Article

Novel $\alpha + \beta$ Type Ti-Fe-Cu Alloys Containing Sn with Pertinent Mechanical Properties

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Abstract: Rising demand for bone implants has led to the focus on future alternatives of alloys with better biocompatibility and mechanical strength. Thus, this research is dedicated to the synthesis and investigation of new compositions for low-alloyed Ti-based compounds, which conjoin relatively acceptable mechanical properties and low elastic moduli. In this regard, the structural and mechanical properties of $\alpha + \beta$ Ti-Fe-Cu-Sn alloys are described in the present paper. The alloys were fabricated by arc-melting and tilt-casting techniques which followed subsequent thermo-mechanical treatment aided by dual-axial forging and rolling procedures. The effect of the concentrations of the alloying elements, and other parameters, such as regimes of rolling and dual-axial forging operation, on the microstructure and mechanical properties were thoroughly investigated. The Ti-3Fe-4Cu-0.7Sn alloy with the most promising mechanical properties was subjected to thermo-mechanical treatment. After a single rolling procedure at 750 °C, the alloy exhibited tensile strength and tensile plasticity of 1300 MPa and 6%, respectively, with an elastic modulus of 70 GPa. Such good tensile mechanical properties are explained by the optimal volume fraction balance between $\alpha$ and $\beta$ phases and the texture alignment obtained, providing superior alternatives in comparison to pure $\alpha$-titanium alloys.

Keywords: titanium-based alloys; mechanical properties; thermo-mechanical treatment; tensile strain and plasticity

1. Introduction

Titanium-based alloys have shown tremendous potential in different lightweight applications. These alloys have found their way in various application fields, such as the aeronautic industry, transport engineering, chemical engineering, and medicine, owing to those light weight; high strength, which extends to a wide temperature scale; and its biocompatibility and non-corrosive nature [1–3]. Thus, due to these superior characteristics over other materials, titanium and its alloys have found a special attention in the biomedical field [4–14]. However, to be an ideal candidate as a
replacement material in the case of implants in the human body, along with being biocompatible, it should be able to imitate the native part as closely as possible. This can be explained with a bone implant example where the mechanical properties between the implant and original bone should be close enough to function properly. But, the problem with using Ti-based alloys is that they have very high elastic moduli, which hinders their application in the biomedical field. A good example of this is of commercial Ti and Ti-6Al-4V alloy (most common alloy) having elastic moduli of \( \approx 105 \) GPa and \( \approx 110 \) GPa, respectively [5,15], which surpasses human bone, the latter having elastic modulus of \( \approx 10–30 \) GPa [4,16]. Low elastic modulus close to that of a bone is a desirable characteristic for Ti alloys to avoid the stress shielding effect [17]. Therefore, to attain successful implants, it becomes necessary to decrease the elastic moduli of such materials without forfeiting their supplementary properties.

One of the ways to decrease the elastic moduli of Ti-based alloys, to be close to those of natural human bone, is the formation of a \( \beta \)-Ti structure. In order to stabilize the composition of the \( \beta \)-Ti phase in Ti-based alloys, very often Ti is alloyed with relatively large amounts of Nb and Ta [12,17,18]. Also, nitrogen (N) doping in Ti-based alloys helps reduce the elastic modulus [19,20]. At low concentrations, nitrogen can be embedded interstitially in the lattice of \( \beta \) and \( \alpha \) titanium [21–23] without influencing the size of the unit cell; rather, it tends to form strong covalent bonds with Ti, reducing the interatomic distances. The addition of nitrogen leads to electron localization, consequently reducing the distance and the size of the unit cell. This phenomenon has been well established in our previous report for the Ti\(_{0.4} \)Pd\(_{0.4} \)Ag\(_{0.2} \)Sn\(_{0.2} \) alloy exhibiting a relatively low elastic modulus of \( \approx 65 \) GPa [24]. Moreover, incorporation of tin (Sn) during alloying can also aid in decreasing the elastic modulus in Ti-based alloys. For instance, Ozaki et al. [25] showed that the addition of Sn to binary Ti alloys suppresses or retards \( \beta \) to \( \alpha \) transformation, thereby decreasing the elastic modulus in the \( \beta \)-Ti alloys. A Ti-Nb-Sn alloy with an optimized composition exhibited a very low elastic modulus of about 40 GPa [26–28]. Likewise, Zhao et al. [29,30] revealed that the addition of Sn improves the mechanical performances of Ti-based alloys; their influence is especially prominent on the increased yield stress of the alloy.

Keeping all this in mind, all our previous research was focused on developing low-alloyed \( \beta \) titanium alloys [31–38]. Our group was successful in developing a low-alloyed Ti-based (\( \beta \)-Fe-Cu) alloy with comparatively good mechanical and electrochemical properties by simple thermomechanical treatment following a dual-axial forging procedure. These findings gave way to enhancing the mechanical properties to a further extent [31–34]. Interchanging Fe and Cu with Pd and Ag enhanced the biocompatibility, with a slight effect on the mechanical properties [35–37]. Among them, \( \text{Ti}_8\text{Ag}_3\text{Pd}_3 \) outperformed all the other alloys, exhibiting an optimum combination of physical and biocompatibility owing to the presence of Ag as an antibacterial agent [24,38].

