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Сучасні тенденції у виробництві і застосуванні титанових сплавів

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Current trends in the production and application of titanium alloys

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Анотація. Мета: Аналіз стану наукових досліджень у галузі виробництва і застосуванні титанових сплавів та тенденцій їхнього розвитку протягом останніх 20 років. Методика: Наративний огляд і аналіз літератури з найактуальнішими публікаціями у відкритих джерелах Google Scholar, Sciencedirect, Researchgate, Scopus. Результати: Титан вирізняється міцністю, малою щільністю, корозійною стійкістю, біосумісністю та термостійкістю, що робить його важливим для промисловості. Створено понад 100 титанових сплавів, з яких комерційного статусу досягли лише 20–30. Найпоширеніший – Ti-6Al-4V (понад 50% застосувань), ще 20–30% – сплави чистого титану. Вони використовуються в аерокосмічній, медичній, автомобільній та хімічній сферах. Металургія титану базується на вакуумнодуговому і електронно-променевому переплаві, проте триває активний пошук альтернативних технологій, наприклад електрошлаковий переплав титанових сплавів. Також активно впроваджуються адитивні технології. Наукова новизна полягає в комплексному узагальненні сучасних досліджень, які стосуються виробництва і застосування титанових сплавів із акцентом на сучасні методи переплаву титанової шихти у готовий виріб. Публікація включає найактуальніші джерела, яких ще немає в інших оглядах. Практична значущість. Публікація допоможе науковцям, інженерам, викладачам, студентам швидко зорієнтуватися в масиві існуючих знань, уникнути дублювання досліджень та краще планувати подальшу діяльність.

Ключові слова: титан, сплави, механічні властивості, біосумісність, корозійна стійкість, галузь, переплав, адитивне виробництво.

Abstract. Purpose: Analysis of the state of scientific research in the field of production and application of titanium alloys and trends in their development over the past 20 years. Methodology: Narrative review and analysis of the literature with the most current publications in open sources Google Scholar, Sciencedirect, Researchgate, Scopus. Results: Titanium is distinguished by its strength, low density, corrosion resistance, biocompatibility and heat resistance, which makes it important for industry. More than 100 titanium alloys have been created, of which only 20–30 have reached commercial status. The most common is Ti-6Al-4V (over 50% of applications), another 20–30% are pure titanium alloys. They are used in the aerospace, medical, automotive and chemical sectors. Titanium metallurgy is based on vacuum arc and electron beam remelting, but an active search for alternative technologies continues, such as electroslag remelting of titanium alloys. Additive technologies are also being actively introduced. The scientific novelty lies in the comprehensive generalization of modern research related to the production and application of titanium alloys with an emphasis on modern methods of remelting titanium charge into a finished product. The publication includes the most relevant sources that are not yet available in other reviews. Practical significance. The publication will help scientists, engineers, teachers, and students to quickly navigate the array of existing knowledge, avoid duplication of research, and better plan further activities.

Keywords: titanium, alloys, mechanical properties, biocompatibility, corrosion resistance, industry, remelting, additive manufacturing.

Titanium and its main properties

Titanium was discovered in 1791 by the amateur mineralogist W. Gregor, but it took almost 150 years before its industrial production began [1]. This significant gap between the discovery of a new metal and its use is not accidental, because titanium is an extremely chemically active element. To reduce it from titanium oxide (TiO₂), it is necessary to first chlorinate titanium and obtain TiCl₄. Then purify TiCl₄ by fractional distillation and finally reduce TiCl₄ with molten magnesium or sodium in an argon atmosphere (Fig. 1) [2, 3]. This process was proposed by metallurgist W. Kroll in 1937 and remains the main one in the production of titanium

sponge – a hollow metal raw material that is subsequently processed into titanium using remelting processes of special electrometallurgy (Fig. 1, 2). There are innovative modern processes (FFC, OS, MHR, MIT) that reduce titanium directly from TiO₂ [3, 4].

The high affinity of molten titanium for oxygen, nitrogen and hydrogen requires that melting and pouring be carried out in a vacuum. Vacuum arc or electron beam melting furnaces are commonly used with a consumable electrode made from blocks of pressed titanium sponge, which are connected together by argon arc welding. For casting, the range of forming materials is limited due to the reactivity of titanium, but copper



water-cooled crucibles or pressed graphite are commonly used [2]. Vacuum induction [6] and chamber electroslag processes [7] are also used for remelting titanium.

