EFFECT OF HEAT TREATMENT ANNEALING OF TITANIUM IN WETTABILITY

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Abstract. *Due to its excellent combination of properties (physical and chemical), titanium and its alloys are materials widely used in biomedical applications. Determine the contact angle and surface tension of these surfaces is of fundamental importance to predict and/or control the behavior of biomedical devices since the adhesion and growth of cells on surfaces since these events are strongly influenced by the balance hydrophilicity/hydrophobicity (wettability). In this study samples of titanium in form of discs were subjected to annealing at 700 ° C at different times and subsequently studied the contact angle formed by three liquids: water, formamide and glycerol. With these measured values it was possible to calculate the surface energy using the approach of Fowkers that determine the degree of hydrophilicity of the surface of heat-treated material. It was observed that the disks annealed for 8 h showed the best result of wettability well as presented more hydrophilic.*

Keywords*: Titanium, Wettability, Heat Treatment, Annealing, Surface Energy,*

1. INTRODUCTION

The biomaterials are as old as medicine itself. However in last decades research and applications for such materials have risen sharply mainly by the need to replace or enhance parts of the body. Another possible reason for this growth are technological advances that resulted from the interdisciplinary approach of physicists, chemists, engineers and biomedical scientists and clinical research (Hanker and Giammaria, 1988).

Currently many biomaterials researchers focus his work in developing surface changes especially in titanium. Seeking improvements in the properties of biocompatibility, techniques such as nitriding, oxidation and deposition by plasma, etching, plasma, heat treatment, among others are widely used to modify the topography and in some cases, the surface chemistry (Browne, 1994; Hanawa, 1999). Usually the heat treatment aimed at modifying the microstructure, and consequently, the mechanical properties of alloys. Annealing is a heat treatment in which a material is exposed to high temperature for a prolonged period of time and then cooled slowly. Annealing is usually carried out in order to stress relief making the material softer, ductile and tenacious and/or to produce a specific microstructure (Callister, 2002).

Knowledge of physical and chemical properties of the titanium surface is of fundamental importance for the study of biocompatibility. Properties such as surface energy and wettability play an important role in protein adsorption, increasing the formation of focal adhesions by osteoblasts (Schneider, 1994; Macdonald, 2002) at the implant surface and consequently playing a key role in the bioactivity. Considering the roughness and wettability interference with the processes of protein adsorption it is possible that cells are strongly influenced by both (Macdonald, 2002).

The cellular behavior on biomaterial surfaces depends on the interaction cell-implant correlated with surface properties such as hydrophilicity, roughness, texture, chemical composition, charge and morphology, strongly affect cellular responses in contact with the implant (Oshida, 1994). Hallab et. al. (2001) showed that the surface free energy was the most important feature in the adhesion and proliferation than the surface roughness and that the components of the surface energy of the different materials tested proved to be related to the strength of cell adhesion. Schakenraad et. al. (1988) concluded that despite the large number of parameters that influence cell adhesion and spreading the free energy of a solid surface is apparently a dominant factor in cell adhesion.

The relative importance of wettability in spreading fibroblasts was studied by Webb et. al. (1998). It was demonstrated that the cell adhesion and spreading were significantly higher in hydrophilic surfaces than hydrophobic surfaces, and moderately hydrophilic surfaces promoted greater levels of cell adhesion. Den Braber et. al. (1995) evaluated the effect of microgrooves parallel and surface energy on cell growth. The most significant finding was that physical and chemical parameters such as hydrophobicity and surface free energy influence cell growth. Georgi et. al. (1996) showed that cell proliferation increased with increasing wettability of material.

Based on the importance of studying the properties of wettability and surface tension of Biomaterials the present work studied the effect of annealing on the wettability of discs CP titanium. There are many works that relate these properties to the biological response of the implanted material (Schakenraad et. al. 1988; Webb et. al. 1998; DenBraber et. al. 1995; Georgi et. al., 1996) and suggest heat treatment that can be used to obtain a good biological response. However in this work was not carried out biological tests and suggestions to be here presented are based on test results already made available in the literature.

