1. Introduction

The increase in life expectancy of the population has led to a greater number of older people and this in turn, has increased the demand for materials suitable to biomedical implants. It is estimated that through 2030 will be performed only in the United States per year approximately 272,000 total hip replacements. Biomaterials used for replacement implants have to combine excellent biocompatibility with appropriate mechanical properties. The biocompatibility of a metallic implant is directly determined by its corrosion resistance and the biological effects of released metallic ions. These effects are diverse: cytotoxicity (inducing cell or tissue death), genetic damage or immune response. On the other hand, the most important mechanical requirements for metallic biomaterials are: low Young’s modulus, high yield strength and ultimate tensile strength, good fatigue resistance and sufficient ductility. A low value of Young’s modulus is required in order to minimize the modulus mismatch between implant and surrounding bone tissues. Indeed, this stiffness mismatch can induce the stress shielding phenomenon. Stress shielding occurs where the metal carries a majority of applied load, leaving the more compliant tissue almost unstressed. This will lead to the undesirable effect termed bone disuse atrophy, a form of osteoporosis, around the implant site.

Moreover, the metallic alloys used for implants are also required to have high yield strength in order to support the complex stresses applied to the implants during their lifetime. In general, yield strength and Young’s modulus vary in opposite way for metallic materials. Lower Young’s modulus corresponds to lower yield strength. Therefore, it is necessary to find the best compromise between these two mechanical properties. For this reason, yield strength to Young’s modulus ratio is often used as key indicator in order to evaluate the mechanical performance of metallic biomaterials for implant applications.

The more conventional metallic materials used as orthopedic implants are: stainless steel, Co-Cr alloys and commercially pure Ti (cp) and its alloys. In this last class, the most widely used is the Ti-6Al-4V alloy. The literature indicates that long term health problems would be associated with the release of Al and V ions from the Ti-6Al-4V metallic implants into the human body. The presence of V ions into tissues can alter the kinetics of the enzyme activity associated with the

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inflammatory response cells\cite{18} whereas presence of Al ions increases the potential for the development of Alzheimer’s disease\cite{19}. Eisenbarth et al.\cite{20} mention, on the other hand, that vanadium is toxic both in elemental form and as oxides.

For these reasons, a number of studies have recently focused on the development of metastable β-type Ti alloys with non-toxic elements such as Mo, Zr, Sn, Ta and Nb\cite{21,22,23}. In addition to an excellent corrosion resistance in human body fluids, β-type titanium alloys exhibit lower Young’s modulus than α and α + β alloys. Moreover, the control of thermomechanical processing parameters permits to obtain the microstructure conferring the optimum yield strength to Young’s modulus ratio to the alloy. Typical mechanical properties of conventional metallic biomaterials and β-type Ti alloys are shown in Table 1\cite{24}. In comparison with stainless steel and Co-Cr alloys, β-Ti alloys exhibit a much lower Young’s modulus and a much higher yield strength to Young’s modulus ratio.

Studies realized by Gabriel et al.\cite{26} on the processing of the Ti-12Mo-13Nb alloy with equivalent concentration of molybdenum (15.4) showed that the highest specific hardness modulus ratio was obtained in the condition aged at 500 °C/24 h and this ratio is higher than for Ti-6Al-4V alloy. Therefore, Ti-12Mo-13Nb alloy has a high potential to be applied as a bone substitute in places subjected to mechanical loading. Moreover, a recent in vitro research indicates that the Ti-Mo-Nb alloys show a very good biocompatibility\cite{27}. However, additional studies are needed to optimize the mechanical behavior of the Ti-12Mo-13Nb alloy.

Thus, the aim of this project is to analyze the microstructure and the mechanical behavior of Ti-12Mo-13Nb alloy hot forged and aged for biomedical applications aiming to replace Ti-6Al-4V alloy currently used.

2. Material and Methods

2.1. Material preparation

The Ti-12Mo-13Nb alloy was prepared from commercially pure Ti with the addition of Mo and Nb in an arc melting furnace with a tungsten electrode on a water-cooled copper hearth. The alloy was prepared in a high purity argon atmosphere and the ingot was re-melted five times to improve chemical homogeneity. The obtained ingot (40 g) was solution-treated at 1000 °C under high vacuum for 24 h and this ratio is higher than for Ti-6Al-4V alloy. Therefore, Ti-12Mo-13Nb alloy has a high potential to be applied as a bone substitute in places subjected to mechanical loading. Moreover, a recent in vitro research indicates that the Ti-Mo-Nb alloys show a very good biocompatibility\cite{25}. However, additional studies are needed to optimize the mechanical behavior of the Ti-12Mo-13Nb alloy.

