

Development of Cu-bearing powder metallurgy Ti alloys for biomedical applications

L. Bolzoni, F. Yang

WaiCAM, School of Engineering, The University of Waikato, Private Bag 3105, 3240 Hamilton, NZ

Corresponding author. Tel. +64 7 8379381 Fax. +64 7 8384835

E-mail address: bolzoni.leandro@gmail.com (L. Bolzoni).

Abstract

Cu-bearing Ti alloys could be used as structural biomedical materials where the releasing of Cu ions is beneficial to lower infection incidences associated with surgical implants. The manufacturing of these alloys via powder metallurgy techniques can lower the production costs. In this study three ternary Cu-bearing Ti-xAl-yCu alloys were produced using conventional powder metallurgy. The mechanical properties increase with the amount of alloying elements. Samples of each composition were also forged to clarify the effect of subjecting them to hot deformation. Forging the samples improved the strength of the alloys due to the reduction of porosity and the refinement of the microstructural features. It is found that the Ti-2Al-1Cu is the most ductile, Ti-6Al-4Cu is the strongest and Ti-10Al-5Cu has a purely elastic behaviour. Some of these powder metallurgy Ti-xAl-yCu alloys have better overall mechanical behaviour than their cast counterparts and therefore are valuable alternative to produce medical and dental implants with improved properties and reduced cost.

Keywords: Ti alloys, powder metallurgy, hot deformation, mechanical properties, antibacterial alloy

1. Introduction

The combination of its properties makes titanium ideal for advanced applications such as those related to the aerospace and medical sectors [1, 2]. Ti is a clear choice as structural biomaterial and for dental implants due to its bioinert nature [3, 4] where alpha, alpha+beta and beta Ti alloys are used. Alpha alloys and pure Ti in particular are used due to their excellent corrosion resistance. Alpha+beta alloys, especially the well-established Ti-6Al-4V alloy, are known for their remarkable combination of mechanical properties (strength and ductility). Finally, beta Ti alloys are being developed to address the issue of the stiffness difference between metallic implants and human bones. Regardless of the type of Ti alloy, prosthesis bacterial infection occurring during surgery is a raising issues and infection incidences can be as high as 16% [5]. Alloying with Cu, and in particular the release of Cu ions once the material is implanted, prevents bacterial infection. Nonetheless, the only Cu-bearing commercial alloys is the Ti-2.5Cu, also known as IMI230, which was mainly obtained via thermomechanical deformation to produce billets, bars and rods [6].

Cast Cu-bearing binary Ti alloys have then been considered for dental application as Cu allows the production of low melting point cast alloys [7]. Kikuchi et al. [8] studied the variation of the mechanical properties of cast Ti-xCu (where $x = 0.5-10$ wt.%) achieving an increase of tensile strength of 30% and yield strength of 40% over commercially pure Ti in the Ti-5Cu alloy. Kikuchi et al. [9] also studied the variation of the elastic modulus of cast Ti-xCu (where $x = 5-30$ wt.%) with the Cu content where the increase in Young's modulus of the Ti-Cu alloys was speculated to be due to the precipitation of the Ti_2Cu intermetallic compound. Renewed interest has lately been shown due to the antibacterial activity of Cu where the production and characterisation of binary Ti-Cu alloys manufactured either through conventional metallurgy (i.e. ingot casting in a vacuum non-consumable furnace with six remelting operations [10]) or via sintering (i.e. hot pressing: 5-35 MPa at 850-1080°C for 30-60 min [7]) has been investigated.

The antibacterial ability of Cu has also been sought by studying the addition of Cu to the well-known alpha+beta Ti-6Al-4V alloy. Specifically, Ren et al. [5] investigated the corrosion behaviour and cell viability of cast Ti-6Al-4V-xCu (where $x = 1-5$ wt.%) proving that the addition of Cu resulted in materials with obvious antibacterial ability and excellent corrosion behaviour and cytocompatibility. Wang et al. [11] quantified the tribological behaviour of cast Ti-5Cu and Ti-6Al-4V-5Cu which resulted to be better than the counterpart materials not alloyed with Cu. However, the cytotoxicity of Cu should also be taken into account during the development of medical implants.

Powder metallurgy (PM) is nowadays recognised as green technology and has intrinsic processing advantages (e.g. high material yield) to be able to be used to reduce the materials cost [12] and it is used to design low-cost Ti alloys [13, 14]. Despite these advantages, and the fact that the level of porosity can be changed to tailor the mechanical properties, such as the stiffness, and the bone ingrowth ability [15, 16], PM has highly been disregarded as manufacturing method for biomedical products [17] with antibacterial capability, as casting is commonly used [18, 19]. The work of Liu. et al. [7], who used hot pressing, is one of the few exceptions in the case of Ti alloys containing Cu for biomedical applications. Therefore this study focuses on investigating the production and properties of Cu-bearing Ti alloys via the simplest PM process of pressing and sintering. As the primary aim is to quantify the structural properties of these new alloys, the effect of post processing the PM alloys using hot deformation via forging was also studied. Design of the chemical composition was done on the basis of the binary Ti-Al and Ti-Cu phase diagrams aiming to create Cu-bearing near-alpha and alpha+beta Ti alloys with increasing Al and Cu content.

2. Experimental Procedure

Commercially available powders of hydride-dehydride (HDH) titanium, electrolytic copper, and atomised aluminium were used to produce the alloys. Table 1 shows relevant physical characteristics of the raw powders. Three ternary Ti-xAl-yCu compositions were targeted and they were designed to be near-alpha (Ti-2Al-1Cu) and alpha+beta (Ti-6Al-4Cu and Ti-10Al-5Cu) alloys. If not otherwise indicated, compositions are in weight percentage (wt.%). The theoretical density of the Ti-xAl-yCu alloy shown in Table 1 was calculated using the rule of mixture. The density is higher than that of pure Ti and proportionally increases with the amount of Cu added due to higher density of the latter; however, the Ti-10Al-5Cu alloy has lower density as a consequence of the high amount of Al. The irregular morphology of the HDH Ti powder, which constitutes the great majority of the blend, would guarantee that the powder mixtures can successfully be shaped into solid green compacts.