The high affinity of molten titanium turns sour, it absorbs nitrogen and water so that the melting and pouring can be condensed in a vacuum. Use vacuum-arc or electron-exchange melting furnaces with a vitriol electrode made from blocks of pressed titanium sponge, which are interconnected by argon-arc welding. To cast a range of forming materials, they are formed through the reaction of titanium, or use copper water-cooled crucibles and press graphite [2]. Also, for remelting titanium used vacuum-induction [6] and chamber electroslag process [7].

The complexity and multi-stage nature of the



Fig. 1 – Chlorination of titanium. Zaporizhia Titanium-Magnesium Plant

Titanium is a relatively poor conductor of electricity compared to materials such as copper or aluminum, making it useful for applications where electrical insulation is required. In certain medical applications, such as implanted medical devices, titanium's low electrical conductivity may be useful in preventing unwanted electrical interactions with body tissues [8].

Due to its affinity for oxygen, titanium spontaneously forms a protective oxide layer on the surface when exposed to an oxidizing environment. In biomedical applications, the presence of a natural oxide layer plays a crucial role in biocompatibility, as it forms a barrier between the biological environment and the “reactive” metal underneath [9]. Moreover, bone tissue can adhere and grow on the surface of titanium alloys until complete integration [10]. Titanium and its alloys are generally considered non-toxic and do not release harmful substances into the body. There are some concerns about the potential toxicity of several alloys due to the presence of aluminum, vanadium, and nickel [10, 11].

Titanium alloys demonstrate impressive mechanical strength and stiffness, reaching ultimate loads comparable to those of some steel grades [8].

Titanium alloys

Alloying elements play a key role in shaping the properties of titanium alloys. Traditionally, titanium alloying elements are divided into two groups depending on the phase they seek to stabilize: alpha (α) and beta

casting process for titanium is offset by its outstanding physical and chemical properties. Titanium has a relatively low density of about 4.54 g/cm³, which is about half the density of steel or cobalt alloys. This low density makes it suitable for applications where weight reduction is important, such as aerospace and medical implants [8]. Titanium also has a high melting point of ≈ 1670 °C, which allows the material to withstand high temperatures during manufacturing processes without losing its structural integrity. Titanium also has a low coefficient of thermal expansion, meaning it expands and contracts minimally with temperature changes. This property is advantageous for applications where dimensional stability is critical, such as precision medical devices [8].

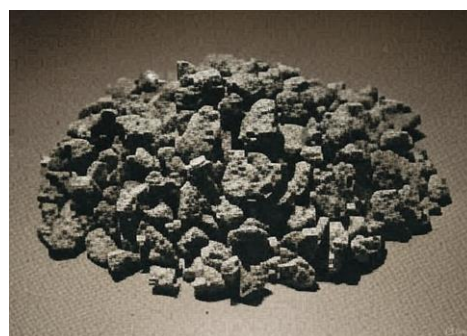


Fig. 2 – Crushed titanium sponge [5]

(β). The α -phase has a hexagonal close-packed structure, and the β -phase has a body-centered cubic (bcc) structure. The distribution between these phases significantly affects the mechanical properties of the material.

Alloying with elements such as aluminum, tin, and zirconium stabilizes the α -phase, increasing strength and hardness and raising the beta transition temperature [12]. Elements such as molybdenum, tungsten, chromium, iron, silicon, and copper stabilize the β -phase, improving ductility and high-temperature properties, and lowering the beta transformation temperature. Vanadium and niobium can act as α - or β -stabilizers depending on the alloy composition. In addition, light elements such as oxygen and nitrogen also have an α -stabilizing effect and a neutral effect on the beta transition temperature [13].

Titanium alloys are usually classified into three main groups, designated α , α/β , and β . The main representatives of α -alloys are commercially pure (CP) titanium alloys, the alloying elements in which are oxygen and nitrogen, which in controlled amounts provide a certain range of titanium strength. Also included in α -alloys are titanium microalloyed with palladium and ruthenium [1]. Alpha alloys cannot be heat treated to improve mechanical properties, since they are single-phase alloys [5].

With a sufficient level of β -favorable elements, a β -phase is formed in the alloy. The resulting structures

are representatives of α/β -alloys. Compared to α -alloys, they are distinguished by high strength combined with improved ductility. The microstructure and properties of α/β -alloys can be changed by heat treatment [5]. An example of an α/β alloy is Ti-6Al-4V, which is the most widely used titanium alloy [1]. This alloy is the benchmark that researchers use to create new, cheaper titanium alloys, while the mechanical properties should not be worse than those of Ti-6Al-4V [4].