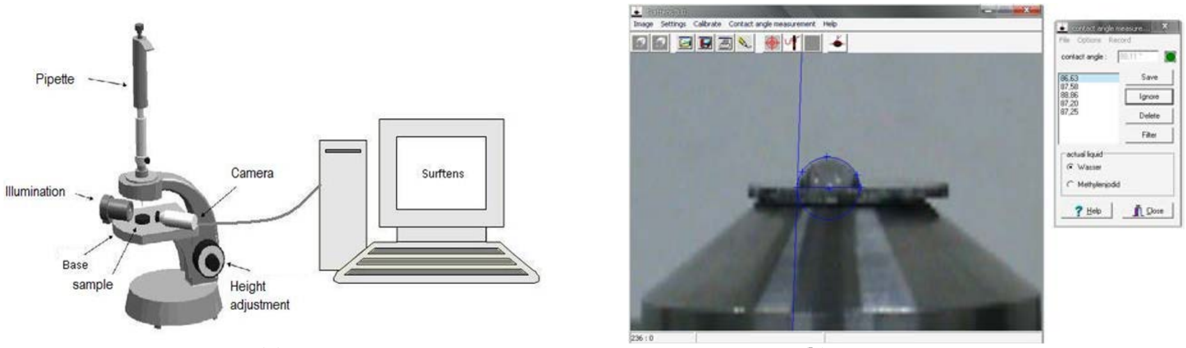
2. **MATERIALS AND METHODS**

This work used 12 discs of CP titanium grade 2 measuring 15m in diameter and 1mm thick. The samples were divided in three groups and subjected to the annealing using resistive furnace with different times of treatment according to “Table 1”. After heat treatments, the disks were prepared metallographic and chemically attacked with Kroll solution.

Table 1. Notations and description of the heat treatments.

Symbol	Heat treatment	Temperature - Time	Cooling
A700-1h	Annealing	700° - 1h	Oven
A700-4h	Annealing	700° - 4h	Oven
A700-8h	Annealing	700° - 8h	Oven
NT	Untreated	-	-

Before the wettability assay the disks have undergone a rigorous process of cleaning with enzymatic detergent, absolute ethyl alcohol and distilled water, 10 min each. The technique used in determining the contact angle is the sessile drop Figure 1a, the liquids used were water, formamide and glycerol. Image acquisition was made using the software Pinnacle studio 8.5 and the measuring of contact angle was performed using the software Surftens 3.0 “Figure 1b”.



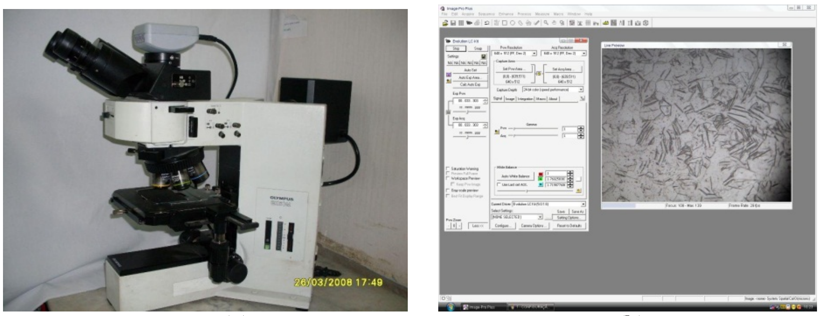
(a) (b)

Figure 1. Schematic of the goniometer used to determine the contact angle (a) and illustration software Surftens 3.0 (b).

To calculate the surface tension was used to approach Fowkers “Equation 1”, which relates the cosine of the angle θ, with the coordinates of the surface tension of the liquid and the coordinates of tension substrate. Where: γ_l - tension total surface of the liquid; γ_l^d - coordinated dispersive surface tension; γ_l^p - coordinated polar surface tension of the liquid; γ_s^d- coordinated dispersive surface tension of solid analysis, γ_s^p - coordinated polar surface tension of solid analysis.

$$\left[\frac{1+\cos\theta}{2}\right]\times\left[\frac{\gamma_l}{\sqrt{\gamma_l^d}}\right]=\left[\sqrt{\gamma_l^p}\right]\times\left[\frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}}\right]+\sqrt{\gamma_l^d} \quad (1)$$

We used the microscope Olympus BX 60M, coupled with a digital camera and Image Pro Plus software for image acquisition “Figure 2”.



(a) (b)

Figure 2. Illustration of microscope Olympus BX 60M (a) and Ilustration of software Image Pro Plus (b).