Table 1. Physical characteristics of the raw powders and designed Ti-xAl-yCu compositions.

| Material | Property | | | |
|-------------|-----------------------------|------------|--------------------------------------|------------|
| | Density [g/cm^3] | Morphology | Max size, D_{90} [μm] | Purity [%] |
| Ti | 4.51 | Irregular | < 90 | > 99 |
| Al | 2.70 | Spherical | < 45 | 99.7 |
| Cu | 8.96 | Sponge | < 63 | > 99 |
| Ti-2Al-1Cu | 4.52 | Blend | < 90 | > 99 |
| Ti-6Al-4Cu | 4.58 | | | |
| Ti-10Al-5Cu | 4.55 | | | |

Powders were mixed in a V-blender at 30 rpm for 30min. 40mm diameter samples were shaped by cold uniaxially pressing the powder for 10s at approximately 700 MPa. Sintering was conducted at 1250°C under vacuum. The heating rate used was 10°C/min and samples were held at temperature for 2 h before furnace cooling. Preheating the samples via induction heating for their forging at 1050°C was done in an inert atmosphere chamber where the oxygen level was kept below 200 ppm.

The applied open die forging ratio resulted in the reduction of the height of the original size of ~30%. As per their binary phase diagrams [20], both the sintering and the forging temperature are in the β field. Figure 1 shows the sketch of the manufacturing route employed.

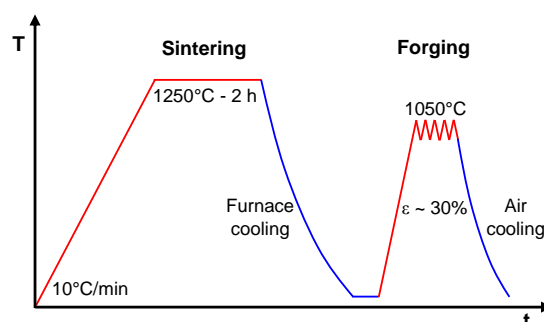


Figure 1. Sketch of the manufacturing route used for obtaining the Ti-xAl-yCu alloys.

Samples for metallographic analysis were prepared following the classical method including grinding and polishing and finally etched with Kroll reactant (2 ml HF, 6 ml HNO₃ and 92 ml H₂O). The microstructure was characterised using optical microscopy (Olympus BX60F5), scanning electron microscopy (Hitachi S4700) equipped with an energy dispersive X-ray spectrometer (EDS) detector used to perform elemental mapping and elemental chemical analysis, and X-ray diffraction (XRD, Philips X'Pert diffractometer). XRD patterns were obtained using: Cu K α radiation, scanning range of 30° to 100°, and scan step size of 0.013°. Mass to weight ratio and Archimedes methods were, respectively, used to determine the density of green samples and sintered and forged specimens. The dimensions were measured using a 2-decimal digital calliper whilst weight measurements were performed on a 4-decimal scale. The shrinkage and densification of the samples due to their sintering was determined via volume variation and the densification parameters [13], respectively. Dogbone-shaped tensile samples (2x2x20 mm³) were cut via electro-discharge machining.

Tensile tests were done on an Instron 33R4204 machine using a loading rate of 0.1 mm/min meanwhile the elongation was measured via an external mechanical extensometer. The offset method was used to calculate the yield strength of the materials.

3. Results

Representative results of the microstructural analysis of the sintered samples are shown on Figure 2 where it can be seen that residual porosity is present and the phases constituting the alloys are α -Ti and β -Ti. The amount of porosity increases with the percentage of alloying elements and is mainly spherical in shape, which is associated with the last stage of sintering. Due to increased amount of Cu, the microstructure gradually transforms into fully lamellar with finer microconstituents and a relative higher amount of β -Ti phase present. The microstructure is the typical of alpha+beta Ti alloys such as Ti-6Al-4V and Ti-6Al-7Nb which are readily used as biomedical materials [21-23].

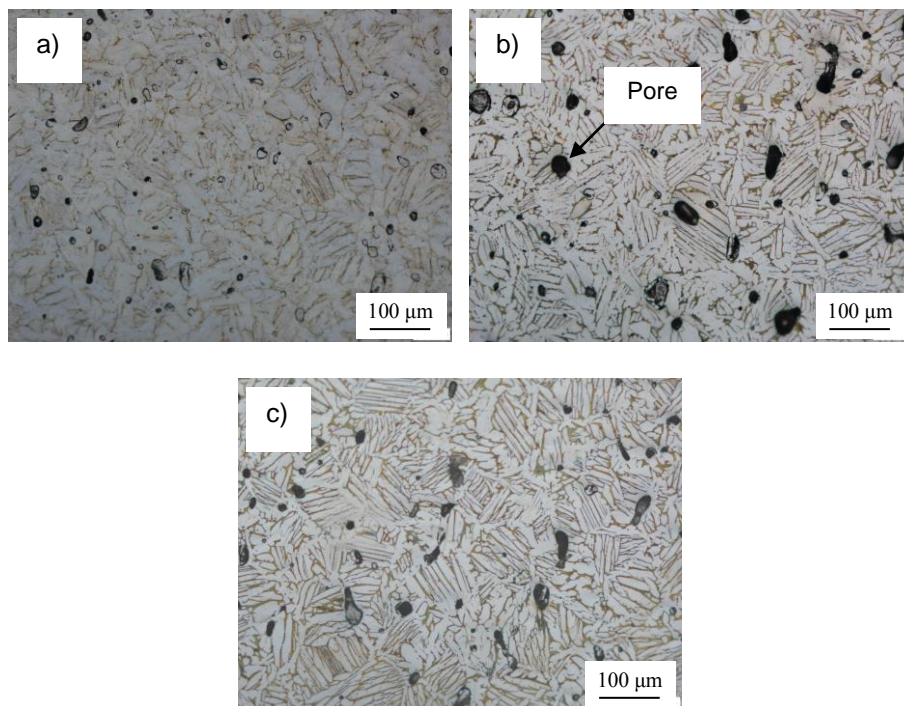


Figure 2. Optical micrographs of the sintered samples: a) Ti-2Al-1Cu, b) Ti-6Al-4Cu, and c) Ti-10Al-5Cu alloy.

Microstructural analysis of the forged samples (Figure 3) reveals quite significant differences with respect to the sintered samples (Figure 2), especially in terms of the microconstituents as noticeable from the smaller marker. The prior β -Ti grain size and the lamella become increasingly smaller as the Cu content increases. The second effect of subjecting the Ti-xAl-yCu alloys to a hot deformation process to be highlighted is the significant reduction of the residual porosity, which is barely visible.

