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STUDIES AND RESEARCH ON TREATMENT OF TITANIUM ALLOYS

Ovidiu DIMA, Petrică ALEXANDRU, Gheorghe GURĂU, Vlad Gabriel VASILESCU, Elisabeta VASILESCU
“Dunarea de Jos” Universityof Galati, Romania
e-mail: odima@ugal.ro

ABSTRACT

Titanium and its alloys have an extended use due to special properties. The paper highlights the TiZr alloy intended to manufacture prostheses, the influence of plastic deformation on the properties and structure. Applied research and technology have shown good deformation behavior of the alloy, good plasticity and a reduced hardening trend. The plastic deformation provides a fine structure and a 50% increase in hardness and strength properties.

KEYWORDS: titanium alloys, direct extrusion, degree of deformation, structure, hardness

1. Introduction

Titanium is a very common element, the ninth in descending order, representing about 0.6% of the Earth's crust. More than 95% of titanium is used in the form of TiO_2 and other compounds in the manufacture of white paints, coating rutile titanium electrodes, etc. Only 5% is used as a pure metal, for micro-alloying of steels or alloy with high strength and low specific weight. The percentage is growing.

Pure titanium has a strength of 434MPa. Commercial purity titanium is 99.2%. In the form alloyed titanium is a very high resistance up to over 1400MPa. Stressed metal reduces its strength when heated to over 430^{o}C. Titanium has two allotropic states: hex to 882^{o}C and the body-centered cubic above this temperature. These structures are found in the case of zirconium with titanium alloy well forming solid solutions with complete solution as shown in the diagram Ti - Zr equilibrium, Figure 1.

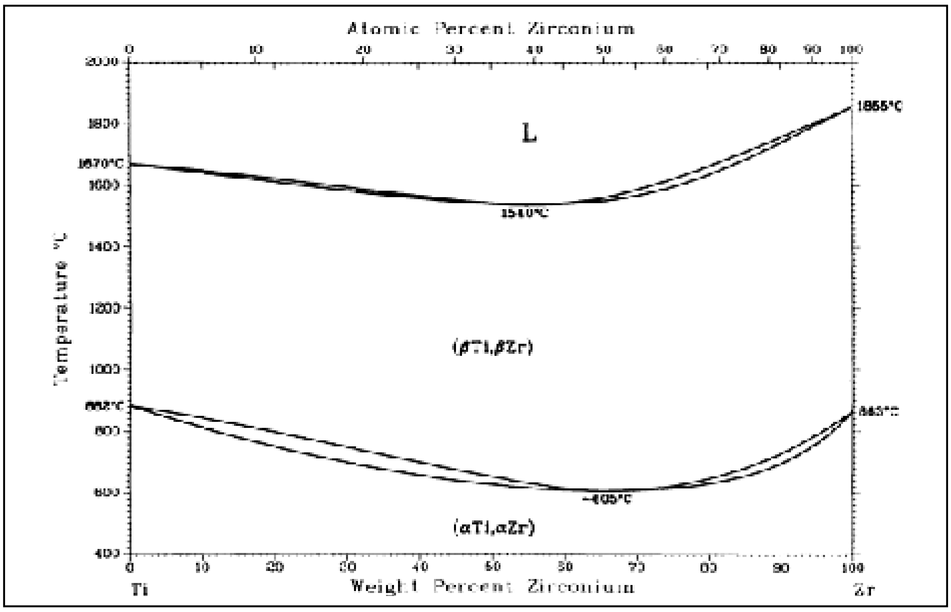

Fig. 1. *The diagram Ti-Zr equilibrium*

A special feature of titanium and its alloys is corrosion resistance. From this point of view it is comparable to platinum. Titanium better resist the attack of acids, solutions of chlorine in water, it is soluble in concentrated acids. Although titanium Pourbaix diagram, Figure 2, shows that it is a very reactive metal, its reaction with water and air are very slow.

