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Effect of heat treatment on microstructure and mechanical properties of Ti30Ta alloy for biomedical applications

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Abstract: As life expectancy increases, further research is needed to develop new materials for biomedical applications. Titanium and its alloys have great potential to be used for such a purpose due to their excellent bulk properties, such as mechanical strength. However, these properties are influenced by their microstructure which varies according to the processing method. Thus, this research aims to evaluate the influence of heat treatment on phase transformation and mechanical properties of Ti30Ta alloy which has been made in an arc melting furnace. The heat treatment has been carried out at 750°C, 800° C and 850°C for 12 hours, followed by water quenching. The β-*transus* temperature was determined by Differential Scanning Calorimetry and High Temperature X-ray diffraction. The phases and structure have been investigated through optical microscopy, scanning electron microscopy and X-ray diffraction. Microscopy images and X-ray diffraction analysis reveal the presence of martensitic phase α'' for the solution treated sample and both α'' and α' phases for recrystallized samples. Mechanical tests show an increase in mechanical strength for all samples after recrystallization and the highest value was observed for the sample treated at 750°C, although there was an undesirable increase of 30 GPa in Young Modulus.

Keywords: Titanium Alloys. Mechanical Properties. Biomaterials. Heat Treatment.

Introduction

In the latest years, new materials must be studied for biomedical implants, since life expectancy has been increasing. Over 500.000 hip replacement surgeries have been performed worldwide from the beginning of this century[1]. Nowadays, biomedical implants are made by using many materials, e.g. metals, ceramics, and polymers. The most common metallic materials used in prosthesis manufacture are stainless steel, cobalt-chromium (Co-Cr) alloys and titanium alloys [2]. However, when implanted into the body, elements like nickel, cobalt and chromium can be released into the patient's body due to corrosion and aggressive environment, thus bringing about toxic effects, as stated by Nicholson [2].

Despite to the toxicity of these materials, stainless steel (200 GPa) and Co-Cr (220 GPa) alloys have a much higher elastic modulus than the human bone (20-30 GPa). This difference of properties can result in an effect called stress-shielding which is an insufficient bone load that leads to bone resorption, implant failure and even another fracture. Thus, according to Kaur and Singh [3], titanium and titanium alloys are ideal replacements for hard tissues due to their lower modulus, higher biocompatibility and corrosion resistance.

In the 1960s, the most widely used titanium alloy in aeronautical applications was Ti-6Al-4V due to desirable properties such as mechanical strength and corrosion resistance. Afterwards, it started being used as material for biomedical applications. However, many studies confirm that its toxicity increases with time due to the fact that Al and V ions are released into the body, which may cause diseases, like Alzheimer's and local pain as stated by Kaur and Singh [3].

Thus, there are new lines of research for developing new titanium alloys without using aluminum (Al-free), such as Ti13Nb13Zr studied by Pérez *et al.*[4], Ti45Nb studied by Völker *et al.*[5], Ti15Mo studied by Chen *et al*. [6] and Ti70Ta [7].

Due to the broad difference between the elastic modulus of pure titanium and pure tantalum when compared to the elastic modulus of bone, these metals cannot be used in their pure form. Thus, an alternative is to use Ti-Ta binary alloys whose mechanical properties can be improved by adding the alloying element tantalum, thence not compromising biocompatibility as studied by Zhou *et al*.[7]. When tantalum was used as an alloying element, Zhou *et al.*[8] verified it acts as a β-stabilizer, which improves the stability field of the β phase and assists in the formation of the α'' martensitic phase, which has a lower elastic modulus and marginally lower mechanical strength than the other phases, thus allowing an improvement of these mechanical properties trough heat treatments and resulting in an alloy which possesses high strength-to-modulus ratio.

A potential replacement for biomedical applications is the Ti30Ta alloy which, according to Zhou *et al*.[8], has a low elastic modulus (69 GPa), high mechanical strength and a high strength-to-modulus ratio when compared to currently used alloys. According to Zhao *et al.* [9], its corrosion resistance is higher than that of Ti-6Al-4V alloy.

Thereby, purpose of this study is to evaluate the influence of heat treatment on phase transformation and

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mechanical properties of the Ti30Ta alloy using different processing routes. It has great potential for biomedical applications and the manufacturing process usually involves plastic deformation at a set temperature, which is generally higher than the β–*transus* temperature. Thus, it is interesting to evaluate its behavior so as to simulate these conditions.