Beta titanium alloys require the addition of sufficient β -stabilizing elements such as vanadium. Beta structures should generally be called metastable beta structures. These are alloys that retain essentially the beta structure when cooled to room temperature. One example of this group is Ti-13V-11Cr-3Al [1, 14].

Today, more than 100 titanium alloys are known, of which, however, only 20–30 have reached commercial status. Of these, the classic Ti-6Al-4V alloy covers more than 50% of the use, another 20–30% are commercially pure titanium alloys [15]. It should be noted that the development of new titanium alloys has reached a new level as a result of the application of the experimental method of high-performance multiple diffusion and machine learning using neural networks. It is believed that this approach will allow the development of high-performance titanium alloys [4].

Applications of titanium alloys

Titanium and its alloys are widely used in many industries. The choice of these materials is based on the main advantages of titanium alloys: corrosion



Fig. 3 – SR71 reconnaissance aircraft (first use of β -Ti alloys [5])

The high corrosion resistance of titanium is the reason for its use in the petrochemical and marine industries [4]. For this purpose, technically pure titanium alloys are usually used, which are corrosion-resistant but have low strength. They are used in tanks, heat exchangers, reactor vessels, for parts of chemical processing, desalination and power generation equipment [17].

In the military field, armor must be subjected to intense shock loads caused by explosions and collisions at hypervelocity, etc. Research is currently underway on the response of titanium alloys to shock, especially

resistance, strength, biocompatibility [16]. The applications of titanium are described below.

The aerospace industry (Fig. 3) is the main application of titanium alloys, in particular, in engine systems and housings, titanium alloys cover 36% and 7% of the mass of parts, respectively. In the USA, about 70-80% of all orders for titanium alloys fall on the aerospace industry [16]. The most important reason for the widespread use of these alloys in the aerospace industry is their high strength-to-weight ratio [4], as well as corrosion resistance [16].

The automotive industry began using titanium and titanium alloys for engine parts of racing cars as early as 1980. However, due to the high cost of these materials, their application has been limited. However, in recent years, titanium and its alloys have been intensively used for the manufacture of various automotive parts [16].

Titanium alloys are widely used in biomedical implants (Fig. 4). This is due to their reduced elasticity, high biocompatibility and increased corrosion resistance compared to conventional stainless steel and Co-Cr alloys. Technically pure titanium (Gr-1, 2, 3, 4) and Ti-6Al-4V alloy are the most widely used titanium materials in medicine [16]. The scope of application of β -titanium alloys in biomedicine is expanding, covering dental implants, joint replacement parts, surgical instruments, etc. [17]. Currently, there have been experiments on the use of porous implants manufactured by additive manufacturing methods, which show good results of compatibility with human tissues [18].



Fig. 4 – Components of a hip joint made of titanium [15]

regarding the microstructural evolution during shock pulses and its effect on mechanical properties [4, 19].

The ability to form various types of attractive/brilliant color shades on the surface during anodizing has led to its use in artificial jewelry and various types of consumer goods: watch bracelets, ornaments, sports equipment, etc. [4].

Methods of processing titanium into a finished product

Vacuum arc remelting (VAR) has been the main method of producing titanium ingots since the commercial introduction of titanium alloys in the 1950s and

remains so today. VAR is a process used to remelt titanium and is carried out in a vacuum using an electric arc (Fig. 5). A cylindrical electrode, consisting of welded blocks of pressed titanium sponge and alloying materials and scrap, is melted by an arc in a vacuum. Subsequently, the liquid titanium solidifies in a copper water-cooled crucible under conditions of directional crystallization. This process provides a high melting rate of titanium, high metal quality due to the removal of gases (oxygen, nitrogen, hydrogen) and non-metallic inclusions, uniformity of structure due to multiple remelting, and effective elimination of defects in the starting material. VDP has many advantages, including high purity, good control and reproducibility [5]. However, the process is performed in a vertical position, which can cause segregation of alloy elements due to gravity [1].

Titanium ingots produced by VAR are about 100 cm in diameter and weigh up to 10-15 tons [1]. Larger ingots are more economical, since losses during the



Fig. 5 – Vacuum arc furnace. Preparation for titanium melting [15]

Melting in electron beam furnaces creates favorable opportunities for refining and forming a dense ingot. One of the main factors contributing to the removal of impurity elements and non-metallic inclusions from the metal is the ability to regulate the duration of the metal's stay in a liquid superheated state due to an independent heat source during EBR. This allows for almost complete removal of high and low density inclusions from the metal [20].