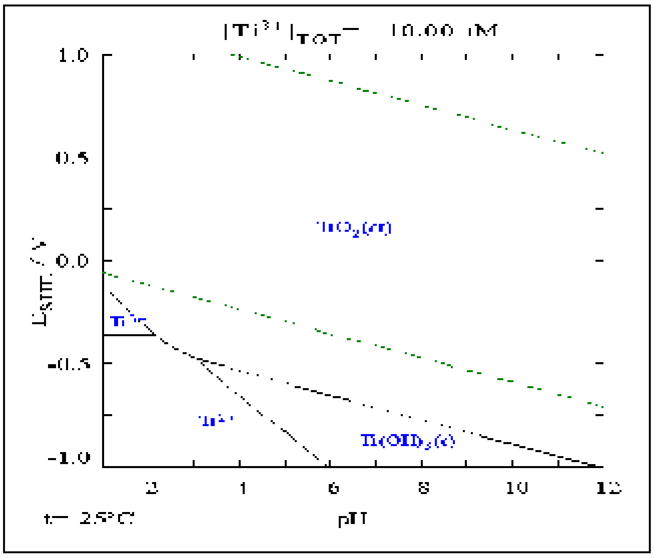

***Fig. 2.** Titanium Pourbaix diagram*

At ambient temperature, in spite of the oxidation resistant titanium has a loss of gloss; formed TiO2 layer thickness of about 2nm. Air temperature increase it was estimated that TiO_2 layer can grow up to 25nm in about four years, enhancing the corrosion resistance of the metal.

Heating to above 1200^{o}C in air causes spontaneous combustion of titanium, so melting, production and casting of titanium and its alloys should be performed in an inert atmosphere or vacuum.

In addition to over 800^{0}C merge seamlessly with nitrogen to form titanium nitride TiN. It is extremely hard and lowers the ductility of the metal or alloy. Titanium is not toxic, even in large amounts and has no impact on tissues or organs of the human body. It was found that it is tolerated by the tissues and also if ingested, its excreted without being absorbed. In power plants, it is found in very small amounts 2ppm, exception being the horse tail and nettle, about 80ppm.

2. Current applications of titanium and its alloys

As a result of its qualities, titanium will become one of the most used metals, the third in terms of global importance.

The growth in the production of titanium, exceeds the growth rate of the world economy and other industries. Initially, titanium has been used in the aerospace industry with spectacular results. Therefore, the enhanced production of titanium explored other potential applications.

Today we distinguish a wide variety of uses such as:

- in the aerospace industry : frames and panels fuselage structure strength, braking, jet engine components, fire walls, etc. Titanium is also used to achieve: turbine blades, compressor blades and disks, hot air pipes, bearings, rotors of helicopters, etc.
- applications that involve the use of titanium due to its outstanding resistance to corrosion, such as: chemical technology, paper manufacturing industry, energy industry, water applications;
- biomedical applications that exploit the inertia of the metal in the human body (biocompatibility): implants dental;
- special applications that appeal to the properties of superconductivity (niobium alloys) or shape memory effect (nickel alloys)
- applications that operate mostly with high specific strength: the automotive industry, vehicles in general;
- applications in consumer goods: cameras, jewelry, musical instruments, sports equipment etc.

3. Aspects of producing Ti

World production of titanium metal is around 100 000 tonnes annually. The most part is produced by the Kroll process that uses TiO_2 and ore concentrates, involving the following reaction sequence:

a) obtaining titanium tetrachloride:

$TiO_2 + 2CI_2 + 2C$ <-> $TiCI_4 + 2CO$

b) reduction of magnesium:

$TiCI_4 + Mg$ <-> $2MgCI_2 + Ti$

Magnezotermic titanium tetrachloride is reduced in a reactor under an atmosphere of argon. Magnesium chloride is formed and the excess of magnesium is washed with water and dilute hydrochloric acid, resulting in the "titanium foam". This was purified by van Arkel - De Boer process played by the reaction:

TiJ_4 <–> $Ti + 2J_2$.

By replacing magnesium with sodium, Degussa method, one can get a pure " titanium sponge ".

Then titanium sponge is melted in a special insullations, such as the electric arc under vacuum. In these furnaces, electric arc generated between a consumable cathode of sponge titanium and copper crucible in a current of 15-40 kA and a vacuum level of 10^{-2} mbar.

In industrial technologies protective atmospheres are used for different heat processing (melting, sintering, plastic deformation, welding, heat treatment, etc.), inert gases such as argon and helium or some controlled atmospheres.

A significant amount of titanium is obtained by recycling waste materials. Recycling waste requires prior preparation, which consists of sorting, cutting, grinding, degreasing and pickling, washing and drying. Degreasing wastes is made alkaline and acid etching. Degreasing wastes is made with alkaline solutions and etching with acid solutions. Operations must preserve the physico- mechanical and chemical properties of the metal or alloy.

Flowsheet melting waste includes the following:

- Obtaining electrodes by compacting waste;
- Melting of the electrode of titanium or alloys waste titanium in the vacuum arc furnaces, or electron beam. In some cases is applied alloy remelting for composition uniformity throughout the length of the ingot;
- Heat treatment and plastic deformation processes;
- Characterization of the products obtained.