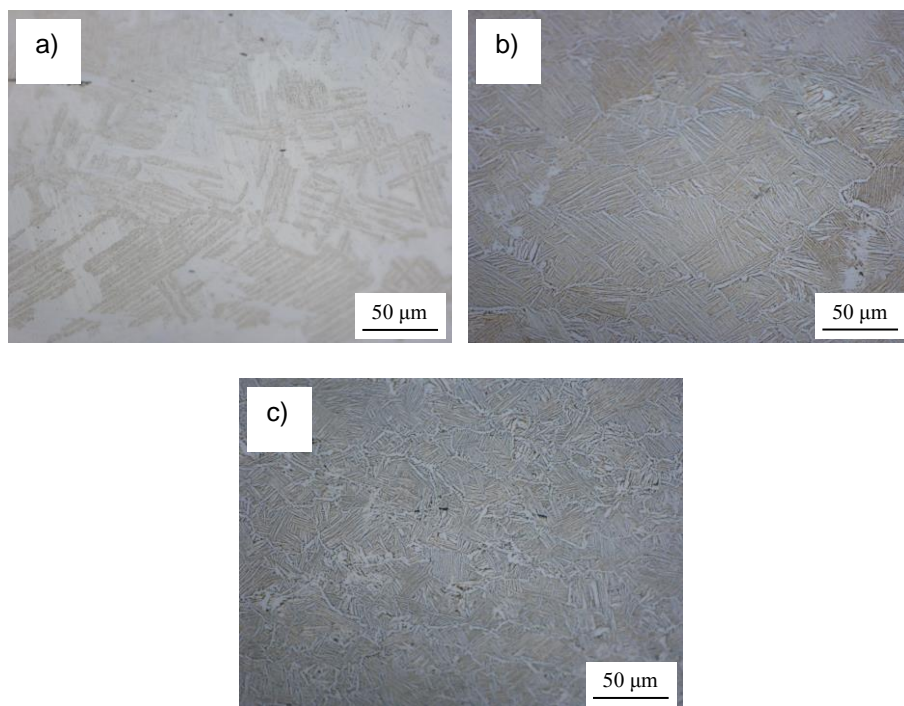


Figure 3. Optical micrographs of the forged samples: a) Ti-2Al-1Cu, b) Ti-6Al-4Cu, and c) Ti-10Al-5Cu alloy.

Elemental mapping and EDS semi-quantitative analysis was performed to check the homogeneity of the alloys. The representative results shown in Figure 4 indicate a completely uniform distribution of the alloying elements. Table 2 reports the results of the EDS analysis for the general composition as well as the composition of the phases.

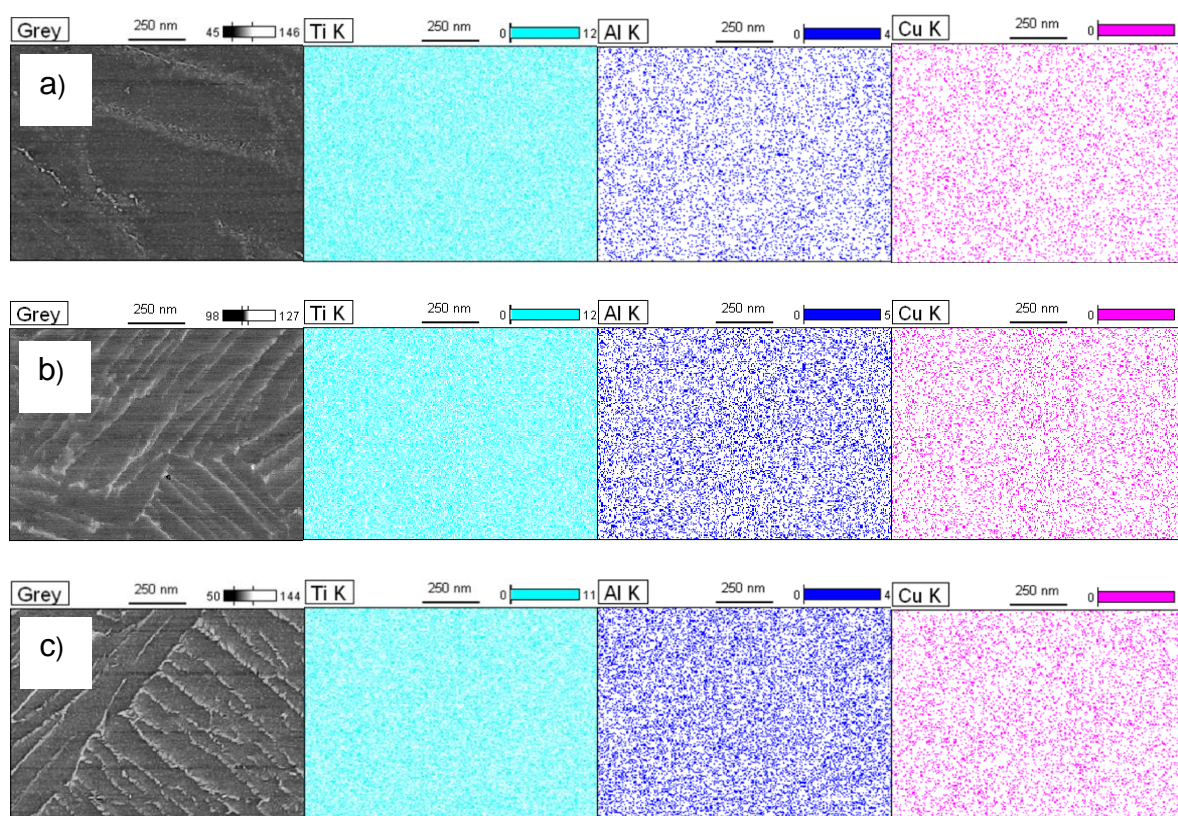


Figure 4. Representative SEM results showing the distribution of the alloying elements: a) Ti-2Al-1Cu, b) Ti-6Al-4Cu, and c) Ti-10Al-5Cu alloy.

Table 2. Average atomic composition of the Ti-xAl-yCu alloys and of the main phases constituting them.

| Alloy | Element | Overall [at.%] | α -Ti [at.%] | β -Ti [at.%] |
|--------------------|---------|------------------|---------------------|--------------------|
| <i>Ti-2Al-1Cu</i> | Al | 1.86 ± 0.19 | 8.96 ± 0.50 | 8.76 ± 0.51 |
| | Ti | 96.07 ± 0.88 | 91.04 ± 1.48 | 85.8 ± 1.44 |
| | Cu | 2.07 ± 0.42 | - | 5.45 ± 1.0 |
| <i>Ti-6Al-4Cu</i> | Al | 7.37 ± 0.23 | 4.9 ± 0.41 | 4.89 ± 0.54 |
| | Ti | 89.46 ± 0.80 | 95.1 ± 1.36 | 88.3 ± 1.48 |
| | Cu | 3.17 ± 0.42 | - | 6.81 ± 1.18 |
| <i>Ti-10Al-5Cu</i> | Al | 10.47 ± 0.23 | 8.67 ± 0.43 | 7.94 ± 0.47 |
| | Ti | 85.42 ± 0.69 | 91.33 ± 1.29 | 82.7 ± 1.26 |
| | Cu | 4.11 ± 0.39 | - | 9.36 ± 1.70 |

X-ray analysis was done for each material to identify if there were any changes occurring on the crystal structure and the results are summarised in Figure 5. The Ti-2Al-1Cu samples

show only α -Ti peaks. The Ti-6Al-4Cu and Ti-10Al-5Cu alloys show additional peaks that matched to the pattern of β -Ti. After forging the relative intensity of the α (002) peak increased. An extra peak at 44° , due to the formation of the Ti_2Cu phase, was detected for the alpha+beta Ti alloys.