Experimental procedure

Ti30Ta alloy processing

The binary Ti30Ta was processed using sheets of Ti (grade 2) and Ta (99.99%). All ingots were melted and remelted over ten times due to having different melting points. Then, they were homogenized under vacuum at 950°C for 24 hours in order to eliminate any residual chemical segregation and worked into bars of 10 mm in diameter by cold swaging. Bars were treated under vacuum at 900°C for 2 hours and then water quenched.

The subsequent treatments were carried out at 750°C (R750), 800°C (R800) and 850°C (R850) for 12 hours followed by water quenching.

A DSC analysis was carried out so as to determine the β–*transus* temperature. For such a purpose, it was used a small sheet made with the Ti30Ta alloy in a platinum crucible, and one crucible was used as reference (empty). Under vacuum, the system was heated from room temperature to 1000°C and then cooled and registered at 100°C. A plate of 0.2 mm in thickness was cut from the solution treated and heat treatment was performed at 750°C, 800°C and 850°C.

A high temperature X–Rays diffraction analysis was carried out with the purpose of determining the α to β phase transformation. It was performed using a Copper Kα irradiation at temperatures ranging between 15° and 100°, accelerating voltage of 40kV, current of 30mA at 0.2°/sec of scanning speed and a heating rate of 2°C/min using a PANalytical equipment, model X'Pert Pro.

The alloy's microstructure was analyzed using a Zeiss optical microscope, model Axio Imager.Z2m, and a Zeiss scanning electron microscope (SEM), model Evo LS–15, operated at 20kV. The samples were ground with sandpaper whose grit sizes ranged between 220 and 1500, polished with colloidal Silica and etched in a solution composed of 5 vol.% HF, 35 vol.% HNO_3 and 65 vol.% H_2O. Phase identification was performed by means of X–Ray diffraction analysis of bulk samples at room temperature using Copper Kα irradiation between 15° and 100°, accelerating voltage of 40kV and current of 30mA at a scanning speed of 0.2°/sec in a PANalytical equipment, model Empyrean.

Tensile specimens were machined by following the specifications laid down by the ASTM E 8M with 6mm in diameter and gauge length of 25mm. A strain gage was attached to the gage section of each specimen. A uniaxial tensile test was conducted at speed of 0.5mm/min and room temperature using a MTS 810 testing system and a MTS– 632.24C–50 extensometer.

Microhardness test of samples were the same as those which had been previously used for microstructural characterization. Vickers microhardness was measured with a Shimadzu model HMV 2T microdurometer and conducted with 1.961N of load for 15s.

Results and discussion

For the initial characterization of the alloy, samples were used in the following conditions: as cast, after homogenization treatment (24 hours at 950°C), after cold swaging and after solution treatment (2 hours at 900°C). During the melting process, the alloy surface in contact with the copper crucible underwent rapid cooling while the surface that was not in contact with the crucible which was slowly cooled. The resulting microstructure under such condition was a two–phase dendritic structure, due to the different cooling rates on the sample, which can be seen in Fig.1 (a). The homogenization treatment turned the microstructure into a secondary stable two–phase acicular α structure spread over a β matrix structure which had also been observed by Du *et al.* [10] and can be seen in Fig.1 (b). The cold swaging caused a severe plastic deformation in the alloy microstructure, but it has not altered the present phases, which is shown in Fig.1(c). The solution was then treated, thus resulting in a martensitic α'' phase and removing the structural deformation caused by cold working (Fig.1 (d)).

β phase formation temperature, also known as β–*transus*, has been studied using High Temperature X–Ray diffraction and DSC analysis. The high temperature X–Ray diffraction analysis showed a stable α" phase until reaching 600°C and a β phase was formed at 700°C and higher temperatures (Fig. 2). In the DSC analysis, endothermic reactions were defined as upright peaks and exothermic reactions were defined as downright peaks, whose results can be seen on Figure 3 which shows an exothermic reaction at 650°C followed by an endothermic reaction at 750°C. This means that there has been transformation from phase α to β, thus β–*transus* temperature is 700°C for this alloy. According to Mantani and Tajima[11], for CP Ti, the β phase is stable between 800 and 1000°C, which indicates that the addition of Ta has led to β phase stabilization at lower temperatures.