However, it should be noted that Fe is considered to be amongst the most efficient \( \beta \)-phase stabilizing elements, having the ability to increase the mechanical strength and improve the hot cracking resistance of Ti-based alloys [39–42]. Based on the literature it is advised to maintain the Fe composition between 1% and 4% to yield maximum tensile mechanical properties [43]. In a similar manner, copper also functions as a \( \beta \)-stabilizing element; which can provide superior hardness, high strength, and good wear resistance [44–47]. Besides, the presence of low amounts of Cu has enabled adequate cell biocompatibility to Ti-based alloys without influencing cell proliferation and differentiation [48]. Moreover, Cu has been already used as an antibacterial agent [49,50].

With all the development achieved so far, the focus of this research was to synthesize inexpensive, low-alloy \( \alpha + \beta \) titanium alloys. This was based on Ti-Fe-Cu elements to achieve a synergetic effect of high strength and plasticity together with low elastic modulus via dual-axial forging and rolling methods. Besides, the influence of Sn addition on the mechanical properties and the elastic modulus of the fabricated alloys was analyzed.

2. Materials and Methods

2.1. Alloy Preparation
Different compositions of titanium alloy rods, namely, Ti95FeCuSn, Ti92FeCuSn, Ti94FeCuSn, Ti92FeCuSn, and Ti94FeCuSn, were prepared by arc melting technique using metal mixtures having a purity of ≥99.9%. All the compositions are presented in their atomic percentage values. Each rod had dimensions of 5 and 50 mm for diameter and length respectively. The entire experiment was carried out under argon atmosphere followed by purification using Ti getter, and finally, the alloys were tilt cast into a Cu mold. To achieve homogenous composition throughout the rod, the ingots were turned over and re-melted for five times.

2.2. Analysis of the Crystalline Structure

X-ray diffraction (XRD) was carried out to study the phase composition of alloys under monochromatic Cu-Kα radiation and the horizontal position of the sample (2θ angles: from 20° to 80°. Step: 0.02. Exposition time per step: 2 s). An accuracy of ±0.0001 nm and ±5% was obtained for lattice parameters and volume fraction of crystalline phases, respectively [51]. The size of the coherent-scattering region (CSR or crystallites) and the root-mean-square (RMS) microstrain were determined from the broadening of the diffraction peaks by Rietveld refinement of the X-ray spectra using dedicated software packages [51]. The Cauchy function was used as an approximating function. The error in the crystallite size and root-mean-square microstrain evaluation were ±5 nm and ±0.005% respectively [51].

Scanning electron microscopy (SEM, produced by Carl Zeiss Group, Oberkochen, Germany) facilitated with an energy dispersive X-ray spectrometer (EDS) was employed to capture the microstructure morphology of the ingots at 15 kV was employed to study the microstructure of the ingots. Before the imaging, the samples were mechanically grounded and etched using Kroll’s reagent (1–3 mL hydrofluoric acid and 2–6 mL nitric acid dissolved in 100 mL of water) for 3–10 s [52].

2.3. Dual-Axial Forging Procedure and Mechanical Testing

Dual-axial forging was carried out based on our previous studies [24,31–38] and Ti-Fe-Cu-Sn phase diagrams. In brief, the initial forging procedure was carried out along the long axis with 15 cycles of ingot rotation at a constant temperature of 900 °C, which corresponds to β-Ti region. Around 60–70% of the dimensional reduction was achieved during the first forging cycle. All the initial rolling was carried out at 900 °C, whereas the single-cycle rolling operation was undertaken at 750 °C which mainly corresponds to the α + β Ti region.

All the tensile mechanical parameters were measured with a standard mechanical testing machine (Zwick Roell Group, Ulm, Germany) by applying a strain rate of 5 × 10−4 s−1 at room temperature (25 °C). Rectangular alloy samples with a cross-section area of 2 × 2 mm and 33 mm in length were tested. Application of KYOWA DPM-912A strain gage allowed measuring real strain.

Microhardness of the alloys was measured using the “Mitutoyo hardness micro wizard testing” machine (Mitutoyo, Kawasaki, Japan) at 500 g load.

3. Results and Discussion

The present investigation on titanium-based alloys follows the direction of low alloying of titanium with non-expensive beta-phase stabilizing elements along with the incorporation of tin to reduce the elastic modulus. Table 1 summarizes the mechanical properties of the alloys investigated in the present work in the as-cast state and the changes after different kinds of thermo-mechanical treatment. Among all the compositions studied, the Ti94FeCuSn alloy samples exhibited the best results. That was because for that alloy, it was possible to improve the mechanical properties with the help of thermo-mechanical processing, i.e., it was strengthened by simple forging or rolling operations. It was also possible to slightly reduce the elastic modulus from >100 GPa to 70–75 GPa, compared to the conventional Ti alloys and pure Ti (Table 1.1 in [26]). It should be noted, that even in the as-cast state this alloy has promising tensile mechanical properties, which can be improved by a single rolling procedure (at 750 °C) without hampering ductility (Table 1). The microhardness of
each sample can be increased by thermo-mechanical treatment but most of the samples remain brittle (Table 1).

