working in an enclosed space. Adequate ventilation must be established and maintained until the work is completed. There must be no steam, chemicals or other hazardous substances or flammable liquids in the enclosed space. All flammable materials should be stored outside the enclosed space [14].

3.3. Hazards for employees in the titanium alloys production

In the metalworking industry, every piece of equipment or tool poses a potential danger to the worker. An even greater hazard is posed if protective equipment that complies with the relevant regulations, standards or measures is not used at work. Hazardous places are places and spaces where the following can occur due to dangerous movements: Entrapment, cuts, entrapment by rotating parts, cuts, electric shocks, harmful effects of hazardous substances, etc. Hazardous movements are defined as movements of tools, shafts, power transmissions, etc. that can create hazardous places or spaces. A hazardous area is defined as a specific place or space where injuries may occur if certain parts of the body or clothing are caught by the moving parts of the equipment [16].

3.4. Hazards from electrical current

The danger of electric current is imminent when a person is connected to an electric circuit during which a current of a certain strength flows through his body. The extent of the consequences depends on the strength of the current and the duration of its passage through the body. The passage of electric current through the human body causes burns, which may be external or internal, destruction of blood plasma, muscle spasms, nervous system disorders and, in the worst case, death. Electrical hazards arise from direct contact with or proximity to live parts. Hazards to the worker are also possible due to a defect in, for example, the insulation or the passage of current through the earthing devices, or due to the occurrence of an electric arc. Such hazards most frequently occur at switches, electrical cables, plug-in devices and electrical mobile consumers.

Therefore, protective measures against electric shock must be taken in accordance with existing regulations and standards. This refers to protective measures on all electrical installations, equipment and apparatus, regardless of the type of premises or room in which they are installed. This is achieved by using suitable equipment and materials for electrical installations and by applying rules of conduct in accordance with the standards and regulations [16].

3.5. Technical measures of protection

At work, all machinery, equipment, devices and other tools used must be fitted with a protective device to protect workers who handle or come into contact with them from possible injury. This is because the guard protects the worker's hand during work, i.e. the guard protects the hand from possible breakage, spillage, splashing,

fire, corrosion, poisoning, hazardous radiation, etc. The guards are built into the tool and set to stop the drive in the event of a malfunction, thus preventing possible injury to the worker. If the safety risk cannot be sufficiently prevented or reduced by collective protective measures or technical measures and organisational measures and procedures, measures relating to the worker are used. These measures enable the worker to control hazards through instruction in the safe operation of machinery or work equipment, vocational training and the use of personal protective equipment [16].

3.5.1. Personal protection equipment

Personal protective equipment is used by workers at work when it is not possible to eliminate risks to safety and health and when the employer cannot sufficiently reduce the risks by applying the basic rules of safety at work or by an appropriate work organisation. Personal protective equipment is divided into protective equipment for the head, eyes and face, hearing, respiratory organs, hands (protective gloves protect hands from possible mechanical, thermal, chemical and other hazards), legs (to protect against cold, against heavy objects falling on legs, against punctures and cuts, against slipping, against oils, greases and chemicals, e.g. safety shoes, safety boots). There is also equipment to protect against ionising radiation, falls from height/depth and adverse climatic conditions [16].

4. Casting of titanium alloys for use in dentistry

In dentistry, titanium is used to make crowns and bridges. It does not cause allergic reactions, is fracture-resistant and has pronounced biocompatibility. Titanium alloys are being introduced in dentistry as an alternative to gold alloys after the price of gold has risen considerably [17] [18].

There are still no titanium alloys exclusively for casting, nor is there a single aggregate for casting. Titanium casting can be improved by adding chromium (Cr) or palladium (Pd), which reduce the melting interval. There are ten different titanium casting processes: Pressure/vacuum casting in separate melting and casting chambers, pressure/vacuum casting in one chamber and centrifugal casting in a vacuum, in an argon atmosphere or in a combination of two atmospheric media: argon and vacuum. Most often, casting is done in an atmosphere of protective argon gas. Pure argon prevents contamination of the molten alloy, does not cause porosity and does not change the microstructural appearance of the casting, but it does contribute to better mechanical properties and thus to clinical applications. The purity of the argon does not influence the microhardness of the titanium casting and its alloy. Pure titanium is also used in dentistry due to its high corrosion resistance, excellent biocompatibility and good mechanical properties. The contamination of titanium with oxygen, hydrogen and nitrogen during the casting process leads to a change in its physical and mechanical properties. Its reactivity with oxygen at high temperatures and its low density complicates the casting process. The surface of titanium castings has a layered structure as a result of the reaction with the moulding materials. In order to obtain high-quality dental casting, the difference between the dimensional accuracy and the surface reaction of pure titanium should not be too great. Relatively high temperatures of the investment casting mould can cause sufficient thermal expansion, but can also lead to considerable oxidation of the surface. Porosity, casting contraction and surface roughness are often the result of casting. Contamination of titanium and its alloys with oxides, hydroxides and nitrites during casting changes their properties. Tensile strength and stiffness increase, while ductility decreases. In terms of dynamic resistance, the increase in tensile strength is positive, but the decrease in elongation and the resulting microcracks have a negative effect [18].

5. Conclusion

Titanium alloys have many good properties, but also some shortcomings. They can be produced by an electric arc melting and casting. During this process, hazards can occur that endanger the production process itself and the safety of those involved in the titanium alloy production process. Possible hazards are fire, explosion, lack of oxygen, etc. To prevent these hazards, it is necessary to invest in equipment and new technologies, train employees, etc. Because of the expected increase in the use of titanium alloys, especially in dentistry, it is necessary to comply with the relevant regulations during production to avoid undesirable consequences.

6. References

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