Optical microscopy images show the α'' phase decomposition into α› and β phases during heat treatment recrystallization, which can be seen in Fig. 4 (a) as one phase only and in (b), (c) and (d) as two phases. According to optical microscopy, the solution treated sample exhibits only one phase (α") while recrystallized samples show two phases (α" and α'). The same result was obtained by Zhou *et al*. [8] who submitted the alloy to heat treatment at a lower temperature.

Figure 1– SEM images of the Ti30Ta alloy in the following conditions: (a) as cast (100x) (b) homogenized (5000x) (c) after cold swaging (5000x) (d) after solution treatment (1000x).

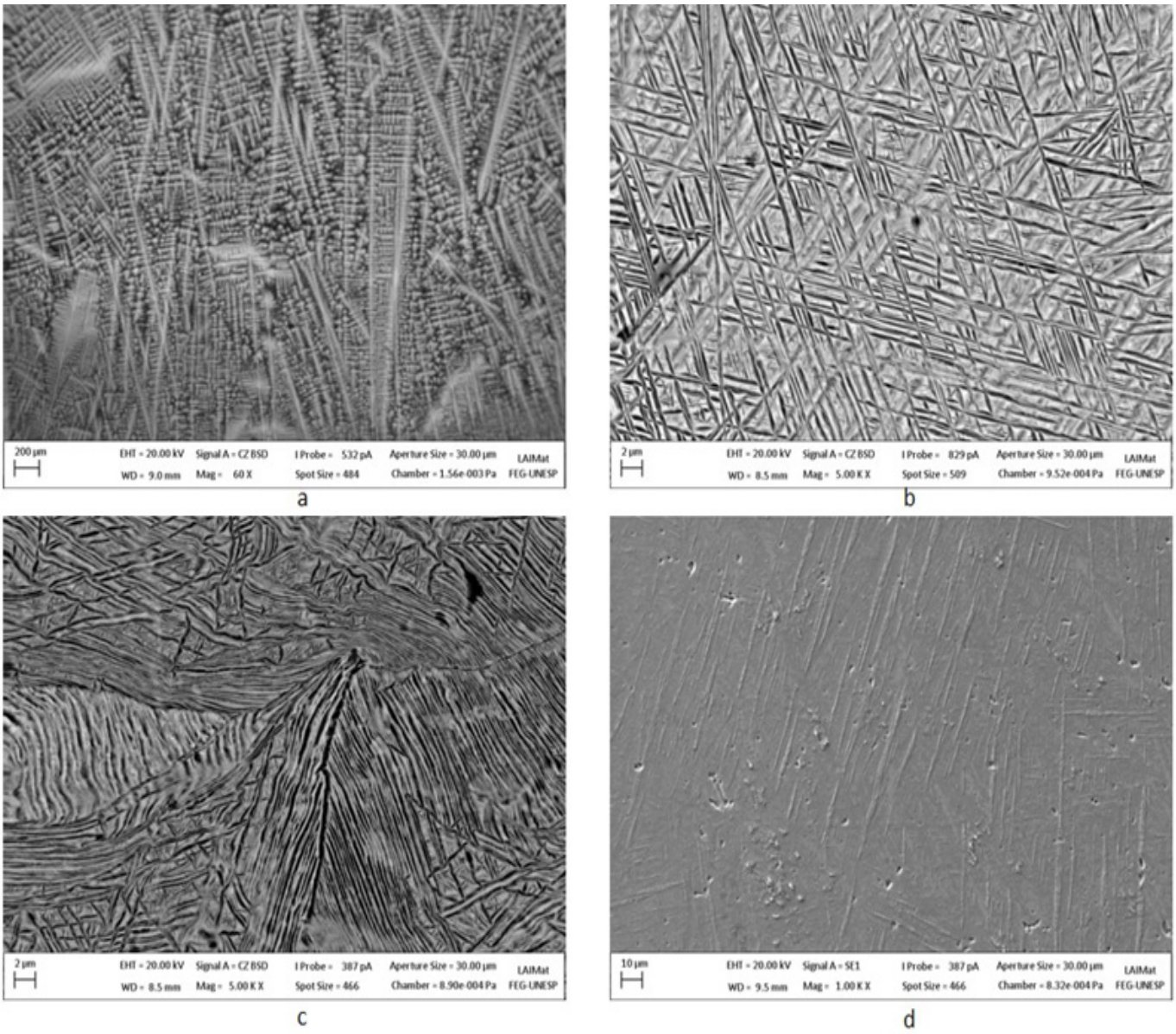


Figure 2 – High temperature X–Ray diffraction analysis of the Ti30Ta alloy after solution treatment at 900°C for 2 hours.