All the other alloy compositions (Ti₉₀Fe₄Cu₃Sn₄, Ti₉₀Fe₄Cu₂Sn₄, Ti₈₅Fe₃Cu₂Sn₂ and Ti₈₅Fe₃Cu₂Sn) show quite poor mechanical properties with high brittleness and lack of plasticity in the as-cast state and after thermo-mechanical treatment (Table 1). Such poor results in mechanical properties can be explained based on the formation of α phase. It is observed that in some cases, that Fe plays the role of α - phase stabilization element which embrittle Ti-based alloy samples [53,54]. Besides, in our previous research on Ti-based alloys containing Fe, which exhibited brittleness during tensile tests [24,36], the formation of the α phase was clearly detected (by TEM and XRD). Therefore, finding the combination of the alloying elements that can partially or completely suppress the formation of α phase is highly desirable. Thus, due to the brittleness, these alloys (Ti₉₀Fe₄Cu₃Sn₄, Ti₉₀Fe₄Cu₂Sn₄, Ti₈₅Fe₃Cu₂Sn₂ and Ti₈₅Fe₃Cu₂Sn) were not used for further experiments.

**Table 1.** Mechanical properties of the investigated alloys in the as-cast state and after thermomechanical treatment (σₜₘₜ—ultimate tensile strength; σₜₛₘₜ—yield strength; δ—tensile plasticity; E—elastic modulus; HV—microhardness).

| Alloy Composition | Treatment | σₜₘₜ, MPa | σₜₛₘₜ, MPa | δ, % | E, GPa | HV |
|-------------------|-----------|-----------|-------------|------|--------|----|
| Ti₉₀Fe₄Cu₃Sn₄     | As-cast   | 520 ± 20  | -           | 0    | 98 ± 10 | 492 ± 30 |
|                   | Rolled at 900°C | 750 ± 20  | -           | 0    | 501 ± 30 | 513 ± 20 |
|                   | Forged at 900°C for 15 times | 460 ± 20  | -           | 0    | 513 ± 20 | 440 ± 20 |
| Ti₉₀Fe₄Cu₂Sn₄     | As-cast   | 1000 ± 30 | 950 ± 20    | 0.3 ± 0.2 | 93 ± 10 | 562 ± 30 |
|                   | Forged at 900°C for 15 times | 880 ± 20  | -           | 0    | 93 ± 10 | 558 ± 20 |
| Ti₉₀Fe₃Cu₃Sn₄     | As-cast   | 720 ± 20  | -           | 0    | 75 ± 10 | 513 ± 40 |
|                   | Rolled at 750°C | 920 ± 20  | 860 ± 40    | 7 ± 1 | 75 ± 10 | 437 ± 15 |
|                   | Rolled at 900°C | 1300 ± 30 | 1070 ± 30   | 6 ± 1 | 70 ± 10 | 401 ± 30 |
|                   | Forged at 900°C for 15 times | 1080 ± 30 | 900 ± 20    | 0.7 ± 0.5 | 95 ± 10 | 440 ± 20 |
| Ti₈₅Fe₃Cu₂Sn₂     | As-cast   | 800 ± 20  | -           | 0    | 100 ± 10 | 587 ± 30 |
|                   | Forged at 900°C for 15 times | 740 ± 20  | -           | 0    | 100 ± 10 | 555 ± 40 |
| Ti₈₅Fe₃CuSn      | As-cast   | 1000 ± 30 | -           | 0    | 100 ± 10 | 323 ± 20 |
|                   | Forged at 900°C for 15 times | 290 ± 50  | 280 ± 40    | 0.5 ± 0.5 | 280 ± 50 | 323 ± 20 |
| Ti₈₅Fe₃Cu (large amount of β-Ti phase) [31] | 1200 ± 30 | 1050 ± 20 | 8 ± 2 | 70 ± 10 | 430 ± 20 |
| Pure Ti (for comparison, as-cast state [38]) | 400 ± 50 | 320 ± 40 | 50 ± 5 | 110 ± 10 | 145 ± 15 |

It was noticed that even conducting different types of thermo-mechanical treatments did not change the phase composition, and therefore, the elastic moduli in almost all of the alloys (except for Ti₈₅Fe₃CuSn) were high. The approximate value of the elastic modulus of each alloy is presented in Table 1.

