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Measurement of the grain boundary energy of commercially-pure grade 2 titanium at high temperature

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Abstract The formation of grains and their growth based on the elimination of other grains, before thermal cycles are imposed, are essential for the correct conformation of a material and to control the microstructure, texture and orientation relationships between phases. However, when the boundary of a polycrystalline grain intersects the outer surface and the material is exposed to temperatures higher than half of its fusion temperature, a crack or groove appears. This research aims to apply a method to evaluate the energy of the grain boundary (GB) and also to compare the energy values of the faces of the GB, and to investigate commercially-pure grade 2 titanium in relation to the action of forces on the grain boundary of the free surface. The thermal attack under vacuum technique was used to reveal, at high temperatures, the titanium microstructure, which is preserved under a very thin oxide layer even when the sample is brought to room temperature. Thus, at room temperature, it was possible to analyze the Ti surface viewed at high temperature. The thermal cracks or grooves appearing due to the selective vaporization of atoms at the GB were measured geometrically using atomic force microscopy. The energy relationship of the GB was determined from the microstructural appearance at high temperatures and applying the equation $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi$ to the thermal crack formed between two grains.The results were compared experimentally with others reported in the literature. With the method applied in this study it was possible to evaluate the energy of the GB and it was verified that this energy was anisotropic for the material under study.

Keywords Titanium, Grain boundary energy, Atomic force microscopy, Thermal attack under vacuum.

Medida de energia de contorno de grão do titânio comercialmente puro – grau 2 – em alta temperatura

Resumo *A formação e o crescimento de grãos a partir de outros existentes, perante ciclos térmicos impostos, são fundamentais para a conformação adequada do material, para controlar a microestrutura, textura e relações de orientação entre as fases. Com o princípio da formação de uma fenda térmica á partir da exposição do material a temperaturas maiores que a metade de sua temperatura de fusão, esta pesquisa visa a comprovação de um método para avaliar a energia de contorno de grão (CG), comparar os valores da energia das faces do CG e investigar a ação das forças na superfície livre dos CGs do titânio comercialmente puro grau 2. A técnica de ataque térmico sob vácuo foi empregada para revelar, em altas temperaturas, a microestrutura do titânio, esta técnica permite a manutenção da estrutura "congelada" sob uma camada de óxido de pequena espessura mesmo quando a amostra é trazida à temperatura ambiente. Com este método foi possível analisar a superfície do Ti em temperatura ambiente, como se estivesse sendo visualizada em altas temperaturas. As trincas ou fendas térmicas provenientes da vaporização seletiva de átomos no CG foram medidas geometricamente utilizando Microscopia de Força Atômica. A energia do contorno de grão foi determinada, com aplicação da equação $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi$ entre dois grãos. Os resultados foram comparados com os da literatura. O método aplicado possibilitou a avaliação da energia do CG e a comprovação de que essa energia é anisotrópica para o material em estudo.*

Palavras-chave *Titânio, Energia de contorno de grão, Microscopia de força atômica, Ataque térmico.*

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Introduction

Titanium is an allotropic element and it has more than one crystallographic direction. At room temperature Ti has a hexagonal close-packed (hcp) structure, alpha phase (α), and at 883 °C it presents a body-centered cubic (bcc) structure, beta phase (β) (Matysina *et al.*, 1995). Thus, from a metallurgical view, titanium can be divided into three classes: α, α + β and β. The change in the crystalline structure of α to β performs an important role in defining the properties of titanium (Matysina and Chuprina, 1992).

Commercially-pure titanium has been investigated as a biomaterial considering several aspects ranging from the development of alloys to reducing or eliminating the cytotoxicity of the material (Fukuda, 2011). Also, surface modifications have been performed to enhance the osseo integration between an implant and bone tissue (Hamlet and Ivanovski, 2011; Zhang *et al.*, 2010; Variola *et al.*, 2008).Titanium has been widely studied as a biomaterial (Chang *et al.*, 2010; Choubey *et al.*, 2004; Hryniewicz *et al.*, 2009; Mendez-Vilas *et al.*, 2007) and the importance of this material has been reported, promising results being obtained with respect to the proposed objectives.

Many researchers have investigated the corrosion and mechanical properties of the metal titanium (Chang *et al.*, 2010; Choubey *et al.*, 2004; Hryniewicz *et al.*, 2009; Zhang and Jin, 2011; Matysina, 1999; Padilha, 1997). However, in the literature little attention has been given to the detailed characterization of this material in its equilibrium state (less energy: the only energy involved is the grain control), where the angle between the grains is 120° and the Ti structure tends to be hexagonal. These aspects are relevant to gaining a better understanding and developing potential applications for commercially-pure titanium.