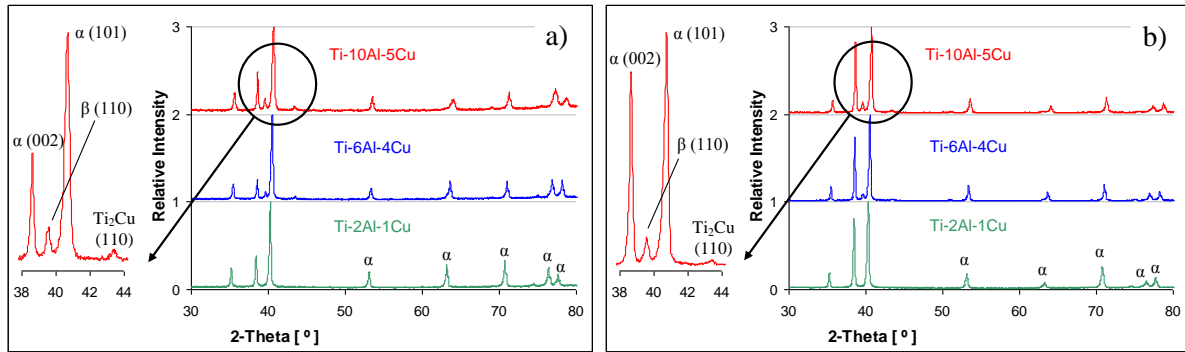


Figure 5. XRD patterns of the (a) sintered and (b) forged Ti-2Al-1Cu, Ti-6Al-4Cu, and Ti-10Al-5Cu alloys.

The variation of the physical properties, in particular of the volumetric shrinkage and relative density, experienced by the Ti-xAl-yCu alloys is shown in Figure 6 where it can be seen that the higher content of alloying elements the lower the shrinkage and the relative density achieved. Consequently, the densification is also lower for higher amounts of alloying elements.

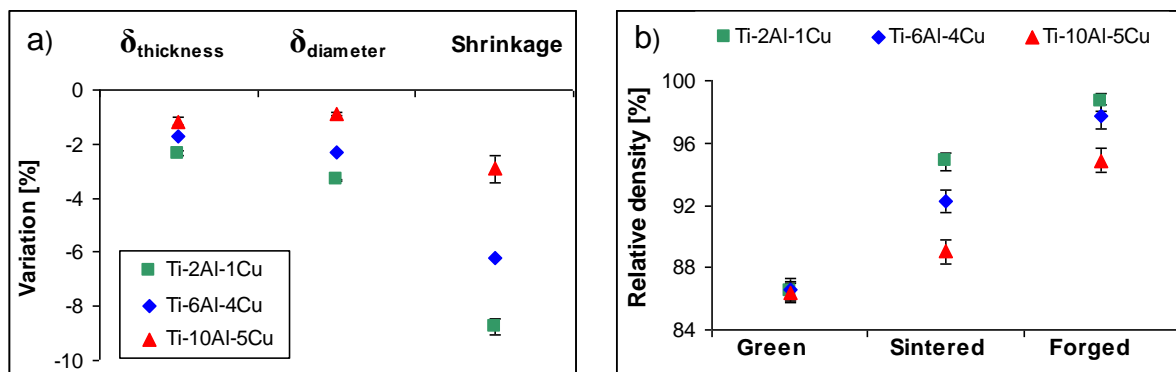


Figure 6. Variation of the physical properties of the Ti-xAl-yCu alloys: a) volumetric shrinkage, and b) relative density.

Figure 7 reports the typical stress-strain curves of the sintered and forged Ti-xAl-yCu alloys showing that Ti-2Al-1Cu has the highest ductility, Ti-6Al-4Cu has the highest strength and Ti-10Al-5Cu is characterised by a purely elastic behaviour and it fractures before deforming plastically. The average Young modulus of the sintered alloys is 104 ± 4 GPa, with the Cu content having a mild effect, which increases to 118 ± 7 GPa after hot forging due to the reduction of the residual porosity (Figure 6).

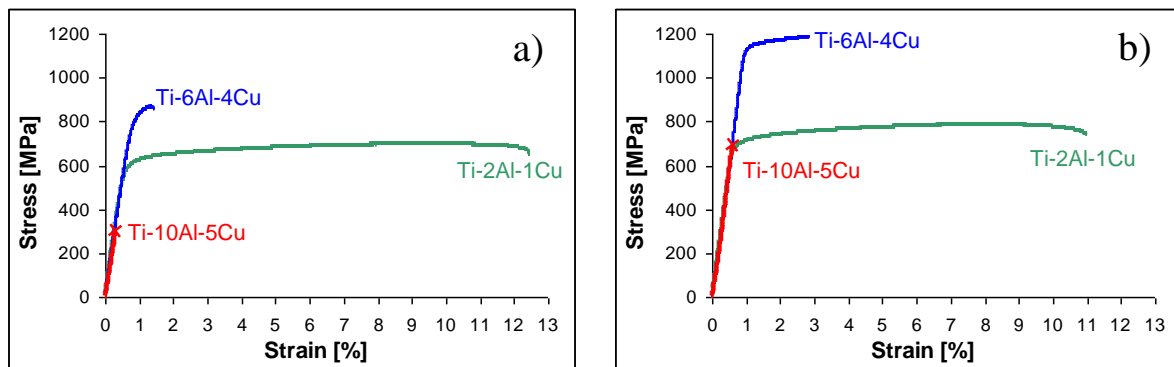


Figure 7. Stress-strain curves of the (a) sintered and (b) forged Ti-2Al-1Cu, Ti-6Al-4Cu, and Ti-10Al-5Cu alloys.

The average values of the ultimate tensile strength (UTS) and elongation at fracture are shown in Figure 8 confirming the behaviour discussed on the basis of the stress-strain curves. The data highlight that forging is beneficial to increase the mechanical properties regardless of the alloy composition; however, the residual porosity has a much stronger effect on the strength, rather than the ductility, as a linear correlation is found (Figure 8b).

