Műszaki Tudományos Közlemények vol. 21. (2024) 56–60.
DOI: Hungarian: https://doi.org/10.33895/mtk-2024.21.08
English: https://doi.org/10.33894/mtk-2024.21.08

HEAT-TREATING PROCESSES OF THE TITANIUM ALLOYS

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Abstract

Titanium is a metal with a short history and is the ninth most abundant element in the Earth's crust. It is expensive to produce but is increasingly used for its many useful properties. The application of titanium alloys has been increasing in recent decades because titanium is a low-density, high-strength, highly corrosion-resistant and biocompatible material. Its different alloys exhibit different mechanical properties. Heat treatments can be applied to achieve the required mechanical properties. These typical heat treatments achieve the desired properties by phase transformation of the microstructure or reduction of stress. In this summary study, the authors aim to present the typical heat treatments of titanium and its alloys.

Keywords: *titanium alloy, heat treatment, precipitation hardening, annealing.*

1. Introduction

Heat treatment is a technological process used to modify the mechanical, technological and/or chemical properties of materials.

Heat treatment technology is a process consisting of heating a material to a predetermined temperature, removing heat and then cooling it in order to achieve the desired properties or combination of properties, e.g. an increase in hardness, a softening of the material or an appropriate strength/heat ratio **[1]**.

Heat treatment can be a process with or without a change in chemical composition. Chemical composition changes usually involve the diffusion of some chemical element into the surface of the material, e.g. carbon during cementation, and nitrogen during nitriding, to help achieve the desired mechanical properties such as hardness, and wear resistance.

The importance of heat treatments carried out without changing the chemical properties is relevant in the field of heat treatments, where changes in the fabric structure over the whole volume can be used to achieve changes in mechanical and other properties.

Titanium is a "new" metal, discovered in 1795 by the German chemist Martin Heinrich Klaproth and named after the mythological titans (which were symbols of strength and toughness). In 1932, Wilhelm Kroll developed a process for extracting titanium, and in the 1940s, based on this process, commercially pure titanium began to be produced in industrial quantities **[2]**.

The Kroll process produces pure titanium from ores (rutile (TiO_2), ilmenite ($FeTiO_3$)). In the first step, pure titanium dioxide is produced chemically or metallurgically, then it is heated together with carbon and chlorine to produce titanium tetrachloride ($TiCl_4$), which is reduced with magnesium melting at 900 °C. **[2]**. Reduction results in the formation of powdery or spongy titanium. The titanium sponge or powder is cleaned of magnesium residues by aqueous washing and dilute hydrochloric acid treatment, possibly by vacuum distillation. The resulting titanium is 99.4–99.9% pure followed by further processing. The high-purity titanium powder is powder metallurgically combined into blocks and then processed by a remelting process in a neutral protective gas or vacuum.

Titanium is the ninth most abundant element in the earth's crust, but its use has not been widespread because of the cost of its production. Titanium is an environmentally and human-friendly material. Its main properties are: low density (ρ = 4500 kg·m^{-3}), high strength (e.g. ASTM Grade 4 R_m = 550 MPa), high corrosion resistance, biocompatibility [2, 3, 4].

Titanium and titanium alloys are now widely used in many areas of aerospace, energy, chemicals and automotive production. Many titanium alloys, due to their biocompatibility, are excellent materials for surgical prostheses and medical devices. With the advent of additive technologies, it has become even more widespread, particularly in the field of dental implants.

The heat treatment technology for titanium and titanium alloy products has evolved significantly in recent decades [5, 6]. In this paper, the authors have aimed to collect and systematize the main heat treatment technologies used in practice.

2. Titanium and alloys

Titanium is an allotropic metal, composed of αTi (hexagonal close-packed) and βTi (body-centred cubic) phases depending on temperature (Fig. 1.) [7]. The temperature of the phase transition is 900 °C [1].

Different alloys change the transformation or precipitation temperature of the resulting phases depending on the type and amount of the alloy. Alloying elements can be classified into three categories based on their effects [2]: -α phase stabilizing elements such as Al, O, N and C; -β phase stabilizing elements such as Mo, V, Ta, Nb (isomorphic elements), Fe, Mn, Cr, Co, Ni, Cu, Si, H (eutectoid forming elements) and -neutral elements such as Sn, Zr and Hf. The elements O, N, C and H form an interstitial solid-solid solution with titanium. All other elements form a substitution solid solution with titanium. The elements that stabilise the α phase expand the range of the α phase, and the elements that form the β phase expand the range of the β phase and simultaneously narrow the α phase field. Neutral elements have only a minor