Waste titanium and titanium alloys generally have high concentrations of impurities compared to sponge titanium source in the preparation. The reason is that, although the melting takes place in vacuum or in an inert gas atmosphere in the atmosphere of the oven where melting occurs, there is always a certain amount of oxygen and hydrogen, as a result of freeing the waste gases adsorbed on the electrode, or oven walls. These gases are almost entirely related to the melted titanium and therefore the amount of impurities in the remelted ingot is always higher than that of primary sponge. These impurities will be found in pieces and manufactures cast, which will add other impurities absorbed during plastic deformation.

Technological scheme for obtaining plastic deformation elements include the following:

- pre-treatment consisting of a homogenizing annealing at about 1000^{o}C and may be followed by a quenching of sample to eliminate the grain boundaries of the eutectic formed with some accompanying parts ;
- hot plastic deformation which can consist of a rolling at temperatures of 800 - 850^{o}C or forging or extrusion. Hot plastic deformation will be in controlled atmosphere furnace or vacuum;
- plastic deformation by cold rolling;
- final treatment comprising recrystallization annealing at 800°C and stress relief annealing at a temperature of 570 ^{o}C . Heating the thermal treatment should be performed under vacuum or in a controlled atmosphere, the duration of the treatment and several days depending on the size of the blanks.

Application of thermomechanical treatments, which combines the various thermal treatments to the plastic deformation, has a high potential for improving the mechanical properties of titanium alloys, and as a results it can be taken into account.

4. Deformation of titanium alloy semi-products laboratory

The blank was originally a cast titanium alloy bar with 10% zirconium, machined by turning. It has a diameter of 18mm and length of 35mm. It has been subjected to heating at 850^{0}C, in the electrical resistance furnace with maintaining equalization for 10 minutes. The temperature was chosen in view of the equilibrium diagram such as Ti-Zr alloy has a solid solution structure of the beta crystalline crystal structure solid solution centered cubic system with a better plasticity.

The blank/semi-product was subjected to heating hot extrusion to a diameter of 10 mm into a mold preheated to about 400°C to avoid cooling of the blank during deformation. Also in this regard, we performed a valuable rapid transfer of the blank from the furnace in the extrusion die container. After forming, the preform was cooled in air.

The second extrusion blank was cut to a length of 35mm, consistent with the increased dimensions.

The Φ10x35mm new blank was subjected to heating at 850^{o}C and was hot extruded to a diameter of Φ5mm and cooled in air.

Finally Φ5mm extruded preform was cold rolled to a diameter of Φ3mm sizes.

For evaluation of materials, all stages of research in all the blanks were sampled by cutting by milling.

Sample preparation and analysis of the structure and hardness.

Titanium alloy samples at each stage of processing: molding, 1 extrusion 1, 2 extrusion 2, cold rolling, were embedded in an acrylic solution.

Sample preparation was done by metallographic grinding paper to very fine grained, scoring 1200 and then fine polishing felt or velvet, with fine alumina paste with high humidity and moderate pressure. To highlight the microstructure of the samples they were attacked with Kroll solution, and 1.5ml HF, HNO_3, 4ml, 94.5ml H_2O.

To determine the Vickers hardness, a test was applied with small tasks HV_{100}. The values obtained as the average of at least three tests were as follows: 212daN/mm^2 for cast, 290daN/mm^2 for extrusion 1, 306daN/mm^2 for extrusion 2 and 320 daN/mm^2 for cold rolled. They show as expected a significant improvement of the properties after deformation. This is confirmed by microstructural analysis. The cast sample has an inhomogeneous structure, consisting of large grains aspect of dendritic cells, Figure 3. Improvying this structure can be achieved by applying a homogenization treatment or hot plastic deformation.

In the research we have done hot plastic deformation by direct extrusion in two stages: extrusion 1 from Φ18mm to Φ10mm and extrusion 2 from Φ10mm to Φ5mm. Metallographic analysis shows a gradual completion of the structure and its uniformity and homogenization.

It also highlighted the lines of flow of the material during deformation, Figure 4 and Figure 5. Moreover, the effect of hot plastic deformation was highlighted as shown by hardness increase from 212 to 306 daN/mm^2. Deformation by cold rolling marked the same trend finishing and smoothing of the structure (figure 6) and increasing hardness from about 320 daN/mm^2. With relatively small increase in cold rolling, the alloy showed good plasticity and a reduced hardening trend. Table 1 and Figure 7 show the trend of hardening of titanium alloy and influence of the degree of deformation expressed by coroiaj C_T on hardness HV_{100}.