In the case of a polycrystalline object free from various kinds of macroscopic defects and microscopic distortions, the presence of excessive free energy (the sum of the surface energy of the polycrystalline object itself and the energy of the interfaces between the elements of the structure - grains, mosaic blocks, etc.) is the only condition that stimulates processes by which the polycrystalline object approaches true equilibrium, i.e., processes tending to convert this object into a single crystal with an equilibrium boundary. Thus, when the grain boundary (GB) of a polycrystalline material intersects its external surface and the material is exposed to a temperature higher than half of its melting temperature, a crack appears due to a thermal reduction in the free energy of the system (Matysina and Chuprina, 1992).

The thermal cracks obtained from the selective vaporization of the peripheral atoms of grains were measured geometrically, using atomic force microscopy (by means of Nanoscope software) and the energy relationship of the grain boundary was determined from the microstructural appearance at high temperatures and by applying Equation 1 (Lozinskii, 1967):

$$\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi \quad (1)$$

Where γ_{gb} is the grain boundary energy of the titanium, γ_s is the surface energy of the metal / free surface, φ is the angle for each GB of a certain area selected near of the energy equilibrium.

The grain boundaries are the regions which separate two-dimensional crystals of different orientations in a polycrystalline aggregate. The differences in the approaches of neighboring grains can be tens of degrees, and this type of defect is called a high-angle grain boundary (Figure 1).

The GBs in polycrystalline materials can be revealed by chemical, electrochemical and thermal attack (Geguzin and Ovcharenko, 1962).

A certain measure of energy per area unit or surface tension is associated with the GB. This energy is almost a constant of the material, and has been related to the GB energy (Equation 1). Overall, using the control equation, the average energy of the external surface (γ) is around 0.45 to 0.75 of the energy of the material (Lozinskii, 1967).

For a given material to achieve a lower-energy state (microstructural stability), it is necessary to eliminate the energy associated with the interfaces between the grains, which remain in the material after the primary recrystallization (Hull *et al.*, 1991). Thus, the driving force behind the process of grain growth is a decrease in the interfacial free energy until the material assumes a state of minimum energy. This process occurs due to a migration of the grain boundaries of smaller grains, which tend to be eliminated, giving rise to larger grains.

According to Mullins (1958), when the material is warm enough (temperatures higher than half of its melting temperature) a microscopic crack will develop along the line where the GB intercepts the surface. The formation of a crack is dependent on the probability of the GB shrinking in order to reduce its area and hence there is a heat-induced reduction in the free energy of the system. The transport processes which lead to microscopic transformations are evaporation, surface diffusion and metric diffusion, surface diffusion being the predominant process.

After the process of grain growth at high temperatures, the material assumes a lower-energy

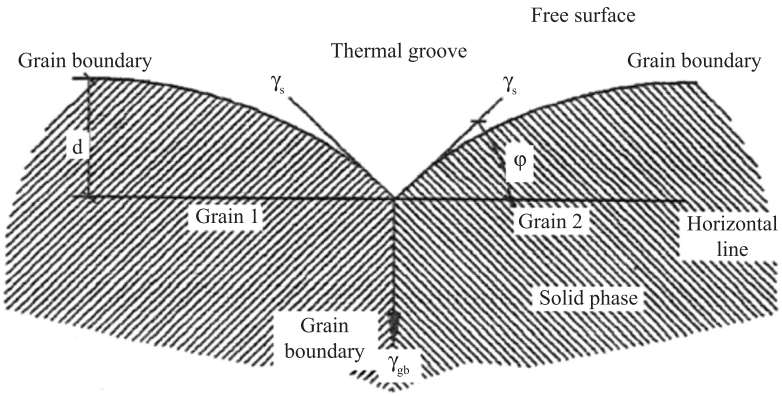

Figure 1. Illustration of a thermal groove formed between two adjacent grains. The surface energy of the metal / free surface $\gamma_s = 2\ J/m^2$.

state. An indication of the lowest energy state of a material is the hexagonal shape of one or more faces of the grain (this format is associated with an angle of 120° between the grains), where the only energy involved is the grain control. From a spatial viewpoint, the above-mentioned 120° angle (the plane) will be 109.28°, occurring between four grains (and the solid is called an orthotetrakaidecahedron, according to Geguzin and Ovcharenko (1962)).