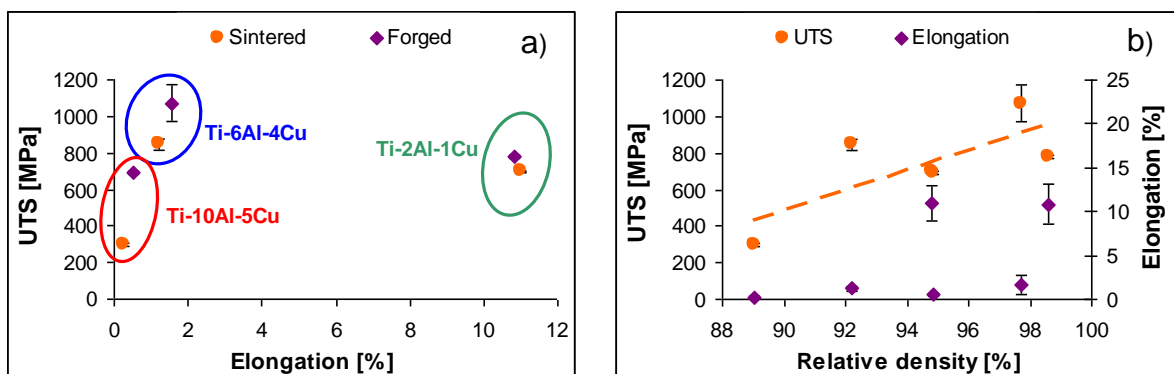


Figure 8. Variation of the tensile properties of the Ti-xAl-yCu alloys: a) UTS vs. elongation, and b) UTS and elongation vs. relative density.

The microhardness values of the sintered and forged Ti-xAl-yCu alloys of Figure 9 show that the hardness of the material increases with the amount of alloying elements and the post-processing via hot forging permits to obtain slightly harder materials.

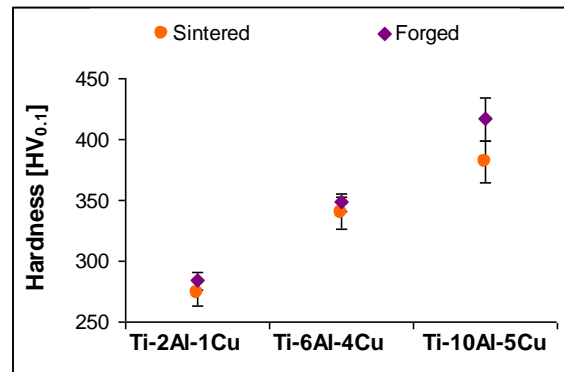


Figure 9. Variation of the microhardness of the sintered and forged Ti-xAl-yCu alloys.

4. Discussion

From the microstructural analysis (Figure 2) it is found that the porosity of the sintered Ti-xAl-yCu alloys is characterised by spherical morphology indicating that the alloys reached the last stage of sintering during the dwell time at maximum temperature but the amount of porosity and its size increase with the amount of Cu. This seems to be due to the fact that the higher the amount of alloying elements, the higher the thermodynamic energy invested in diffusion of these elements. The data of the physical properties (shrinkage and relative density displayed in Figure 6) reveal that progressively lower values are obtained as the amount of alloying elements increases despite of the comparable green density; this confirms that more energy is spent in homogenisation of the composition. Sintering of the Ti-xAl-yCu alloys induces a reduction of the final dimensions, both thickness and diameter, which is generally higher for the latter, resulting an overall shrinkage of the samples. The actual shrinkage is significantly affected by the chemistry of the alloy where the higher the amount of alloying elements the lower the shrinkage.

This reflects in a final lower relative density after sintering as the three Ti-xAl-yCu alloys have fairly similar green density (Figure 6). Apart from the value of the sintered Ti-10Al-5Cu alloy, the relative density achieved in Ti-xAl-yCu alloys is comparable to that of other PM Ti materials [10, 24-27] as they are in the range between 92% and 95%. The alloys experience, then, different level of densification which varies between 17% for Ti-10Al-5Cu and 59% for Ti-2Al-1Cu due to the sintering stage.

Figure 2 also shows that the microstructure of the sintered Ti-xAl-yCu alloys is lamellar regardless of the composition as the alloys were slow cooled from a temperature above their respective β transus and therefore $\alpha+\beta$ lamellae nucleated and grew through the centre of prior β grains following favourable crystallographic planes and directions. However, there are significant differences in terms of amount of the two phases as the relative amount of β -Ti proportionally increases with the amount of Cu. Being a near-alpha alloy, Ti-2Al-1Cu has a coarse lamellar structure where the β phase is primarily found at the grain boundaries between equiaxed α -Ti grains although some $\alpha+\beta$ lamellae grains are also present (Figure 2a). Both the sintered Ti-6Al-4Cu and Ti-10Al-5Cu alloys have a fully lamellar structure, typical of alpha+beta alloys Ti alloys, but α -Ti lamellae are coarser in the former (Figure 2b) and the β -Ti lamellae are coarser in the latter (Figure 2c) due to the relative content of each of the alloying elements and their stabilising effect on the Ti phases. The reach of the third stage of sintering suggested by the microstructural analysis indicated that, via the sintering parameters employed, a homogenous distribution of the alloying elements could be expected. This was confirmed by elemental mapping and EDS analysis (Figure 4). Although the resolution of the equipment could not definitively discern the precise distribution of the alloying elements into the Ti phases, Al is present in α -Ti whereas Cu is in β -Ti (Table 2) as Cu has no solubility in α -Ti at room temperature [20]. The average atomic percentage found for the three Ti-xAl-yCu alloys is 96.07Ti-1.86Al-2.07Cu, 89.46Ti-7.37Al-3.17Cu and 85.42Ti-10.47Al-4.11Cu, respectively.

From the X-ray patterns shown in Figure 5, the sintered Ti-xAl-yCu alloys are predominately composed of α -Ti and, as expected, the amount of stabilised β -Ti increases with the Cu content as the β (110) peak becomes stronger. Even though β -Ti is present in the microstructure of the Ti-2Al-1Cu alloy, the corresponding peak was not detected due to the low amount of stabilised β -Ti, which is thus lower than the detection limit of the equipment. It should also be noticed that when the Cu content is greater than 2%, such as for both Ti-6Al-4Cu and Ti-10Al-5Cu alloys, the (110) peak of the Ti_2Cu phase was also detected. The $[010]_\alpha \parallel [100]_{\text{Ti}_2\text{Cu}}$ orientation relationship has been previously reported for the precipitation of eutectoid Ti_2Cu particles at α -Ti grain boundaries [28]. From the low relative intensity, it is inferred that the amount of precipitated Ti_2Cu is fairly small and increases with the Cu content.