According to the XRD analyses, the optimal Ti₈₅Fe₃CuSn alloy shows α + β-Ti phase composition in the as-cast state and after thermomechanical treatment (Figure 1a). It should be also pointed out that even in the as-cast state this alloy has relatively high tensile strength (σₜₘₜ ≈ 920 MPa), yield strength (σₜₛₘₜ ≈ 860 MPa) and plasticity (δ ≈ 7%). These values are very promising compared to the results displayed by other alloy compositions (Figure 1e and Table 1). The tensile strength of the alloys showed further improvement after dual-axial forging, but at the cost of plastic strain (Figure
1e and Table 1). Hence, due to the relatively insufficient influence of dual-axial forging on tensile plasticity, single rolling operation at low temperature (750 °C) was attempted, as in our previous work [24]. Contrary to the results obtained from dual-axial forging, the low-temperature rolling operation led to an increase in tensile strength ($\sigma_{ut} \approx 1300$ MPa) and in yield strength ($\sigma_{0.2} \approx 1050$ MPa), while it retained tensile plasticity of $\approx 6\%$ (Figure 1e and Table 1).

![Figure 1. XRD analyses of the Ti$_{94}$Fe$_{1}$Cu$_{1}$Sn$_{4}$ alloy samples in the (a) as-cast state, (b) rolled at 900 °C, (c) rolled at 750 °C, and (d) forged at 900 °C 15 times with sample rotation along the long axis, and (e) the tensile mechanical properties of all the samples investigated.](image)

Table 2 summarizes the phase composition, lattice parameters, size of coherent X-ray scattering regions, and the root-mean-square microstrain of the Ti$_{94}$Fe$_{1}$Cu$_{1}$Sn$_{4}$ alloy samples in the as-cast state and after different types of thermo-mechanical treatment.

| Alloys Composition | Phase Composition, vol. % | Lattice Parameter, nm | Coherent-Scattering Region Size, nm | Root-Mean Square Microstrain, % |
|--------------------|---------------------------|-----------------------|-------------------------------------|-------------------------------|
| As cast            | $\alpha$-Ti, 80           | a: 0.2899             | $\geq 500$                          | 0.218                         |
|                    | (type A3)                 | c: 0.4615             | -                                   | -                             |
|                    | $\beta$-Ti, 20            | a: 0.3195             | $\geq 500$                          | 0.042                         |
|Rolled at 900°C    | $\alpha$-Ti, 98           | a: 0.2905             | 20                                  | 0.292                         |
|                    | (type A3)                 | c: 0.4618             | -                                   | -                             |
|                    | $\beta$-Ti, 2             | a: 0.3260             | 15                                  | 0.013                         |
|Rolled at 750°C    | $\alpha$-Ti, 70           | a: 0.2916             | 35                                  | 0.381                         |
|                    | (type A3)                 | c: 0.4667             | -                                   | -                             |
|                    | $\beta$-Ti, 30            | a: 0.3204             | 10                                  | 0.248                         |
|Forged at 900°C    | $\alpha$-Ti, 98           | a: 0.2986             | 15                                  | 0.31                          |
|                    | (type A3)                 | c: 0.4651             | -                                   | -                             |
|                    | $\beta$-Ti, 2             | a: 0.3304             | 10                                  | 0.331                         |

Table 2 reveals that the $\alpha + \beta$-Ti phase mixture is heavily deformed in the Ti$_{94}$Fe$_{1}$Cu$_{1}$Sn$_{4}$ alloy after thermo-mechanical treatment. At the same time, the mechanical properties also depend on the phase composition of the alloys. For example, the volume ratio between $\alpha$ and $\beta$ phases after the
rolling operation at 750 °C (Table 2) is close to 70 to 30. Moreover, XRD analyses (Figure 1c) revealed that the rolled samples are textured. This can be seen by the significant integral intensity of the (002), (102), and (103) reflexes of the α-Ti phase and the low integral intensity of the (101) reflexes of the β-Ti phase. Such preferred orientation of the grains also contributes to the enhancement of mechanical properties, i.e., the increase in tensile strength, while retaining its tensile plasticity. On one hand, the increase in tensile strength is due to the deformation of the alloy’s microcrystalline structure (increase in the dislocation density, grains fragmentation, etc.). On the other hand, the retention of the tensile plasticity is owed to the formation of oriented microcrystalline structure (preferred deformation in the direction of oriented texture).

From the SEM analysis, relatively large grains, approximately ranging between 100 and 150 μm, can be observed in the images of the as-cast samples (Figure 2a). The fractured surface exhibits viscous, brittle features (Figure 2a–c) after undergoing room temperature tensile testing. The structure of the rolled samples (single cycle rolling operation at 750 °C) consists of α- and β-Ti phase layers, with each layer thicknesses between 5 and 10 μm (Figure 2d). The features observed on the fracture surface also indicate viscous, brittle failure (Figure 2e,f).

Figure 2. SEM images of the Ti–Fe–Cu–Sn alloy samples surfaces before and after the single cycle rolling operation at 750 °C. (a) As-cast sample: sample surface, (b) fracture surface of tensile sample, and (c) a viscous, brittle fracture. (d) Rolled sample: sample surface, (e) fracture surface, and (f) viscous-brittle fracture.