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| Alloy            | YM (GPa) | YS (MPa) | strength-to-modulus ratio(×10⁻³) | EL (%) |
|------------------|----------|----------|----------------------------------|--------|
| V 316(stainless steel) | 379      | 793      | 2.1                              | 22     |
| (Co–Cr–Mo)       | 220      | 448      | 2.0                              | 8      |
| Ti (cp)          | 103-104  | 170-485  | 1.6-4.7                          | 15-24  |
| Ti–6Al–4V        | 124      | 896      | 7.2                              | 13-16  |
| Ti–50Ta (aged)   | 77       | 612      | 7.9                              | 11.6   |
| Ti–13Nb–13Zr (aged) | 79-84  | 836-908  | 10-11.5                          | 6-10   |
| Ti–15Mo (annealed)| 78       | 544      | 7.0                              | 21     |
The bright-field micrograph of aged Ti-12Mo-13Nb alloy obtained by TEM is shown in Figure 2. After the aging treatment, fine α precipitates (in white) with platelet morphology were observed dispersed in the β matrix. These precipitates are a few nanometers thick and a few hundreds of nanometers long.

3.2. Mechanical characterization

The values obtained for the measurements of Young’s modulus using the nanoindentation technique were 140 GPa for the reference Ti–6Al–4V alloy and 110 GPa for β-Ti–12Mo–13Nb alloy. This indicates a 21% reduction in the Young’s modulus of the alloy described in the present work.

The lower Young’s modulus of the Ti-12Mo-13Nb alloy can mainly be attributed to the Mo and Nb atoms in solid solution. Niobium and molybdenum have high solubility in titanium but also larger atomic radius. The calculated atomic radius is 248 pm for Ti whereas it is 320 pm for Nb and 306 pm for Mo. At the contrary, the atomic radii of Al and V are smaller, respectively 118 pm for Al and 171 pm for V[30]. It has been shown that a decrease of Young’s modulus is associated with the presence of substitutional atoms with larger atomic radius in the Ti lattice. This presence reduces the binding force of the lattice by expanding unit cell volume[31].

Figure 3 shows the stress-strain curves at room temperature for the aged Ti-12Mo-13Nb alloy and the Ti-6Al-4V alloy.

The obtained yield strength, ultimate tensile strength and elongation are given in Table 2 along with Young’s modulus and yield strength on Young’s modulus ratio values for both tested alloys.

The strengthening effect of fine α precipitation during the 24 h aging heat treatment at 500 °C gives a higher strength to Ti-12Mo-13Nb alloy compared to Ti-6Al-4V alloy.

On the other hand, Young’s modulus does not only depend on chemical composition but it depends also on the applied thermomechanical process.

For β-Ti alloys, aging treatments induce a strengthening of the material due to fine α or ω phase precipitation but this precipitation also leads to an increase of Young’s modulus. This increase is much more important for α phase precipitation than for ω phase precipitation[3,32]. The structural characterization by XRD and transmission electron microscopy has shown that the aging heat treatment at 500 °C during 24 h avoids the precipitation of the most deleterious ω phase and permits so to obtain the highest yield strength to Young’s modulus ratio with only the fine precipitation of α phase. However, this fine precipitation also induces a lower ductility for the aged Ti-12Nb-13Mo compared to Ti-6Al-4V alloy. Nevertheless, the elongation of 6% at rupture, revealed by the tensile test, indicates that the aged Ti-12Nb-13Mo does not show any brittle behavior. On the other hand, a high ductility is, in fact, only required for the forming operations. Therefore, the Ti-12Nb-13Mo alloy has to be hot or cold formed before the aging treatment when its structure consists of 100% of more ductile β phase. In this work, the material was hot swaged at 900 °C-1000 °C. This range of temperatures lies inside the stability area of β phase.
### Table 2. Mechanical properties of Ti-6Al-4V and aged Ti-12Nb-13Mo alloys.

| Alloy       | YM (GPa) | YS (MPa) | UTS (MPa) | strength-to-modulus ratio($\times 10^{-3}$) | EL (%) |
|-------------|----------|----------|-----------|--------------------------------------------|--------|
| Ti–6Al–4V   | 140 ± 3.36 | 930      | 966       | 6.6                                        | 14.2   |
| Ti-12Nb-13Mo (aged) | 110 ± 2.62 | 981      | 1111      | 8.9                                        | 6.3    |

### 4. Conclusions

The results show that the Ti-12Mo-13Nb alloy hot forged and aged at 500 °C for 24 h presented a microstructure consisting of very fine dispersed α phase in a β matrix and consequently with good mechanical properties. The values obtained for the ratio of strength to Young’s modulus of the present alloy are higher than those of the commercially available Ti-6Al-4V alloy. The results indicate that Ti-12Mo-13Nb alloy is competitive compared to the other β-Ti alloys listed in Table 1 and can be a promising alternative for biomedical applications.

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