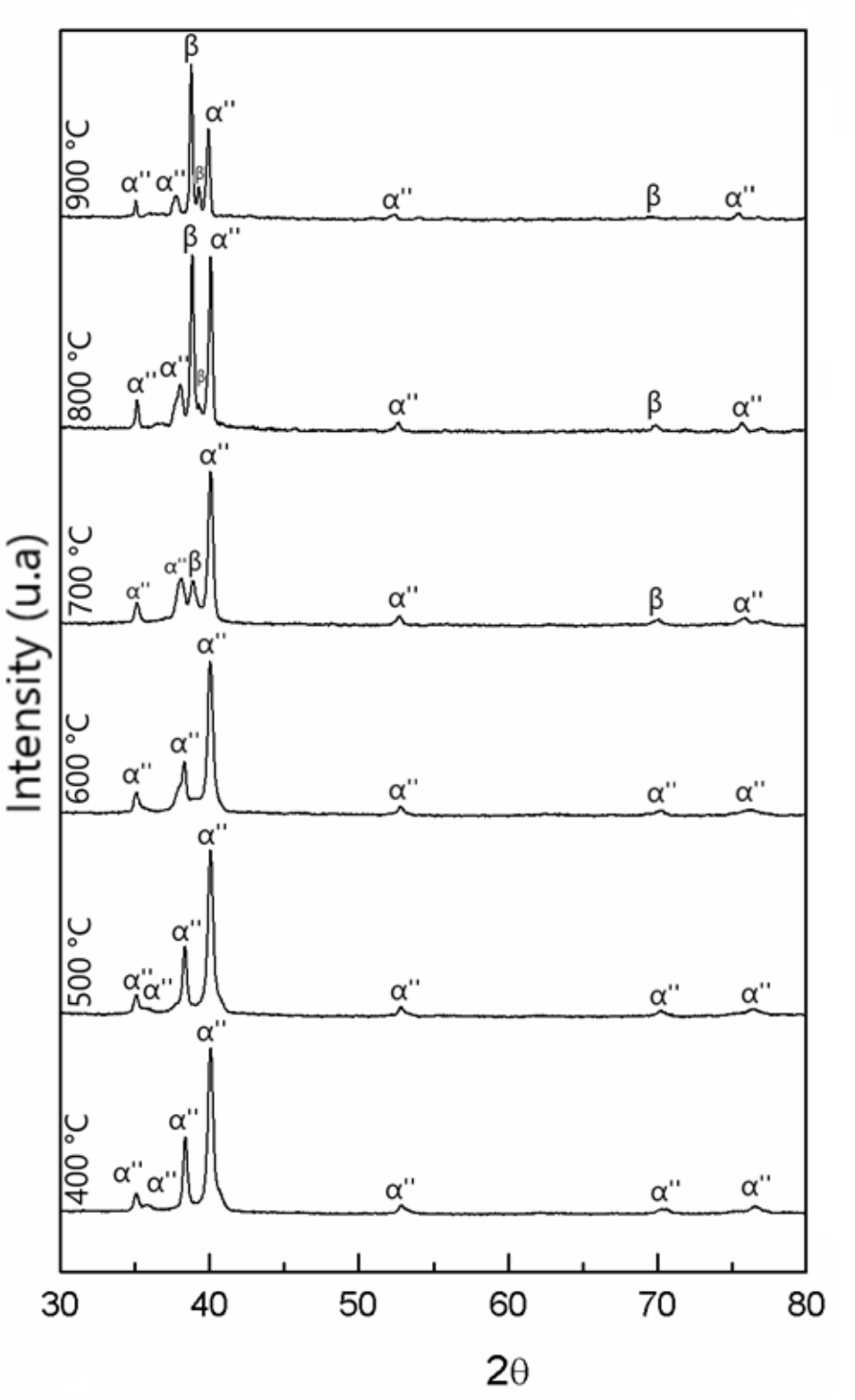


Figure 3 – DSC analysis of the Ti30Ta alloy after solution treatment at 900°C for 2 hours.