The differences between the chemical compositions of α and β-Ti phases are presented in Figure 3. Figure 3a depicts an SEM image of the layers of α and β-Ti grains after the rolling operation. An EDS line scan was performed across different phases. It is evident that the grains of β-Ti phase contain a significantly larger amount of the alloying elements (Cu, Fe) than the α-Ti grains. For α-Ti, the concentration of Ti is much higher (Figure 3b). A similar trend with respect to the EDS line scan was visualized by the element mapping of the same alloy sample (Figure 3c–g). This result depicted in Figure 3 has a good correlation with the binary phase diagrams of Ti-Fe and Ti-Cu [52] alloys. For example, the maximum amount of Fe in the α-Ti is approximately 0.04%, but the maximum amount of Fe in the β-Ti is 22%, whereas, in the case of Ti-Cu binary system, the maximum amount of Cu in the α-Ti is around 2%, but the maximum amount of Cu in the β-Ti is almost 13%. Therefore, the β-Ti phase is enriched in the alloying elements (especially with Fe and Cu), but the α-Ti phase is mostly free of these alloying elements (Figure 3b–d). Also, according to the XRD patterns, only α-Ti and β-Ti phases are found in this sample (Figure 1c); i.e., no intermetallic compounds are formed.
Figure 3. SEM images of the Ti₉₄Fe₁Cu₁Sn₄ alloy sample, etched in the Kroll’s reagent, (a) after a single cycle rolling operation at 750 °C, with the marked line of the EDS line scan; and (b) the normalized intensity distribution of the Ti and further alloying elements along the marked line. Typical chemical analysis (elemental mapping) of the same alloy sample: the local distributions of (c) Cu, (d) Fe, (e) Sn, and (f) Ti, and (g) the general view of the same structure.

The optimal balance between the content of α and β phases (80:20) allows achieving a relatively low elastic modulus for the as-cast Ti₉₄Fe₁Cu₁Sn₄ alloy sample. The rolling operation at 750 °C mostly retains the balance between α and β phases (70:30) obtained in the as-cast sample. In Table 2 it can be visualized that there is only a minor decrease in the amount of α-Ti phase (approximately 10% less compared to the as-cast state) and a further decrease of the elastic modulus (approximately 5 GPa less compared to the as-cast state). Hence, the obtained textured orientation and relatively strong crystalline lattice deformation (Table 2) allows the improvement in the tensile strength of the Ti₉₄Fe₁Cu₁Sn₄ alloy.

It is evident that in comparison with the model alloy of Ti₆₃Fe₂₄Cu₁₃ from our previous work [31], the Ti₉₄Fe₁Cu₁Sn₄ alloys are more stable during preparation by tilt casting in terms of the ratio between α and β phases, and the mechanical properties obtained by thermo-mechanical treatment. For example, as it has been already mentioned above, that an increase in the amount of Fe in the Ti₆₃Fe₂₄Cu₁₃ alloy may cause the formation of the ω-phase, which increases the brittleness of the samples [24]. Therefore, it can be hypothesized that the formation of ω-phase does not take place in the present Ti₉₄Fe₁Cu₁Sn₄ alloy, in both the as-cast and thermo-mechanically treated condition. Thus, explaining the effect of retention of tensile plasticity in the alloy.

The mechanical properties of Ti-based alloys mostly depend on the subsequent heat-treatment procedure. We used a low-alloyed alloy (i.e., relatively inexpensive), with relatively high and stable mechanical properties already in the as-cast state or after a very simple single-cycle rolling operation.
For comparison, e.g., pure Ti in as-cast state has relatively high plasticity, but not very high tensile strength (see Table 1), and the most popular Ti-6Al-4V alloy has relatively high strength and plasticity only after a rather complicated heat-treatment procedure (see [52]). Some other examples of Ti-based alloys with good mechanical properties in the as-cast state are quite troublesome to alloyed using relatively expensive alloying elements (like Ta, Zr, Mo, Nb, Hf, etc.). Therefore, the low-alloyed Ti-based alloy obtained in the present research work opens up various paths ways for different applications and further investigation owing to its relatively low cost and adequate mechanical properties in the as-cast state or after a single-cycle rolling operation.

The results obtained in the present research work and thermo-mechanical treatment used are very close to those of the earlier work [55], where relatively high tensile mechanical properties (strength up to 870 MPa) and relatively low elastic modulus (of about 42 GPa) were obtained for Ti-25Nb-16Hf alloy, with a β-Ti single phase structure. But, in contrast to the low-alloyed alloy composition of the current research (Ti_{84}Fe_{15}Cu_{7}Sn_{4} alloy), the Ti-25Nb-16Hf alloy [55] was highly alloyed by Nb (of about 17 at. %) and Hf (of about 6 at. %). The low elastic modulus obtained in the work of [55] was explained by the nanocrystalline structure formed during the cold rolling treatment, which was also well documented in the work of Mishra et al. [56]. It has been found that the elastic moduli of nanocrystalline materials are usually lower than those of the corresponding coarse-sized crystalline materials [57]. Elastic moduli tend to decrease as a consequence of the large fraction of atoms in the grain boundaries having a lower elastic modulus [58,59].