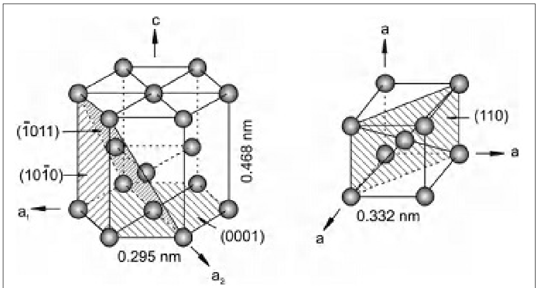
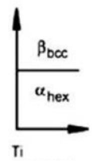
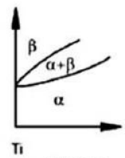
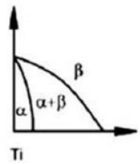
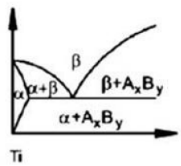


Fig. 1. *Crystal structure of pure titanium α (hexagonal close-packed crystal lattice) and β (body-centred cubic crystal lattice)* [7]

effect on the βt temperature. The effect of alloying elements on the phase diagrams of titanium alloys is summarised in Table 1.

Table. 1. *Titanium alloy types* [7, 8]

Type	Alloy	Typical equilibrium diagram
Pure Titanium	–	
α solid solution	Al, O, N, C	
β stabilized	Mo, V, Ta, Nb	
Eutectoid	Fe, Mn, Cr, Co, Ni, Cu, Si, H	

2.1. α Titanium phase alloys

A single-phase alloy consisting of an α-phase solid solution. Whether at room temperature or higher practical application temperatures, it is α-phase, has a stable structure, higher wear resistance, is more stable than pure titanium and has strong corrosion resistance. At 500°C ~ 600°C, it still retains its strength and creep resistance, but cannot be heat treated to increase its strength.

A significant group of α-phase alloys are near α titanium alloys, which also contain small amounts of β-phase alloys, for which strength-enhancing heat treatment can already be applied. Typical examples of near α alloys are Ti-8Al-1Mo-1V and Ti-6Al-5Zr-0.5Mo-0.2Si alloys [9].

2.2. (α + β) Titanium phase alloys

A two-phase alloy with good structural stability, good toughness, good ductility and high-temperature ductile properties, which can be processed by hot forming and the strength of the alloy can be increased by ageing. The strength after heat treatment is about 50-100% higher than in the annealed condition. The strength after heat treatment is about 50-100% higher than in the annealed state. This alloy retains its strength at high temperatures and can operate at temperatures between 400°C and 500°C for long periods [10, 11].

The α-phase is stabilised by Al, the main β-stabilisers are V, Mo, Nb and Cr, and the alloys often contain neutral elements such as Zr and Sn. Major biphasic (α + β) alloys include Ti-6Al-4V, Ti-6Al-6V-2Sn and Ti-6Al-4Zr-2Sn-1Mo [9].

The Ti6Al4V alloy is a typical (α + β) phase alloy. The schematic phase diagram (Fig. 2) shows the phases as a function of the alloy contents.

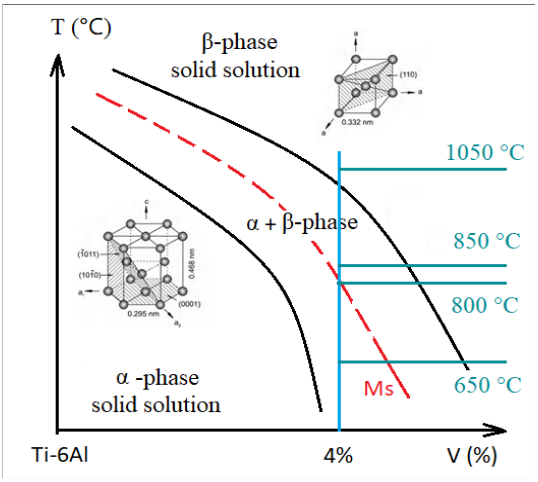


Fig. 2. *Schematic phase diagram of the Ti6Al4V alloy.*

2.3. β Titanium phase alloys

Metastable β titanium alloys, which typically consist of a β-phase solid solution, have high strength before heat treatment. After solution annealing and subsequent ageing (precipitation hardening), the strength of the alloy can be further increased and the strength measured at room temperature can reach 1400 MPa. The most common β phase-forming alloys are V, Mo, Nb, Cr and Si, the α phase-forming alloys 3% Al and the neutral alloys Sn and Zr. Widely used β-titanium alloys include Ti-3Al-8V-6Cr-4Zr-4Mo (Beta C), Ti15Mo-3Nb-3Al-0.2Si (Timetal 21S) and Ti-15V-3Cr-3Sn-3Al [5]. Fig. 2 shows the area of the β-phase solid solution of Ti6Al4V alloy. The β stabilizer in this alloy is vanadium.