In terms of tensile behaviour, for both Ti-2Al-1Cu and Ti-6Al-4Cu the yield strength could be calculated and it is 618 ± 10 MPa and 830 ± 10 MPa, respectively. Generally, the mechanical properties of the sintered Ti-xAl-yCu alloys increase with the amount of alloying elements as the Ti-6Al-4Cu alloys is stronger than Ti-2Al-1Cu alloys, but Ti-10Al-5Cu alloys has the lowest strength (Figure 7). This behaviour is due to the combined effect of the phases present and the residual porosity left after the sintering stage. A linear relationship is found between the UTS and the relative density although alpha+beta alloys, such as Ti-6Al-4Cu are intrinsically stronger than near-alpha alloys (i.e. Ti-2Al-1Cu) due to the higher amount of stabilised β -Ti phase and the precipitation of the eutectoid Ti_2Cu intermetallic phase (Figure 8b). A greater amount of the latter in the sintered Ti-10Al-5Cu alloy and a higher amount of residual porosity with irregular morphology (Figure 2c) are the responsible for the brittle behaviour of this alloy which also results in a very low tensile strength. Above the solubility limit of $\sim 2.1\%$ Cu, the relative amount of Ti_2Cu precipitates increases and consequently the ductility of the alloy decreases.

This is represented in Figure 10a) where the elongation of the PM Ti-xAl-yCu alloys of this study is compared to that of other Cu-bearing Ti alloys found in the literature [29-31]. It is worth mentioning that the latter are made via casting rather than PM. The tensile properties of the sintered and forged Ti-xAl-yCu alloys are also comparable to those of other wrought alpha+beta Ti alloys used in biomedicine [4, 32, 33].

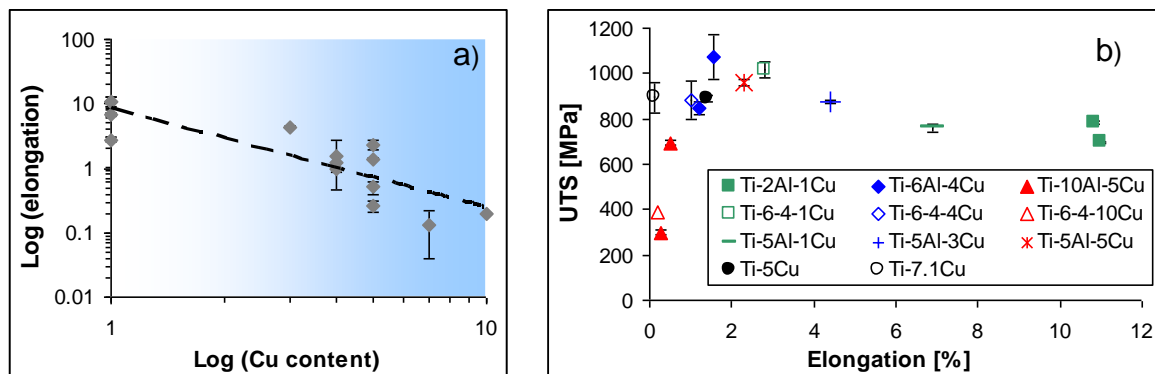


Figure 10. Variation of the tensile properties of the Ti-xAl-yCu alloys compared to other Cu-bearing Ti alloys [29-31]: a) elongation vs. Cu content, and b) UTS vs. elongation.

From Figure 9, the hardness of the Ti-xAl-yCu alloys increases along with the content of alloying elements. The increase in microhardness (i.e. $HV_{0.1}$) is primarily due to the phases constituting the alloy and that is why the Ti-10Al-5Cu alloy has much higher hardness than the Ti-2Al-1Cu alloys although the latter has much higher relative density or, in turns, less pores present in the microstructure. Therefore, there is no relationship between the microhardness and the level of relative density achieved via either sintering or forging. It is worth mentioning that the residual porosity would have affected the measurements of macrohardness. The measured values presented in Figure 9 are very common among other wrought Ti-based biomedical alloys [3, 4, 21-23].

The hot deformation via forging of the Ti-xAl-yCu alloys reduces the residual porosity but the results are influenced by the previous thermal history of the alloy. From the micrographs shown in Figure 3 it seems that almost full density was achieved in all the alloys.

Nevertheless, Archimedes density data reported in Figure 6 indicate that residual porosity is still present. The discrepancy is due to the fact that during hot forging the material in the middle of the sample experiences the highest load and thus the porosity is completely sealed (Figure 3). Conversely, porosity is left on the periphery of the forged samples. In terms of absolute values, the post processing via hot deformation leads to an increase in relative density between 3.8% for Ti-2Al-1Cu and 5.8% for Ti-10Al-5Cu which is the opposite trend of that found during sintering where Ti-2Al-1Cu alloy underwent the highest increment. The apparent densification experienced by the alloys via hot forging, due to the sealing of the residual porosity, is in the 55-75% range. The Ti-2Al-1Cu has the coarsest microstructure of the three alloys and it is composed of elongated α -Ti grains grew inside the prior β -Ti grains with the β -Ti phase found at the grain boundaries. Because of the deformation of the α -Ti grains, the microstructure has a much higher resemblance to a lamellar structure. Both Ti-6Al-4Cu and Ti-10Al-5Cu α + β alloys are still characterised by a fully lamellar structure but the size of the prior β -Ti grains and of the α + β lamella are much finer and, consequently, the interlamellar spacing is also smaller. In the micrographs of Figure 3 it can also be noticed that there is some prominent α -Ti phase at the grain boundaries, which was the first to nucleate during the relatively fast cooling imposed by the hot deformation process resulting in a refined lamellar structure. Regarding the deformation of the alloys at high temperature, the XRD patterns shown in Figure 5b) clearly indicate that hot forging does not change the nature of the phases composing the different Ti-xAl-yCu alloys but imposes some texture as the relative intensity of the $\alpha(002)$ peak, which corresponds to the basal plane of the h.c.p. structure, becomes more pronounced.

The post processing of the Ti-xAl-yCu alloys via hot forging induces a general increment of the tensile performances though the behaviour is still greatly affected by the chemistry of the alloy. Therefore, the near-alpha alloys has intermediate strength but high elongation while the ductility and strength of the alpha+beta alloys decreases with the increment of the Cu content due to the higher number of Ti₂Cu precipitates. Although the tensile behaviour is still purely elastic, the strength of the Ti-10Al-5Cu alloy greatly benefits from the sealing of the residual porosity as a linear relationship is found between these two properties (Figure 8b). The forged alloys generally have higher microhardness with respect to the sintered ones (Figure 9), due to the characteristics of the microconstituents, as the forged alloys have finer microstructures (Figure 3) than their sintered counterparts (Figure 2).