In addition, it is necessary to mention that Cu and Sn, are good β-Ti phase stabilizers [60–62]. Thus, adding β-stabilizers reduces the temperature requirement for β → α-transformation and increases the amount of β-phase in the alloy, as a result slowing down the growth of β-grains; i.e., it inhibits the growth of the grains and contributes to the reduction of all the structural components. Moreover, Sn can noticeably reinforce Ti-based alloys and improve the alloy’s corrosion resistance [63], at the same time inhibiting excessive ω phase precipitation in metastable β Ti alloy [61,62]. It was also proven that Sn is a non-toxic and non-allergenic element [64]; all the above-mentioned facts play important roles in improving the mechanical properties or potential biocompatibility of the investigated Ti_{84}Fe_{15}Cu_{7}Sn_{4} alloy and will aid in future research.

The mechanical properties of the Ti_{84}Fe_{15}Cu_{7}Sn_{4} alloy are comparable to the existing analogues. However, the investigated alloy exhibits a lower elastic modulus (Table 1.1 in [26]). Furthermore, it should have an acceptable level of antimicrobial activity, due to the presence of Cu [63]. This allows for avoiding risks of implant rejection as a result of sepsis or infections, the probability of which is very high during implantation [65,66]. Therefore, the Ti_{84}Fe_{15}Cu_{7}Sn_{4} alloy can be a very attractive choice for biomedical applications and will be very attractive for further investigations, including biocompatible tests.

4. Conclusions

The structural and mechanical properties of Ti-based alloys containing low amounts of Sn (Ti_{84}Fe_{15}Cu_{7}Sn_{4}, Ti_{75}Fe_{15}Cu_{7}Sn_{4}, Ti_{65}Fe_{15}Cu_{7}Sn_{4}, Ti_{55}Fe_{15}Cu_{7}Sn_{4}, and Ti_{45}Fe_{15}Cu_{7}Sn_{4}) subjected to thermo-mechanical treatment (by applying dual-axial forging and rolling methods), were investigated. The Ti_{84}Fe_{15}Cu_{7}Sn_{4} alloy samples demonstrated good mechanical properties in both the as-cast state and after the single-cycle rolling operation carried out at 750 °C. The rolling operation at 750 °C helps to increase the tensile strength while keeping a relatively low elastic modulus. After a single rolling operation at 750 °C, the alloy shows an increase in tensile strength up to 1300 MPa and tensile plasticity of about 6%, with an elastic modulus close to 70 GPa. Such promising tensile mechanical properties are owed to the balance between α and β phases and the texture obtained upon rolling. The present results of Ti_{84}Fe_{15}Cu_{7}Sn_{4} alloy are very appealing for its use in biological applications, which will be dealt with in the future course of work.