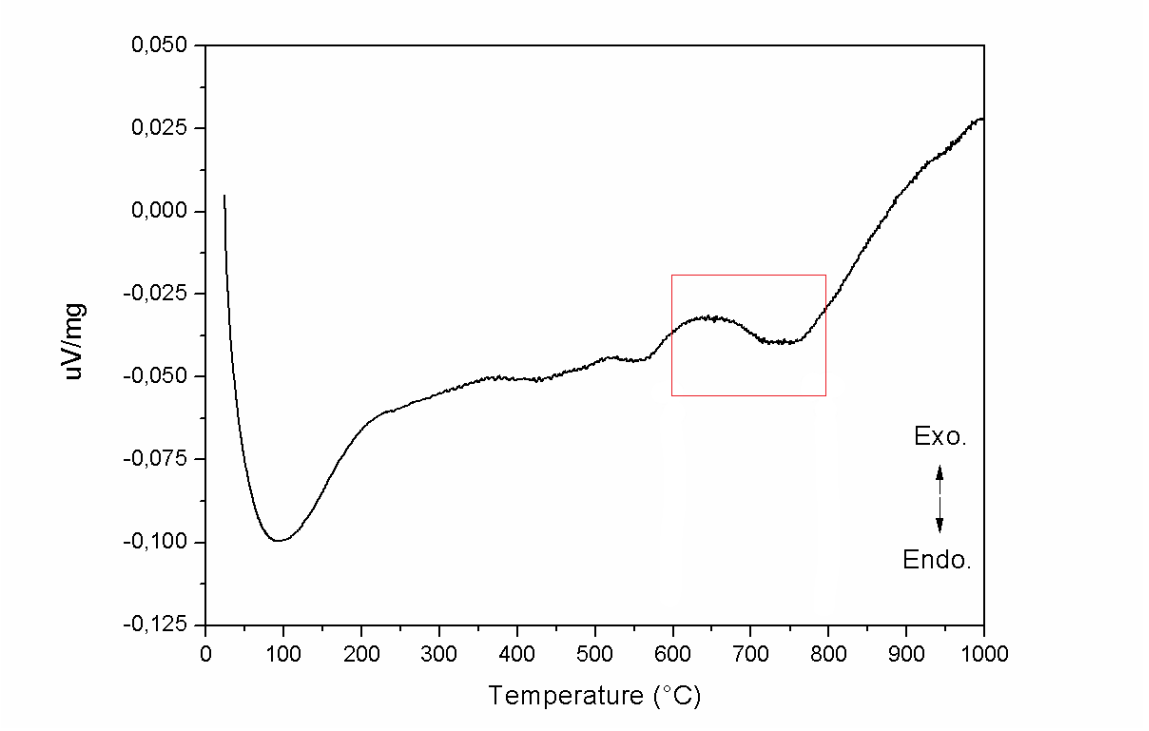
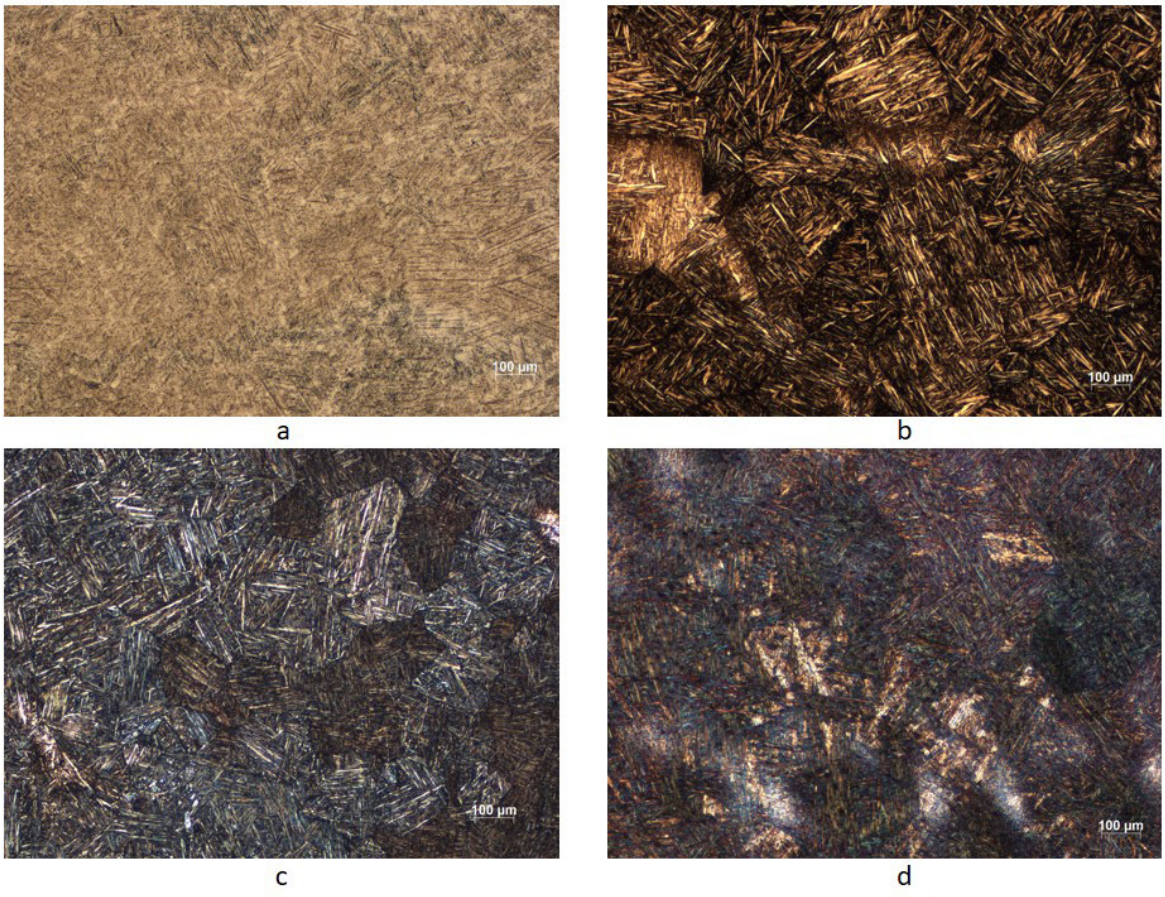