From Figure 10b), the PM Ti-xAl-yCu alloys mostly perform better than their cast counterparts, especially if the fact that the sintered alloys have residual porosity that can be sealed via post processing is taken into account. For example, the sintered Ti-2Al-1Cu is the most ductile (better than cast Ti-6Al-4V-1Cu) and has strength comparable to that of cast Ti-5Al-1Cu. The sintered Ti-6Al-4Cu has comparable or better properties (i.e. strength) than the cast Ti-6Al-4V-4Cu where the exclusion of V is valuable both in terms of reducing the cost of the alloy as well as reduce its cytotoxicity [34]. The sintered Ti-10Al-5Cu has higher strength than the cast Ti-6Al-4V-10Cu although all of them are brittle. Due to the lower amount of residual pores, the forged Ti-xAl-yCu alloys have normally better properties than both the sintered and cast counterparts. Figure 11 shows a comparison of the hardness of the Ti-xAl-yCu alloys with other Cu-bearing cast Ti alloys. It can be noticed that similar values are obtained if the matrix is the same, such as when comparing PM Ti-2Al-1Cu with cast Ti-5Al-1Cu, but the hardness is lower with respect to Cu-bearing cast Ti alloys with a different based alloy such as in the case of Ti-2Al-1Cu versus Ti-6Al-4V-1Cu.

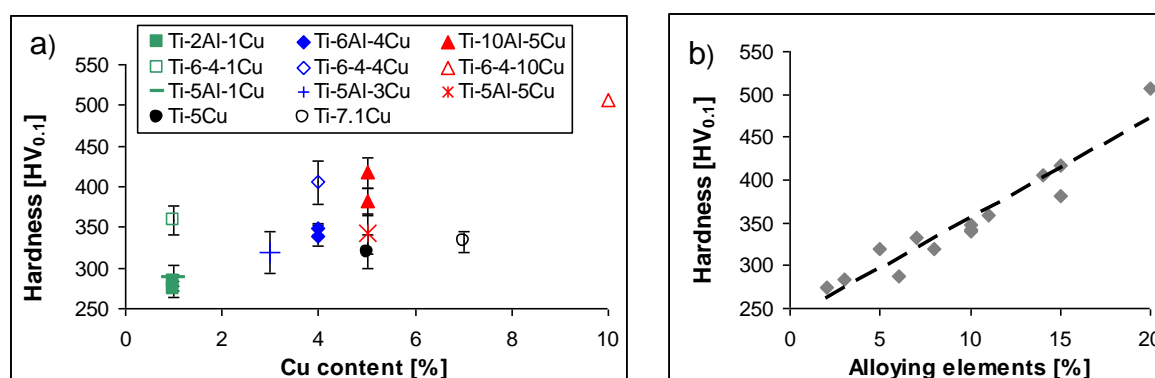


Figure 11. Variation of the hardness of the Ti-xAl-yCu alloys compared to other Cu-bearing Ti alloys [29-31]: a) microhardness vs. Cu content, and b) microhardness vs. total amount of alloying elements.

The same trend does apply to other alloys with higher amount of Cu where the pure Ti-based alloys are softer than other alloys where Cu was added to starting alpha+beta alloys (i.e. Ti-6Al-4V). Even though there is a correlation with the amount of Cu, the microhardness of the Cu-bearing Ti alloys has a better correlation with the total amount of alloying elements (Figure 11b) as they determines the features of the α -Ti, β -Ti and any other phase that might be present, such as Ti_2Cu , including their size, distribution, interspacing and relative content. The hardness of the forged alloys is comparable to that of cast alloys with the exception of when Cu is added into the Ti-6Al-4V alloys rather than to pure Ti.

The antibacterial properties of Cu-bearing Ti alloys have been previously tested and it was demonstrated that the materials exhibit antibacterial activity against *E. Coli* and *S. aureus* where strong and stable antibacterial activity are found for Cu around 5% [7]. Cu bearing Ti-alloy also have excellent corrosion resistance and cytocompatibility [5]. The new PM Ti-xAl-yCu alloys are then potential candidates to be used for manufacturing structural biomedical implants and prostheses with suitable mechanical properties, biocompatibility, low cost, and expected antibacterial properties.

5. Conclusions

From this study considering the effect of alloying element content and hot processing on the properties of Cu-bearing powder metallurgy Ti alloys it is found that the amount of Cu is critical in determining the microstructure (phases) and mechanical properties of the materials and it is expected to also affect the antibacterial properties of the alloy. Powder metallurgy is a viable process to manufacture biomedical materials where a combination of processes can be used to regulate the level of porosity to be able to tailor the mechanical response and bone ingrowth ability.

Acknowledgements

The authors are thankful for the financial support from the New Zealand Ministry of Business, Innovation and Employment (MBIE) through the UOWX1402 research contract. L. Bolzoni would also like to acknowledge the technical support from Mr. Daniel Hishon.

References

- [1] C. Leyens, M. Peters, *Titanium and Titanium Alloys. Fundamentals and Applications*, Wiley-VCH, Köln, Germany, 2003.
- [2] R. Narayan, *Biomedical Materials*, Springer, 2009.
- [3] M. Niinomi, Recent Metallic Materials for Biomedical Applications, *Metallurgical and Materials Transactions A*, 33 (2002) 477-486.
- [4] M. Niinomi, Mechanical Biocompatibilities of Titanium Alloys for Biomedical Applications, *Journal of the Mechanical Behavior of Biomedical Materials*, 1 (2008) 30-42.
- [5] L. Ren, Z. Ma, M. Li, Y. Zhang, W. Liu, Z. Liao, K. Yang, Antibacterial Properties of Ti-6Al-4V-xCu Alloys, *Journal of Materials Science & Technology*, 30 (2014) 699-705.
- [6] R. Boyer, G. Welsch, E.W. Collings, *Materials Properties Handbook: Titanium Alloys*, in: A. International (Ed.), Ohio, USA, 1998.