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References
1. Ilyin, A.A.; Kolachev, B.A.; Polkin, I.S. Titanium Alloys. In Composition, Structure, Properties, Reference Book; VILS-MATI publishing: Moscow, Russia, 2009.
2. Donachie, M.J., Jr. Titanium: A Technical Guide, 2nd ed.; ASM International, Materials Park, OH, USA, 2000.
3. Helth, A.; Siegel, U.; Kühn, U.; Gemming, T.; Gruner, W.; Oswald, S.; Marr, T.; Freudenberger, J.; Scharnweber, J.; Oertel, C.-G.; et al. Influence of boron and oxygen on the microstructure and mechanical properties of high-strength Ti0.95Nb0.05CuNi5.8Al2 alloys. Acta Mater. 2013, 61, 3324–3334, doi:10.1016/j.actamat.2013.02.022.
4. Niinomi, M.; Nakai, M.; Hieda, J. Development of new metallic alloys for biomedical applications. Acta Biomater. 2012, 8, 3888–3903, doi:10.1016/j.actbio.2012.06.037.
5. Niinomi, M. Recent research and development in titanium alloys for biomedical applications and healthcare goods. Sci. Technol. Adv. Mater. 2003, 4, 445–454, doi:10.1016/j.stam.2003.09.002.
6. Long, M.; Rack, H.J. Titanium alloys in total joint replacement-a materials science perspective. Biomaterials 1998, 19, 1621–1639, doi:10.1016/S0142-9612(97)00146-4.
7. Atapour, M.; Pilchak, A.L.; Frankel, G.S.; Williams, J.C. Corrosion behavior of β titanium alloys for biomedical applications. Mater. Sci. Eng. C 2011, 31, 885–891, doi:10.1016/j.msec.2011.02.005.
8. Rack, H.J.; Qazi, J.I. Titanium alloys for biomedical applications. Mater. Sci. Eng. C 2006, 26, 1269–1277, doi:10.1016/j.msec.2005.08.032.
9. Wang, K. The use of titanium for medical applications in the USA. Mater. Sci. Eng. A 1996, 213, 134–137, doi:10.1016/0921-5093(96)01243-4.
10. Miura, K.; Yamada, N.; Hanada, S.; Jung, T.K.; Itoi, E. The bone tissue compatibility of a new Ti-Nb-Sn alloy with a low Young’s modulus. Acta Biomater. 2011, 7, 2320–2326, doi:10.1016/j.actbio.2011.02.008.
11. Liu, H.; Niinomi, M.; Nakai, M.; Obara, S.; Fuji, H. Improved fatigue properties with maintaining low Young’s modulus achieved in biomedical beta-type titanium alloy by oxygen addition. Mater. Sci. Eng. A 2017, 704, 10–17, doi:10.1016/j.msea.2017.07.078.
12. Liu, H.H.; Niinomi, M.; Nakai, M.; Cho, K.; Narita, K.; Sen, M.; Shiku, H.; Matsue, T. Mechanical properties and cytocompatibility of oxygen-modified β-type Ti-Cr alloys for spinal fixation devices. Acta Biomater. 2015, 12, 352–361, doi:10.1016/j.actbio.2014.10.014.
13. Liu, H.H.; Niinomi, M.; Nakai, M.; Hieda, J.; Cho, K. Changeable Young’s modulus with large elongation-to-failure in β-type titanium alloys for spinal fixation applications. Scr. Mater. 2014, 82, 29–32, doi:10.1016/j.scriptamat.2014.03.014.
14. Niinomi, M. Design and development of metallic biomaterials with biological and mechanical biocompatibility. J. Biomed. Mater. Res. A 2019, 107, 944–954, doi:10.1002/jbm.a.36667.
15. Pilliar, R.M. Modern metal processing for improved load-bearing surgical implants. Biomaterials 1991, 12, 95–100, doi:10.1016/0142-9612(91)90185-D.
16. Rho, J.Y.; Tsui, T.Y.; Pharr, G.M. Elastic properties of human cortical and trabecular lamellar bone measured by nanoindentation. Biomaterials 1997, 18, 1325–1330, doi:10.1016/S0142-9612(97)00073-2.
17. Li, Q.; Ma, G.; Li, J.; Niinomi, M.; Nakai, M.; Koizumi, Y.; Wei, D.-X.; Kakeshita, T.; Nakano, T.; Chiba, A.; et al. Development of low-Yang’s modulus Ti-Nb-based alloys with Cr addition. J. Mater. Sci. 2019, 54, 8675–8683, doi:10.1007/s10853-019-04357-0.
18. Homma, T.; Arafah, A.; Haley, D.; Nakai, M.; Niinomi, M.; Moody, M.P. Effect of alloying elements on microstructural evolution in oxygen content controlled Ti-29Nb-13Ta-4.6Zr (wt%) alloys for biomedical applications during aging. Mater. Sci. Eng. A 2018, 709, 312–321, doi:10.1016/j.msea.2017.10.018.
19. Tahara, M.; Kim, H.Y.; Hosoda, H.; Miyazaki, S. Shape memory effect and cyclic deformation behavior of Ti-Nb alloys. *Acta Mater.* **2005**, *4*, 79–82, doi:10.1016/S0921-5093(97)00800-6.

20. Ramarolalhy, A.; Castany, P.; Prima, F.; Labeurte, P.; Peron, I.; Gloriant, T. Microstructure and mechanical behavior of superelastic Ti-24Nb-0.5O and Ti-24Nb-0.5N biomedical alloys. *J. Mech. Behav. Biomed. Mater.* **2012**, *9*, 83–90, doi:10.1016/j.jmbbm.2012.01.017.

21. Bars, J.-P.; David, D.; Etchessahar, E.; Debuigne, J. Titanium α- nitrogen solid solution formed by high temperature nitriding: Diffusion of nitrogen, hardness, and crystallographic parameters. *Metall. Trans. A* **1983**, *14*, 1537–1543, doi:10.1007/BF02654379.

22. Tahara, M.; Kim, H.Y.; Inamura, T.; Hosoda, H.; Miyazaki, S. Role of interstitial atoms in the microstructure and non-linear elastic deformation behavior of Ti–Nb alloy. *J. Alloys Compd.* **2013**, *577*, S404–S407, doi:10.1016/j.jallcom.2012.11.113.

23. Tahara, M.; Kim, H.Y.; Inamura, T.; Hosoda, H.; Miyazaki, S. Lattice modulation and superelasticity in oxygen-added β-Ti alloys. *Acta Mater.* **2001**, *59*, 6208–6218, doi:10.1016/j.actamat.2011.06.015.

24. Zadorozhnyy, V.; Kopylov, A.; Gorshenkov, M.; Shabanova, E.; Zadorozhnyy, M.; Novikov, A.; Maksimin, A.; Wada, T.; Louguine-Luzgin, D.; Kato, H. Structure and mechanical properties of Ti-Based alloys containing Ag subjected to a thermomechanical treatment. *J. Alloys Compd.* **2019**, *781*, 1182–1188, doi:10.1016/j.jallcom.2018.12.152.