Another advantage of the electron beam remelting technology is that titanium sponge of various fractions and lump waste from titanium production can be used as the starting charge for EBR. In this case, the proportion of waste in the charge can reach 100% [20].

Currently, the technological scheme of EBR with an intermediate capacity developed at the E.O. Paton Institute of Electric Welding has become widespread. It allows you to separate the processes of melting and refining from impurities in the intermediate capacity, as well as the solidification of the metal in the crystallizer [20]. The metal obtained using EBR technology meets the standards set for US aerospace materials [4, 22] and for medical products [23]. EBR technology with an intermediate capacity allows you to obtain Ti ingots

transformation of the ingot into the final product are smaller, and the melting time, including furnace reloading, is shorter. Both of these factors, plus the minimization of the number of VDP furnaces required for production, lead to a decrease in cost. VDP is able to process up to 25-30% of waste from the total mass of the charge [1].

Electron beam remelting (EBR) (Fig. 6) is a promising and widely used process for producing titanium ingots [20]. The physical basis of the EBR process is the conversion of the kinetic energy of electrons accelerated in an electric field to high speeds into thermal energy when they are slowed down in the surface layer of the metal. A special device, an electron gun, forms a flow of accelerated free electrons (electron beam). The process of melting titanium is carried out in a vacuum, which prevents contamination of the metal with nitrogen and oxygen impurities from furnace atmosphere, and also improves the conditions for degassing metal [20, 21].



Fig. 6 – Electron beam furnace
Zaporizhzhia Titanium-Magnesium Plant

weighing up to 12 tons and with better metal purity than with vacuum arc remelting [1, 21]. The production of titanium castings in EB furnaces is more economical than vacuum arc and plasma arc remelting [24].

Plasma arc remelting (PAR) is a material processing technology in which the heat of thermal plasma is used to melt the starting material (Fig. 7) [24]. PAR is a promising technology for removing nitrogen-containing inclusions from titanium, since it allows the surface of the melt to be overheated to 200 °C above the melting point and makes it possible to maintain the metal in a liquid state for any required time [21]. A characteristic feature and advantage of plasma heating is the ability to treat the metal melt with various gas mixtures of the appropriate composition at a given pressure [25]. The presence of a flowing inert gas atmosphere above the surface of the liquid metal in a plasma arc furnace makes it possible to create good kinetic conditions for bath degassing [26].

Using plasma heat sources, it is possible to melt primary titanium ingots directly from the sponge, excluding the pressed electrode [26]. In this case, a lump charge is fed to the bath of liquid metal, including the return of titanium production, and its maximum content

can reach 100% under appropriate conditions [26]. In the process of remelting titanium scrap by the PAR method, dense ingots are obtained with a significantly lower content of gas impurities (oxygen, nitrogen and hydrogen) compared to the original charge [21, 27]. The macrostructure of the ingots is characterized by directional crystallization, and the surface is of excellent quality [26]. The biggest disadvantages of PAR are the high cost and complexity of equipment maintenance (plasma torch) and high electricity consumption [25, 26], although modern authors claim that the operating costs of PAR are lower than those of EBR, and the effect of metal purification is higher than that of VAR [27].

One of the advantages of cold hearth melting methods (CHMM), in addition to the control of structure and chemistry, is the possibility of manufacturing shaped ingots with a cross-section other than cylindrical [5].

Vacuum induction remelting (VIR) is a process of remelting and purifying metals under vacuum or in an

inert atmosphere, in which the metal is melted in a crucible by induction heating [5]. VIR of titanium alloys in refractory crucibles is much less energy-intensive than other melting methods, but at the same time it allows high superheating temperatures, thus improving the purity of the metal [6]. In addition, VIR allows for rapid homogenization of the melt by electromagnetic stirring and is less expensive than alternative melting methods [6]. Despite its advantages, VIR is not often used for the industrial production of titanium alloys, mainly due to the lack of stable refractory crucibles resistant to aggressive melt at high temperature and to thermal shock [6].

A promising technology is vacuum induction melting, degassing and pouring (VIMDP). The VIMDP concept allows the crucible to be kept under vacuum at all times. During pouring, the melt is transferred through a ceramic runner into a forming chamber where it fills the mold under vacuum [28].