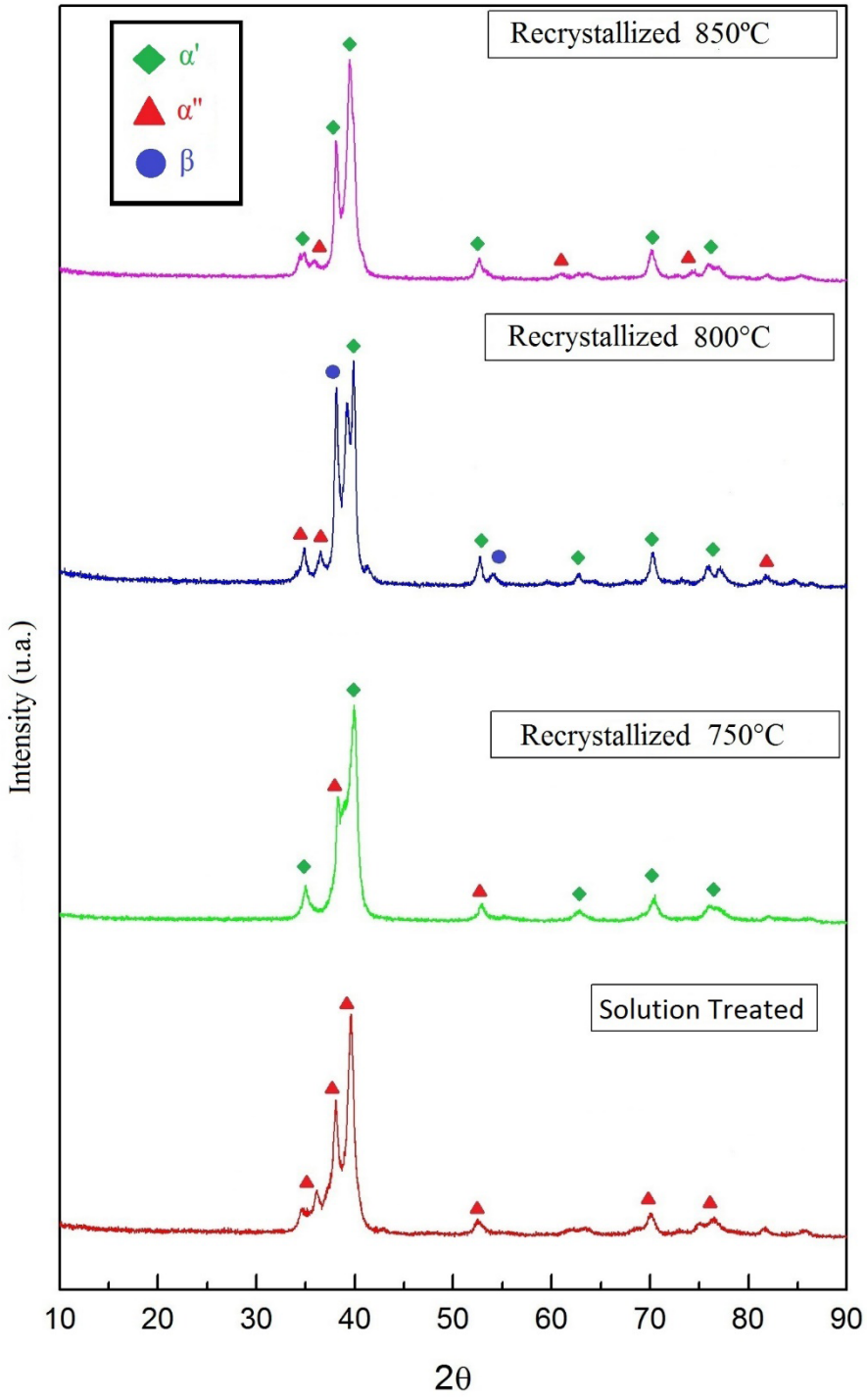