3. RESULTS

The “Figure 3” shows the results of the behavior of the contact angle of water for the treatments of annealing. It was noted that the treatment A700-1h showed higher contact angle (81.91 °) and the treatment A700-8h the lowest value (52.19 °). The A700-4 h treatment showed similar values to samples without treatment at around 62° that means there was no significant difference in wettability for these two cases even occurring microstructural changes of grain size for example.

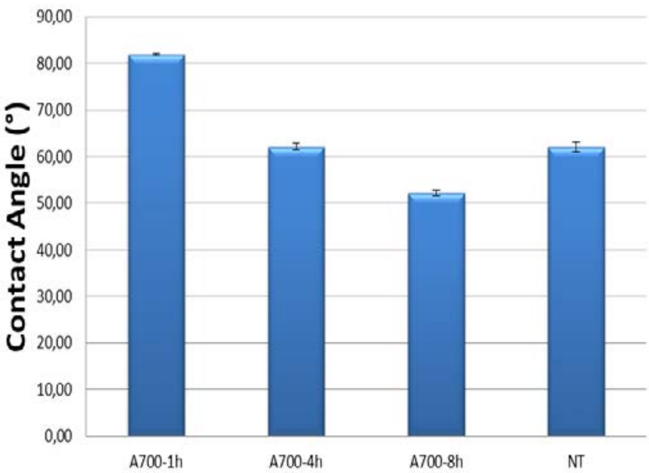


Figure 3. Results of contact angle to water after 60 seconds of accommodation of drop.

The “Tabel 2” shows the mean values of contact angles for three liquids used and measured from the sessile drop method. Considering only water as wetting liquid was observed that treatment A700-8h showed the lowest contact angle, ie, this treatment can be regarded as the best chance of having a good biological response. It was also noted that the samples treated by 8h had the lowest contact angle for the three liquids.

Table 2. Mean values of contact angles for the treatment of annealing.

Liquids	A700-1h	A700-4h	A700-8h	NT
Water	81,91+/-0,22	62,15+/-0,65	52,19+/-0,65	62,09+/-0,52
Formamide	56,65+/-0,76	52,03+/-0,8	48,31+/-0,81	34,56+/-5,6
Glycerol	79,99+/-0,61	76,85+/-0,68	76,13+/-0,54	57,15+/-1,65

Measurements of contact angles indicate that all surfaces are moderately wettable. However, the surface energy components indicate different degrees in relation hydrophilicity/hydrophobicity this relationship is seen as a strong influence on the cell adhesion and proliferation. The “Figure 4” clearly shows that the samples treated R700-8h had a disperssive character (high value γ^d). It can also be observed that the treatment R700-8h had a higher value for γ_s and the prevailing characteristic polar (γ^p) instead of dispersive feature (γ^d). There are studies that relate the influence of component (γ^p) of surface energy with cell adhesion (Ma, et. al. 2003; Wan, et. al. 2003; Tezcan, et. al. 2003; Hallab, et. al ., 1995). So we suggest using long times of annealing if the interest is biological application.

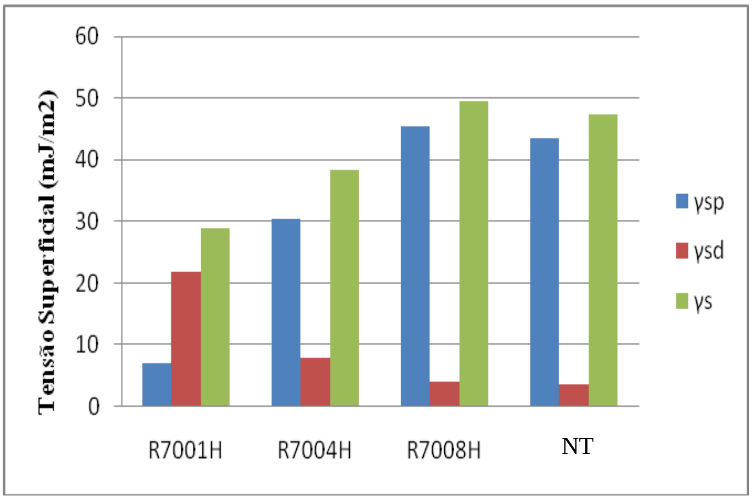


Figure 4. Components of surface energy γ_s - total energy, γ^p - polar component, γ^d - dispersive component for the treatment of annealing.