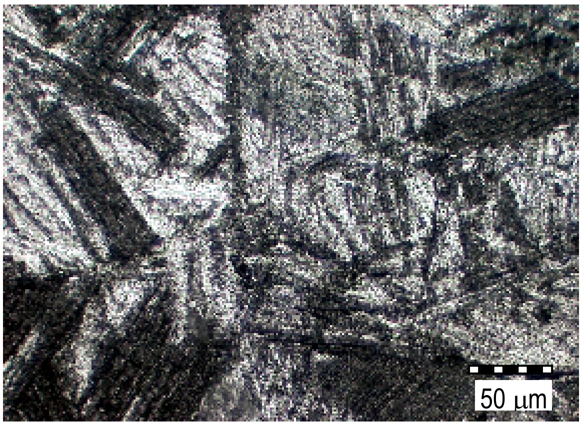

Fig. 3. *Castings microstructure of Φ18mm (X200)*

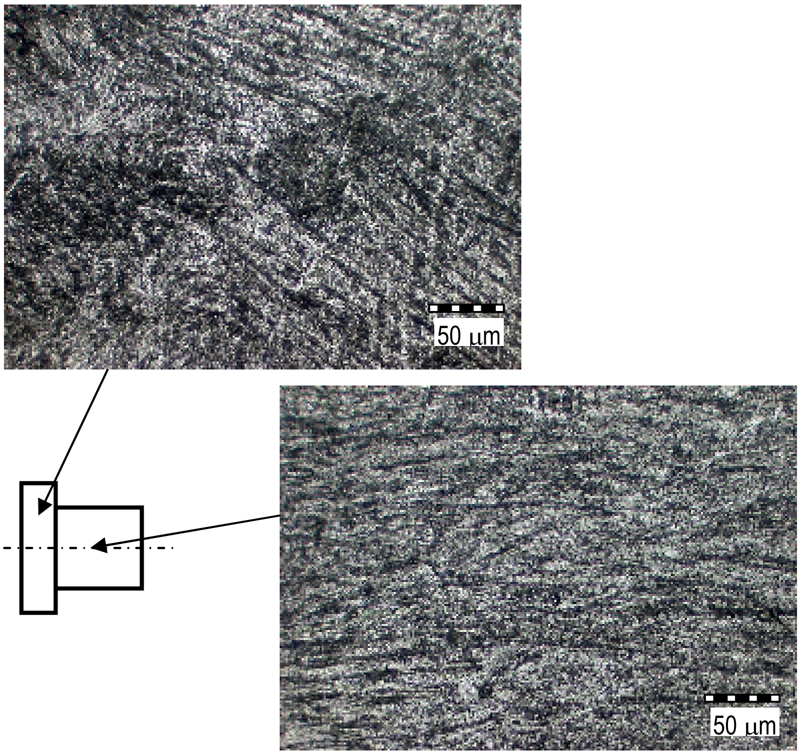

Fig. 4. *Microstructures no.1 extruded 1 from Φ18mm to Φ10mm (X200)*

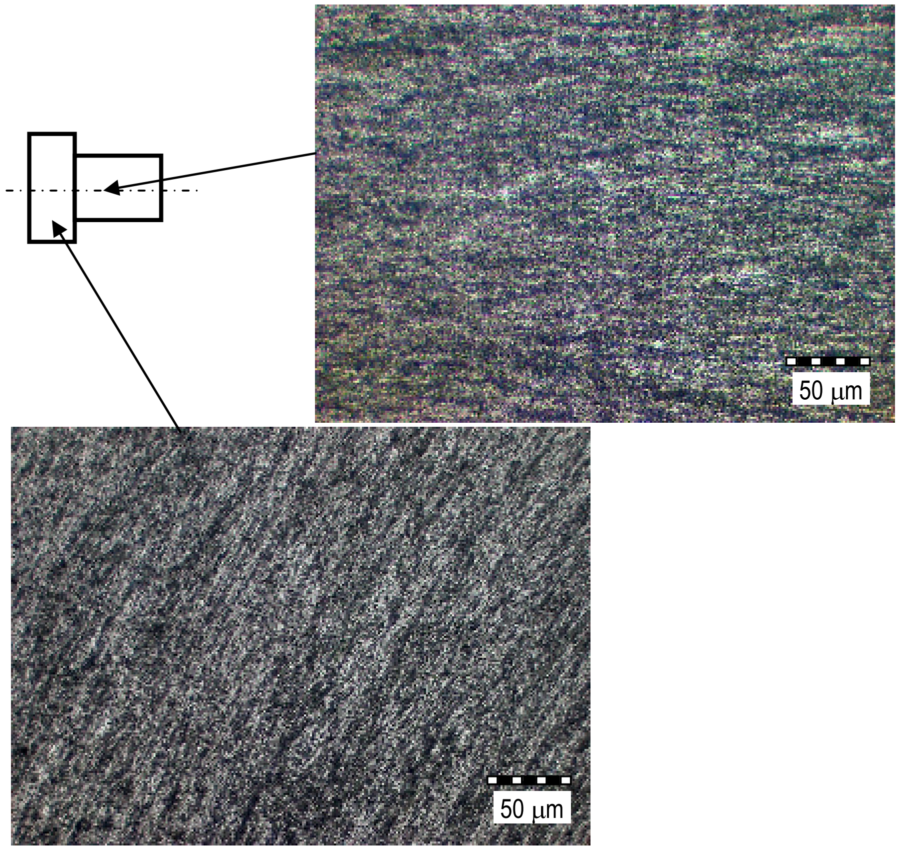

Fig. 5. *Microstructures no.2 extruded from Φ10mm to Φ5mm (X200)*

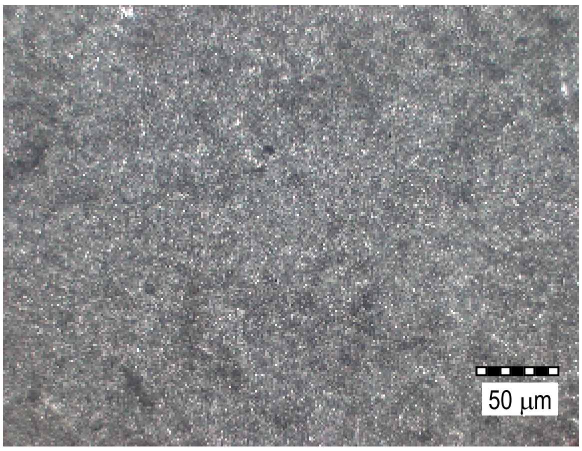

Fig. 6. *Cold rolled Microstructure from Φ5mm to Φ3mm (X200)*

Table 1

Nr.	**The blank Semi-product**	**Stage degree of deformation $C=S_{i-1}/S_i$**	**Total degree of deformation $C_T=S_0/S_i$**	**Hardness HV_{100} daN/mm^2**
1	Cast Φ18	0	0	212
2	Extruded Φ10	3.24	3.24	290
3	Extruded Φ5	4	12.96	306
4	Cold rolled Φ3	2.77	36	320