Fig. 7 – Operation of plasma torches of a plasma arc furnace [25]



Fig. 8 – Laboratory chamber electros slag furnace

Electroslag remelting (ESR) (Fig. 8) was developed in 1953 at the Paton Institute of Electric Welding [29]. Currently, variations of electroslag remelting: inert gas ESR and pressure ESR are common remelting processes. In ESR, the electrode is melted by heating synthetic slag. Due to the superheated slag, which is constantly in contact with the tip of the electrode, a liquid film of molten metal is formed from which droplets are formed. When the droplets pass through the slag, the metal is cleaned of non-metallic inclusions, which are removed by chemical reaction with the slag or by flotation to the upper part of the melt bath. The remaining inclusions are evenly distributed in the remelted ingot. In addition to this refining function, the ESR process allows for the establishment of a specific macrostructure through controlled solidification in a water-cooled copper mold. In this way, segregation is minimized and a uniform distribution of alloying elements can be achieved [28].

Ukrainian scientists continue to develop the ESR technology, they proposed the technology of chamber electros slag remelting (ChESR) [30, 31]. ChESR is based on "classic" electroslag remelting, and the presence of a chamber allows: to use active slags that

contribute to refining; to create a vacuum or any controlled atmosphere in the melting space; to remelt highly reactive metals and alloys [7, 30]; to alloy titanium with oxygen [32] and carbon [33].

Additive technologies (AT) are a generalized name for technologies that involve manufacturing a product according to a three-dimensional digital model using the layer-by-layer addition method. AT is based on the principle of layering liquids, powders, substrates and films to create three-dimensional structures without using a mold [34]. The most common AM methods for metals are powder bed melting processes, such as: selective laser melting (SLM), electron beam melting (EBM), and laser metal deposition (LMD) processes [35].

Selective laser melting (SLM) is a process that uses laser energy to create three-dimensional metal parts by fusing fine metal powders. A thin layer of metal powder is deposited onto a platform using a blade, and the laser beam melts the powder in a controlled inert environment. The platform is then lowered and a new layer is deposited. The process is repeated until the height of the part is reached. The layer thickness can vary from 15 to 150 μm [35].

Electron beam melting (EBM) uses electron beam energy to melt metal powder. Each layer is produced by the following steps: powder distribution, preheating and sintering using a highly defocused beam, which provides mechanical stability and electrical conductivity to the powder layer, and melting using a focused beam. The layer thickness – 50 to 200 μm . The EBM process takes place in a vacuum, so this process is suitable for materials with a high affinity for oxygen [35].

Laser metal deposition (LMD) is a process in which metal powder is introduced into a focused beam of a powerful laser under strictly controlled atmospheric conditions. The focused laser beam melts the powder and creates a layer of molten material. The workpiece is moved by a computer-controlled drive system under the beam/powder interface to form the desired cross-sectional geometry. This is a complex process that is controlled by mass, heat, and fluid flow. Typically, each layer is 0.3–1 mm thick. LMD has been used to fabricate structures with graded porosity and composition from various materials, including Ti [35].

Various industries, from automotive and aerospace to jewelry and biomedical, have adopted AM processes due to the numerous advantages they offer to manufacturers and consumers. The most important advantages include the ability to create strong porous structures, product personalization, reduced tooling costs, machining and energy consumption, and production "flexibility" [35].

Conclusions

The analysis of literature sources showed that:

1. Titanium has a number of unique properties that make it attractive for many industries. These are strength, low density, corrosion resistance, biocompatibility, heat resistance, non-magnetism.

2. At present, more than 100 titanium alloys have been invented and only 20-30 have reached commercial status. The classic Ti-6Al-4V alloy remains the key titanium alloy in the world, used in more than 50% of cases, another 20-30% are alloys of commercially pure titanium.

3. Titanium alloys are widely used for the manufacture of components used in the automotive, chemical, aerospace, and biomedical industries that are exposed to difficult operating conditions. Research is underway into the properties of armor-grade titanium alloys for military applications.

4. The basis of titanium metallurgy remains the processes of vacuum arc, electron beam and vacuum induction remelting. The triple remelting process VIP/ESP/VDP provides optimal purification of materials for aerospace parts. In recent years, AM technologies (SLM, EBM and LMD) have become more popular due to the ability to create metals with customized porous architecture, "flexibility" of production, etc. However, each AM technology has its own limitations and advantages in terms of the materials used and processing technologies, which requires an individual approach to obtain the necessary products.

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