The external surface and GB defects are important in terms of the theoretical background of material designs with commercially-pure titanium. However, the grain formation and growth from other existing grains, before the thermal cycles were implemented, are essential not only for the correct conformation of materials, but also to control their microstructures, textures and orientation relationships between phases and thus to optimize their properties.

The distribution of the orientation of the grains of the metal surface can be tested in an attempt to create more efficient textures, for example, in cases where strict control will be necessary against damage caused by various phenomena such as cavitation in pipes.

However, the area of the boundary has a thickness of two to five interatomic distances and it is a significant defective, although practically invisible. However, the grain boundaries in polycrystalline materials can be revealed by chemical, electrolytic or heat attack.

This research aims to demonstrate the feasibility of a method to evaluate the energy of a GB and compare the energy of the faces of the GB of commercially-pure grade 2 Titanium.

Materials and Methods

The material used in this study is a commercially-pure grade 2 Titanium, according to the B265-79 standard (Titanium and Titanium alloy strip, Sheet and Plate – ASTM) (Fortuna *et al*., 2000). Its atomic composition is shown in Table 1.

The grade 2 titanium sample was cut into a cylindrical shape of 4 mm diameter and 2 mm length for the optical metallography tests with thermal attack under vacuum. The sample was embedded in acrylic resin for polishing. The microstructure of the titanium was revealed after attack with the chemical reagent Kroll and it was photographed in order to view the grain boundaries and compare them with samples that had suffered heat attack at high temperatures.

After the preparation of the metallographic samples, the first test involving a heating attack was carried out, using a hot-stage microscope. In this test the controller (New Control) was scheduled to increase the temperature at a rate of 0.5 °C/s until a temperature of 1100 °C was reached and the material was maintained at this temperature for 20 minutes. It was then cooled at a rate of 1 °C/s. The vacuum was obtained in the order of 10^{-4} mmBar.

To measure the positioning of the grains which were the object of this analysis, three Vickers microhardness (HV) indentations (load of 100 gf) were made in each sample, forming a triangle on the surface. The samples were then subjected to heat attack, using a hot-stage microscope followed by observation by atomic force microscopy (AFM) to determine the angle φ between the boundaries. The appearance of microstructures due to the action of the thermal attack was observed using an image analysis system employing Adobe Photoshop 4.0 and Scion Image software.

The AFM technique was performed to measure the angle between the grain boundaries and the GB energy of the commercially-pure grade 2 titanium, under conditions close to equilibrium state.

The values for the angle φ of each of the three boundaries are shown in Table 2. In each thermal crack

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Table 1. Chemical composition (wt%) of grade 2 Titanium.

Element	% weight
H	0.0290
C	0.1060
S	0.0040
O	0.1811
N	0.0096
Fe	0.0200
Ti	99.6503

Table 2. Angle φ values for each grain boundary of a certain area selected near the energy equilibrium.

Thermal groove between the grains	Arithmetic average one side of the thermal groove	Arithmetic average on the other side of the thermal groove
1-2	15.37	16.45
1-3	15.96	12.92
2-3	16.70	14.22

of beta/beta grains, six different points were selected using Nanoscopic software, first determining a straight line crossing the perpendicular thermal crack and, on this line at the intersection with the GB. The surface topography of the sample along the Z axis could be observed. This procedure was carried out six times for each boundary and an arithmetic average of the values obtained was calculated (Table 2).

Results and Discussion

At the end of the heating, a thin oxide film, which preserved the structure obtained at high temperatures for the consequent determination of the geometry of thermal cracks, was formed, which could be observed by AFM. The image obtained during the heating is shown in Figure 2. For this analysis, the oxide film should be a very thin layer, sufficient only for a light 'freezing' of the structure. If this oxide layer is relatively thick, subsequent AFM analysis would not be viable.

Regions in the sample where the grain surface had one side of a hexagonal visible (division between grain is approximately equal to 120 °C) were selected.

The AFM technique was performed to measure the angle between the grain boundaries and the GB energy of the commercially-pure grade 2 titanium, under conditions close to the equilibrium state. A topographic image taken to calculate the GB energy is shown in Figure 3.