Figure 4 – Optical Microscopy images for Ti30Ta samples: (a) solution treated (b) recrystallized at 750°C for 12 hours (c) recrystallized at 800°C for 12 hours and (d) recrystallized at 850°C for 12 hours.



An X–Ray diffraction analysis was carried out in order to investigate the phases present in all samples, whose results are shown in Figure 5. Its results indicate that an α'' phase was formed for the solution treated sample due to rapid cooling, but there was no time for atomic diffusion and the entire structure transformed into a martensitic α'' phase. Furthermore, Zhou *et al*.[8] has obtained the same result while studying the α" phase decomposition on Ti–Ta binary system alloys. After recrystallization, the X–Ray diffraction analysis of samples have revealed the presence of both martensitic α'' and α' phases, which occurs due to heat treatment temperature and time. When structure β was quenched in water, there was little time for atomic diffusion, thus partially forming α' phase and α'' phase, which has also been observed by Zhou *et al.*[8] when this alloy underwent heat treatment at lower temperatures. According to Zhou *et al.*[12], α" phase decomposition is sensitive to both heat treatment temperature and tantalum content. Matsumoto *et al.*[13] studied a microstructure formed after performing heat treatment using the alloy Ti35Nb4Sn and observed that

Figure 5 – X–Ray diffraction patterns of Ti30Ta samples under the following conditions: solution treated, recrystallized at 750°C, recrystallized at 800°C and recrystallized at 850°C.



the transformation from α'' to β does not follow the same crystallographic path from β to α''. This is an explanation for the α' phase formation during its decomposition.

The results of tension tests are shown in Figure 6, through which it is possible to observe a different mechanical behavior by the alloy under the studied conditions.

According to Hao et al.[14]. the Young modulus of a multiphase material is sensitive to the individual modulus of each phase and their volume fractions, but it is not affected by precipitate or grain sizes. Thus, in a multiphase material, the Young modulus will be strongly influenced by the difference between each phase's modulus. According to Lee et al.[15], the α" phase has a lower Young modulus than the α' phase.

The values of mechanical properties of the alloy in the studied conditions are shown in Table 1, through which it is possible to observe a higher ultimate tensile strength (UTS) by the sample recrystallized at 750°C when compared to other samples on account of the presence of the α" phase and a higher fraction of α' phase. The solution treated sample presented lower UTS, lower Young modulus and higher deformation rate due to the presence of α" phase only. Samples recrystallized at 800 and 850°C have intermediate properties due to a balance between α" and α' phases. These properties make this condition suitable for biomedical applications due to the fact that they are closer to human bone features when compared to CP Ti or Ti–6Al–4V.