- [7] J. Liu, F. Li, C. Liu, H. Wang, B. Ren, K. Yang, E. Zhang, Effect of Cu Content on the Antibacterial Activity of Titanium-Copper Sintered Alloys, *Materials Science and Engineering: C*, 35 (2014) 392-400.
- [8] M. Kikuchi, Y. Takada, S. Kiyosue, M. Yoda, M. Woldu, Z. Cai, O. Okuno, T. Okabe, Mechanical Properties and Microstructures of Cast Ti-Cu Alloys, *Dental Materials*, 19 (2003) 174-181.
- [9] M. Kikuchi, M. Takahashi, O. Okuno, Elastic Moduli of Cast Ti-Au, Ti-Ag, and Ti-Cu Alloys, *Dental Materials*, 22 (2006) 641-646.
- [10] E. Zhang, X. Wang, M. Chen, B. Hou, Effect of the Existing Form of Cu Element on the Mechanical Properties, Bio-corrosion and Antibacterial Properties of Ti-Cu Alloys for Biomedical Application, *Materials Science and Engineering: C*, 69 (2016) 1210-1221.
- [11] S. Wang, Z. Ma, Z. Liao, J. Song, K. Yang, W. Liu, Study on Improved Tribological Properties by Alloying Copper to CP-Ti and Ti-6Al-4V Alloy, *Materials Science and Engineering: C*, 57 (2015) 123-132.
- [12] F.H. Froes, M.N. Gungor, M.A. Imam, Cost-affordable Titanium: The Component Fabrication Perspective, *JOM*, 59 (2007) 28-31.
- [13] L. Bolzoni, E. Herraiz, E.M. Ruiz-Navas, E. Gordo, Study of the Properties of Low-cost Powder Metallurgy Titanium Alloys by 430 Stainless Steel Addition, *Materials and Design*, 60 (2014) 628-636.
- [14] L. Bolzoni, E.M. Ruiz-Navas, E. Gordo, Understanding the Properties of Low-cost Iron-containing Powder Metallurgy Titanium Alloys, *Materials and Design*, 110 (2016) 317-323.
- [15] S. Fujibayashi, M. Neo, H.-M. Kim, T. Kokubo, T. Nakamura, Osteoinduction of Porous Bioactive Titanium Metal, *Biomaterials*, 25 (2004) 443-450.
- [16] C. Torres-Sanchez, F.R.A. Al Mushref, M. Norrito, K. Yendall, Y. Liu, P.P. Conway, The Effect of Pore Size and Porosity on Mechanical Properties and Biological Response of Porous Titanium Scaffolds, *Materials Science and Engineering: C*, 77 (2017) 219-228.
- [17] V.A.R. Henriques, C.E. Bellinati, C.R.M. da Silva, Production of Titanium Alloys for Medical Implants by Powder Metallurgy, *Key Engineering Materials Advanced Powder Technology II* (2001) 443-448.
- [18] P.C. Garcia Oliveira, G. Luis Adabo, R. Faria Ribeiro, S. Soares Rocha, The Effect of Mold Temperature on Castability of CP Ti and Ti-6Al-4V Castings into Phosphate Bonded Investment Materials, *Dental Materials*, 22 (2006) 1098-1102.

- [19] C.-C. Hung, G.-L. Hou, C.-C. Tsai, C.-C. Huang, Pure Titanium Casting into Zirconia-modified Magnesia-based Investment Molds, *Dental Materials*, 20 (2004) 846-851.
- [20] J.L. Murray, *Phase Diagrams of Binary Titanium Alloys*, 1st ed., ASM International, 1987.
- [21] D. Henry, *Materials and Coatings for Medical Devices: Cardiovascular*, ASM International, Ohio, USA, 2009.
- [22] M. Semlitsch, F. Staub, W. H., Titanium-aluminium-niobium Alloy Development for Biocompatible, High Strength Surgical Implants, *Biomedizinische Technik/Biomedical Engineering*, 30 (1985) 334-339.
- [23] M. Semlitsch, H. Weber, R. Steger, Fifteen Years Experience with Ti-6Al-7Nb Alloy for Joint Replacements, in: P.A. Blenkinsop, Evans, W. J., Flower, H. M. (Ed.) *Titanium '95: Science and Technology*, Birmingham - UK, 1995, pp. 1742-1759.
- [24] F.H. Froes, O.M. Ivasishin, V.S. Moxson, D.G. Savvakina, K.A. Bondareva, A.M. Demidik, Cost-effective Synthesis of Ti-6Al-4V Alloy Components via the Blended Elemental P/M Approach, in: W. TMS, PA (Ed.) *Symposium on TMS Symposium on High Performance Metallic Materials for Cost Sensitive Applications*, Seattle, WA, 2002.
- [25] L. Bolzoni, E.M. Ruiz-Navas, E. Gordo, Powder Metallurgy CP-Ti Performances: Hydride-dehydride vs. sponge, *Materials and Design*, 60 (2014) 226-232.
- [26] L. Bolzoni, E.M. Ruiz-Navas, E. Gordo, Feasibility Study of the Production of Biomedical Ti-6Al-4V Alloy by Powder Metallurgy, *Materials Science and Engineering C*, 49 (2015) 400-407.
- [27] D.-W. Lee, H.-S. Lee, J.-H. Park, S.-M. Shin, J.-P. Wang, Sintering of Titanium Hydride Powder Compaction, *Procedia Manufacturing*, 2 (2015) 550-557.
- [28] D.N. Williams, R.A. Wood, *Effects of Surface Condition on the Mechanical Properties of Titanium and its Alloys*, Battelle Columbus Labs Ohio Metals and Ceramics Information Center, 1971, pp. MCIC-71-01.
- [29] A.O.F. Hayama, P.N. Andrade, A. Cremasco, R.J. Contieri, C.R.M. Afonso, R. Caram, Effects of Composition and Heat Treatment on the Mechanical Behavior of Ti-Cu Alloys, *Materials & Design*, 55 (2014) 1006-1013.
- [30] T. Aoki, I.C.I. Okafor, I. Watanabe, M. Hattori, Y. Oda, T. Okabe, Mechanical Properties of Cast Ti-6Al-4V-XCu Alloys, *Journal of Oral Rehabilitation*, 31 (2004) 1109-1114.

- [31] M. Koike, T. Okabe, Properties Characterization of Cast Ti-Al-Cu Alloys for Dental Applications, Medical Device Materials IV: Proceedings from the Materials and Processes for Medical Devices Conference 2007, (2007) 109-113.
- [32] M. Long, H.J. Rack, Titanium Alloys in Total Joint Replacement - A Materials Science Perspective, *Biomaterials*, 19 (1998) 1621-1639.
- [33] M.M. Dewidar, H.-C. Yoon, J.K. Lim, Mechanical properties of metals for biomedical applications using powder metallurgy process: A review, *Metals and Materials International*, 12 (2006) 193-206.
- [34] M.A. Khan, R.L. Williams, D.F. Williams, The Corrosion Behaviour of Ti-6Al-4V, Ti-6Al-7Nb and Ti-13Nb-13Zr in Protein Solutions, *Biomaterials*, 20 (1999) 631-637.