The influence of annealing time on microstructure can be seen in “Figure 5”. Note that the grain size increased significantly. Therefore, it is possible to characterize the material after treatment as single phase with an average diameter of grain (~28.83μm to NT sample and de ~ 108.41 to A700-8h sample, ie there was an increase of ~ 376%), where obviously the increase ingrain size is due to longer periods of annealing.

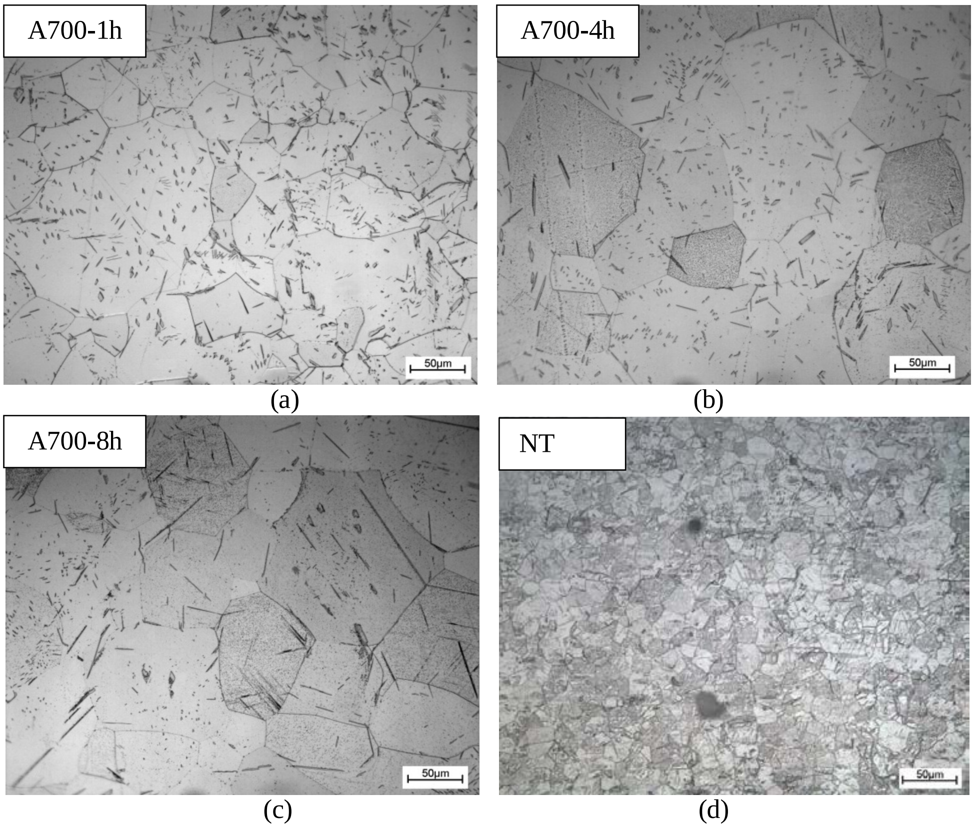


Figure 5. Microstructure of titanium sample using a optical microscope. Samples treated A700-1h(a) treatment A700-4h (b) treatment A700-8h(c) and sample untreated NT (d).

Observing the micrographs “Fig. 5” and the values of contact angles “Figure 3”. It is perceived that the larger the size of the grains smaller the contact angles, ie the long time annealing may have influenced the Wettability since these treatment modified the microstructure and internal stress in the material. Likewise, we can correlate the increase in polar component “Fig. 4” with the increase of grain size, ie, the larger the grains the greater the value of polar component in the surfaces of the discs treated.

3. CONCLUSION

The results showed that the annealing heat treatment influenced the wettability of Ti samples. This type of treatment provides a reduction of internal stress arising the thermo processing undergone by the samples, increasing the grain size. All samples presented moderately wettable. A range of possibilities between the polar and dispersive components of surface energy was obtained by heat treatments. Therefore with the results obtained here can say that the A700-8h treatment showed the best wettability for water as well as the highest value for the polar component among all other treatments could result in a good biological response. We suggest that in vitro biological tests are performed on disks treated for long periods of time.

4. ACKNOWLEDGEMENTS

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6. RESPONSIBILITY NOTICE

Jussier de Oliveira Vitoriano, Haroldo Reis Alves de Macêdo, Marina de Oliveira Cardoso Macêdo and Clodomiro Alves Junior are the only responsible for the printed material included in this paper.