Table 2 shows the microhardness test results which are in agreement with the Tension tests results, thus exhibiting higher mechanical strength for the sample recrystallized at 750°C and lower mechanical strength for the solution treated sample.

Figure 6 – Tensile behavior of Ti30Ta samples in the following conditions: solution treated (ST), recrystallized at 750°C (R750), recrystallized at 800°C (R800) and recrystallized at 850°C (R850).

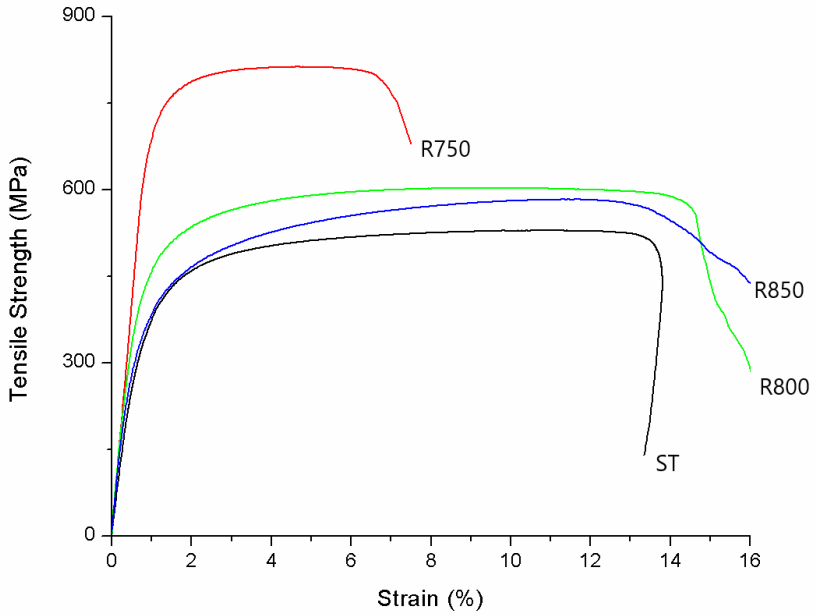


Table 1 – Mechanical properties of Ti30Ta samples in the following conditions: solution treated (ST), recrystallized at 750°C (R750), recrystallized at 800°C (R800) and recrystallized at 850°C (R850)

	Ti30Ta	**Ti30Ta Recrystallization**		
	Sol. Treated	750 °C	800 °C	850 °C
UTS (MPa)	528	812	602	582
σ_e (MPa)	357	711	423	360
E (GPa)	48	80	67	51
ε (%)	13,2	6,8	14	14,8

Table 2 – Microhardness values of Ti30Ta samples in the following conditions: solution treated (ST), recrystallized at 750°C (R750), recrystallized at 800°C (R800) and recrystallized at 850°C (R850).

Sample	Microhardness (HV)
Sol. Treated	194 ± 6,76
Recrystallized 750 °C	282 ± 15,65
Recrystallized 800 °C	227 ± 7,21
Recrystallized 850 °C	213 ± 10,76

Conclusion

The present study investigated how recrystallization heat treatment affects phase transformation, which has revealed the mechanical properties of the Ti30Ta alloy.

In conclusion, high temperature XRD and DSC analyses have determined *β–transus* temperature for the Ti30Ta alloy, i.e. 700°C.

The heat treatment of the solution has removed the structural deformation caused by rotary swaging and formed a new phase: the martensitic α'' phase. Subsequent recrystallization heat treatments have formed another phase, the α' phase, in addition to the α'' phase. Both phases have been identified by the XRD analysis, optical microscopy and scanning electron microscopy.

Mechanical tests showed a significant increase in the tensile strength for the sample recrystallized at 750°C when compared to the other samples, although there was also an unwanted increase in Young's modulus. Therefore, the solution treated sample showed the lowest Young's modulus and high tensile strength, thus being the most suitable for biomedical implants and a promising replacement for mechanical processing due to increasing tensile strength without compromising Young's modulus.

For this material, ideal conforming procedures should be carried out below the *β–transus* temperature, i.e. below 700°C, in order to avoid working the material at higher levels of strength and hardness.

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