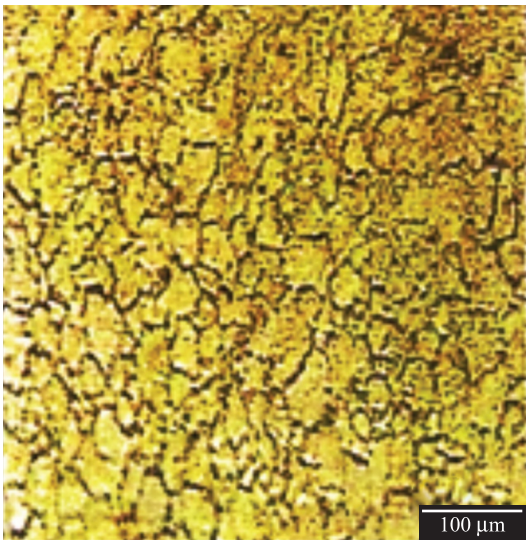

Figure 2. Photomicrographs during heating from room temperature (25 °C) to 1030 °C.

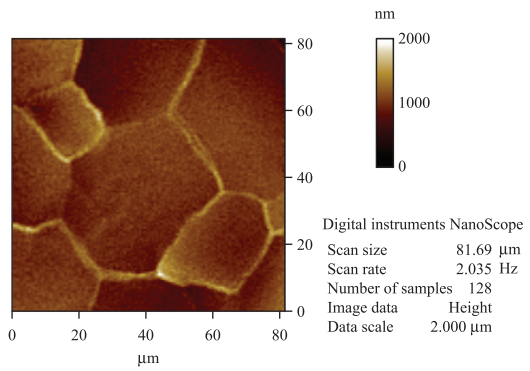

Figure 3. Topography of the grade 2 Ti obtained by atomic force microscopy.

The image processing was carried out using features of the Nanoscopic software as shown in Figure 4.

A change in the macroscopic profile can occur by means of four different mechanisms: transfer of material through the gas phase, surface diffusion, volume diffusion, and viscous flow. Regardless of which of these mechanisms is the main one under certain conditions, the direction of the process is determined by a tendency towards a decrease in the total free energy of the external surface, occurring with the conservation of the volume of the specimen.

According to Padilha (1997) the external surface of crystals and polycrystals is the crystalline defect that causes greatest disorder in the structure and therefore has more energy per area unit. This energy per area