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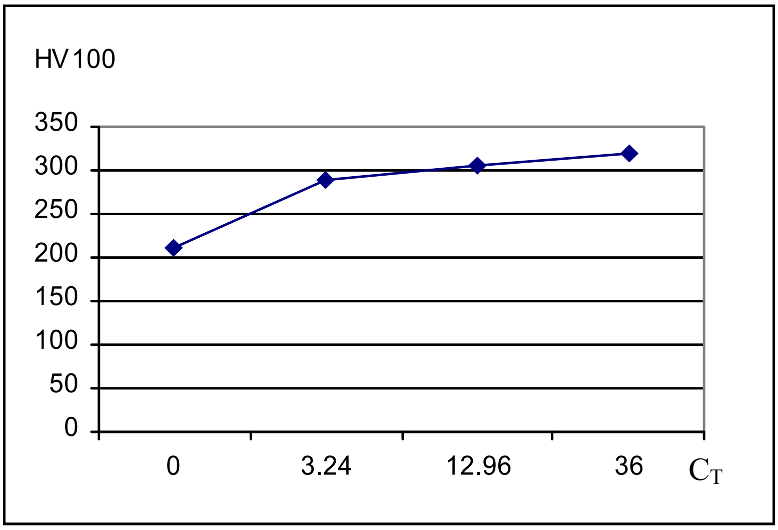

Fig. 7. *Total deformation influence on the hardness of the Ti Zr alloy*

4. Conclusions

The study and research highlight the importance of using titanium alloys both primary development and recovery of waste in the form of ingots of similar dimensions required. Improved performance of these alloys can be achieved by hot-plastic deformation and cold deformation by heat treatment. The applied technology applied to revealed smooth deformation behavior of the alloy, good plasticity and a reduced hardening trend. The deformation process ensures a fine structure and a 50% increase in hardness and strength properties.

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