3.Heat treatment of titanium alloys

3.1. Stress relieving

Stress relief heat treatment is important for titanium alloys, especially for α-solid solution alloys. Stresses from the manufacturing steps can be reduced by this heat treatment. Stress relief heat treatment consists of annealing at 500 °C in a neutral atmosphere followed by slow cooling. The stress-relieving annealing temperature for (α + β) alloys is between 500 °C ~ 700 °C, while that for metastable β alloys is higher, 700 °C ~ 800 °C [12].

3.2. Annealing

Annealing increases fracture toughness, ductility, dimensional and thermal stability, and creep resistance. Annealing is a heat treatment process in which a metal alloy is heated to a temperature slightly higher than the temperature of the solution annealing and then allowed to cool very slowly. The main purpose of the annealing process is to increase ductility and remove stresses from the material [12].

Typical annealing:

1. Recrystallization annealing, the alloy is heated to the upper α−β range, held there and slowly cooled.
2. Duplex annealing improves creep resistance or fracture toughness. It typically consists of solution annealing below $T_β$ and subsequent ageing at 320°C ~ 500 °C.
3. Beta annealing heat treatment to improve fracture toughness, characterised by heat treatment above $T_β$ followed by slow cooling [13].

3.3. Solution annealing

Solution annealing is a process in which the alloy is heated at an appropriate temperature for a specified time to form the desired component in a solid solution, followed by rapid cooling [5].

The three steps of solution annealing are as follows:

a) heating the material to a high temperature to bring the alloying elements in the β-phase into solution,

b) maintaining at this temperature to achieve homogenisation,

c) rapid cooling to room temperature.

For β titanium alloys, the solution annealing temperature is usually above $T_β$, for (α + β) alloys it is usually below $T_β$.

3.4. Ageing

Ageing heat treatment is also called precipitation heat treatment. It is a heat treatment process used to increase the yield strength of materials. During ageing, phase precipitation occurs by decomposition of the β-phase. Through the mechanism of α precipitation, which is finely dispersed in the β matrix, it leads to an increase in the strength of the material.

There are three types of ageing:

– High-temperature ageing,
– Low-temperature ageing,
– Duplex ageing [9].

3.4.1. Ageing at high temperatures

Grain boundaries are the process of decomposition of the β-phase at relatively high ageing temperatures (above 500 °C).

3.4.2. Ageing at low temperatures

Intermediate decomposition products (ω or β' phases) are formed when β-Ti alloys are aged at relatively low (~320 °C) ageing temperatures. If the ageing temperature is particularly low, the transformation takes a long time to complete; the transformation to an equilibrium microstructure consisting of only α and β phases may not be achieved.

The ω phase (hexagonal lattice) causes severe brittleness of the alloy. The coherent ω-particles shear during deformation, causing intense slip localisation and fracture with little or very little ductility.

3.4.3. Duplex ageing

After a rapid cooling (water) following solution annealing (~840 °C) the treatment consists of a long period of low-temperature ageing (~320 °C), followed by a short period of high-temperature ageing (~500 °C). The actual temperature and time chosen for the solution annealing and the two steps should be optimised for the specific alloy composition. The heat treatment results in higher strength and toughness.

3.5. Cryogenic annealing

Cryogenic annealing is the rapid cooling from the homogenizing annealing temperature to −196°C using nitro-gas vapour (boiling point of nitrogen at atmospheric pressure −195,8°C) [14]. This heat treatment significantly increases the ductility of Ti6Al4V alloys (from 5.3% to 8.3%), while the yield strength is reduced by a small amount (2%) [15]. Cryogenic treatment at low temperatures for a long time stabilizes Ti6Al4V alloy by reducing the effect of internal stress, transforming unstable phases into stable phases and improving the mechanical properties and ductility of the material [16].

4. Conclusion

The use of titanium alloys is becoming more widespread despite the fact that they are expensive to produce. Titanium and its alloys have a number of advantageous properties. New alloys are being developed and tested in order to achieve good mechanical, corrosion and wear resistance properties. However, adjusting the chemical composition is not enough, as it is also necessary to create the right microstructure, which can be achieved by heat treatment. In the case of titanium, an alloy-dependent microstructure is formed under equilibrium conditions as shown in **Table 1**. Titanium is an allotropic metal and therefore phase transformations can also occur under equilibrium cooling conditions due to changes in temperature. However, with proper heat treatment, a stable structure can be created which reliably provides mechanical, corrosion resistance and wear resistance properties at the given application temperature.

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