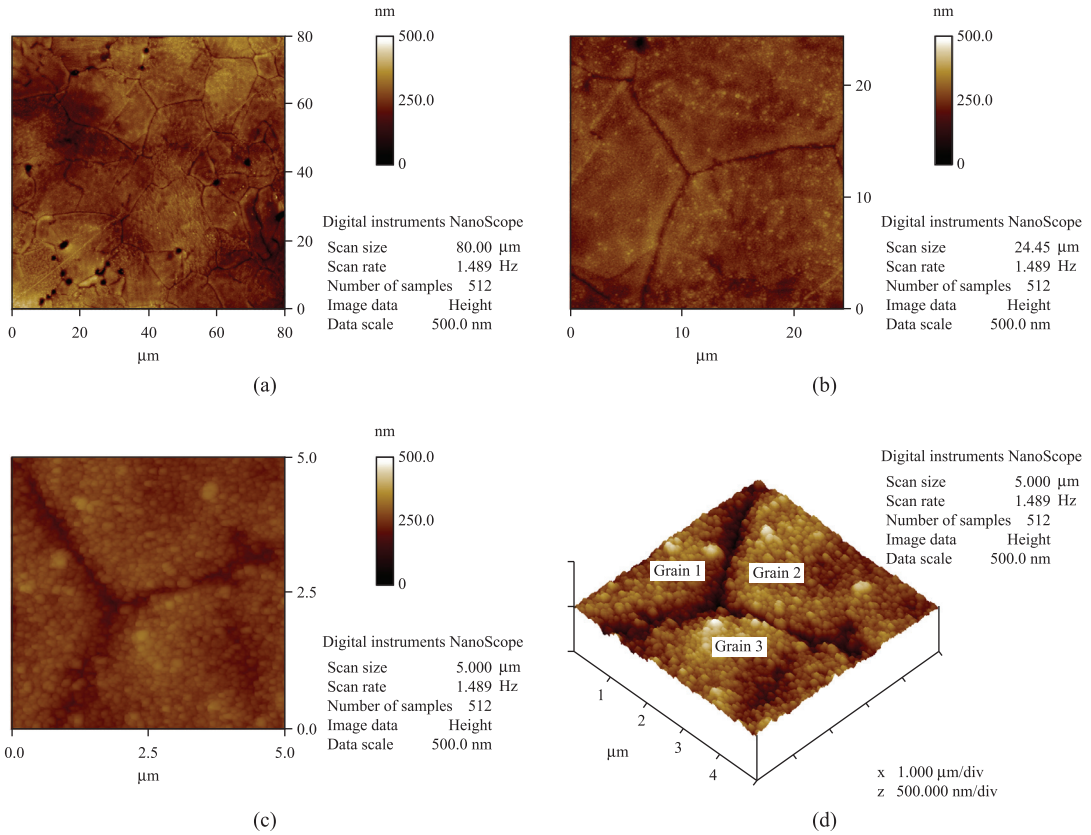

Figure 4. Sequence of images generated by the Nanoscopic software (used for processing of data and images obtained from the atomic force microscopy), through successive approximations: a) surface region selected for examination (containing grains with hexagonal sides), b) Grain boundary of 1, 2 and 3, c) Grain boundary morphology and d) Topographic image used to calculate the grain boundary energy.

unit can be understood as a surface or interfacial tension between the solid and vapor phases, and is associated with broken links on the surface, i.e., the atoms of the crystals are located on the surface, and the coordination number is approximately half that of the crystal bulk. Although the absolute value of this energy is high, its importance is not so great, since the amount of surface area per unit of volume is almost negligible. However, in some areas, such as in powder metallurgy, the amount of surface area per unit of volume is high and the surface energy plays an important role.

After obtaining the values for the angle φ of each GB (Table 2) it was possible to estimate the GB energy for commercially-pure grade 2 titanium using Equation 1. For Ti it was assumed that $\gamma_s = 2\ J/m^2$ is close to the ccf structure of iron, which has a melting point close to that of Ti. Table 3 shows the results for the GB energy.

The values shown in Table 2 are consistent with those reported in the literature. According to Padilha (1997), the energy of the GB is around 0.45 to 0.75 of the surface energy γ_s for a given material, which was confirmed by the data in which the grain energy obtained for titanium ranged from 0.45 to 0.57 of its surface energy.

On increasing the temperature up to 1100 °C it was found that the energy of the GB has different

Table 3. Energy of grain boundary of commercially-pure grade 2 titanium, after increasing its temperature to 1100 °C.

For the thermal crack formed between the grains:
Grain 1 and Grain 2
Side 1: $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi = 2 \times 2 \times Sen15.37 = 1.06\ J/m^2$
Side 2: $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi = 2 \times 2 \times Sen16.45 = 1.13\ J/m^2$
Grain 1 and Grain 3
Side 1: $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi = 2 \times 2 \times Sen15.96 = 1.10\ J/m^2$
Side 2: $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi = 2 \times 2 \times Sen12.92 = 0.89\ J/m^2$
Grain 2 and Grain 3
Side 1: $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi = 2 \times 2 \times Sen16.70 = 1.15\ J/m^2$
Side 2: $\gamma_{gb} = 2 \cdot \gamma_s \cdot \text{sen}\varphi = 2 \times 2 \times Sen14.22 = 0.98\ J/m^2$

behaviors for the two faces. This verifies the anisotropic energy of the GB, where γ_{gb} is the grain boundary energy of titanium, γ_s is the surface energy of the metal / free surface, and φ is the angle for each GB of a certain area selected close to the energy equilibrium (Table 3).

Conclusions

In this study, commercially-pure grade 2 titanium was investigated by hot-stage microscopy and atomic force microscopy (AFM) analysis. For this material, a precise knowledge of the surface structure at high temperatures and measurement of the grain boundary energy are essential to correctly analyze its interactions with different kinds of cells. The use of hot-stage microscopy to monitor the microstructural evolution of titanium, from room temperature (25 °C) to high temperatures (1100 °C), allowed the observation of its microstructure, texture and orientation relationship between phases. The AFM analysis was used to observe the surface roughness and to determine the grain boundary energy by measuring the angle between the grain boundaries of commercially-pure grade 2 titanium under conditions close to the equilibrium state. The energy values for the grain boundary of the titanium, found experimentally by analyzing the geometry of grooves formed after the heating cycle using hot-stage microscopy, are around 0.45 to 0.57, and are in agreement with values reported in the literature. Through this study it was possible to demonstrate a method for evaluating the energy of the grain boundary and determine that its behavior is consistent with an anisotropic sample.

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