25. Ozaki, T.; Matsumoto, H.; Watanabe, S.; Hanada, S. Beta Ti Alloys with Low Young’s Modulus. *Mater. Trans.* **2004**, *45*, 2776–2779, doi:10.2320/matertrans.45.2776.

26. Zheng, H.C.Y.; Xu, X.; Xu, Z.; Wang, J. *Metallic Biomaterials*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2017.

27. Kuroda, D.; Niinomi, M.; Morinaga, M.; Kato, Y.; Yashiro, T. Design and mechanical properties of new β type titanium alloys for implant materials. *Mater. Sci. Eng. A* **1998**, *243*, 244–249, doi:10.1016/S0921-5093(97)00808-3.

28. Tane, M.; Akita, S.; Nakano, T.; Hagiwara, K.; Umakoshi, Y.; Niinomi, M.; Nakajima, H. Peculiar elastic behavior of Ti–Nb-Ta–Zr single crystals. *Acta Mater.* **2008**, *56*, 2856–2863, doi:10.1016/j.actamat.2008.02.017.

29. Zhao, G.-H.; Ketov, S.V.; Mao, H.; Borgenstam, A.; Louguine-Luzgin, D.V. Ti-Fe-Sn-Nb eutectic alloys with superb yield strength and significant strain-hardening. *Scr. Mater.* **2017**, *135*, 59–62, doi:10.1016/j.scriptamat.2017.03.033.

30. Zhao, G.-H.; Ketov, S.V.; Jiang, J.; Mao, H.; Borgenstam, A.; Louguine-Luzgin, D.V. New beta-type Ti-Fe-Sn-Nb alloys with superior mechanical strength. *Mater. Sci. Eng. A* **2017**, *705*, 348–351, doi:10.1016/j.msea.2017.08.060.

31. Zadorozhnyy, V.Yu.; Ioune, A.; Louguine-Luzgin, D.V. Ti-based nanostructured low-alloy with high strength and ductility. *Mater. Sci. Eng. A* **2012**, *551*, 82–86, doi:10.1016/j.msea.2012.04.097.

32. Zadorozhnyy, V.Yu.; Shchetinin, I.V.; Chirikov, N.V.; Louguine-Luzgin, D.V. Tensile properties of a dual-axial forged Ti-Fe-Cu alloy containing Boron. *Mater. Sci. Eng. A* **2014**, *614*, 238–242, doi:10.1016/j.msea.2014.07.017.

33. Zadorozhnyy, V.Yu.; Shchetinin, I.V.; Zheleznyi, M.V.; Chirikov, N.V.; Wada, T.; Kato, H.; Louguine-Luzgin, D.V. Investigation of structure—Mechanical properties relations of dual-axial forged Ti-based low-alloys. *Mater. Sci. Eng. A* **2015**, *632*, 88–95, doi:10.1016/j.msea.2015.02.065.

34. Zadorozhnyy, V.Yu.; Shi, X.; Kozak, D.S.; Wada, T.; Wang, J.Q.; Kato, H.; Louguine-Luzgin, D.V. Electrochemical behavior and biocompatibility of Ti-Fe-Cu alloy with high strength and ductility. *J. Alloys Compd.* **2017**, *707*, 291–297, doi:10.1016/j.jallcom.2016.11.213.

35. Zadorozhnyy, V.Yu.; Kozak, D.S.; Shi, X.; Wada, T.; Louguine-Luzgin, D.V.; Kato, H. Mechanical properties, electrochemical behavior and biocompatibility of the Ti-based low-alloys containing a minor fraction of noble metals. *J. Alloys Compd.* **2018**, *732*, 915–921, doi:10.1016/j.jallcom.2017.10.231.

36. Zadorozhnyy, V.Yu.; Shi, X.; Kopylov, A.N.; Shchetinin, I.V.; Wada, T.; Louguine-Luzgin, D.V.; Kato, H. Mechanical properties, structure, and biocompatibility of dual-axially forged Ti5FeAu, Ti5FeNb5 and Ti5Au2Nb5 alloys. *J. Alloys Compd.* **2017**, *707*, 269–274, doi:10.1016/j.jallcom.2016.11.349.

37. Zadorozhnyy, V.Yu.; Shi, X.; Wada, T.; Kato, H.; Louguine-Luzgin, D.V. Mechanical properties and biocompatibility of the Ti-based low-alloys minor alloying by the noble metals. *Nano Hybrids Compos.* **2017**, *13*, 63–68, doi:10.4028/www.scientific.net/NHC.13.63.
38. Zadorozhnyy, V.Yu.; Shi, X.; Gorshenkov, M.V.; Kozak, D.S.; Wada, T.; Louguine, D.V.; Inoue, A.; Kato, H. Ti-Ag-Pd alloy with good mechanical properties and high potential for biological applications. Sci. Rep. 2016, 6, 25142, doi:10.1038/srep25142.

39. Yang, H.; Su, Y.; Luo, L.; Chen, H.; Guo, J.; Fu, H. Influences of Fe and B on the Columnar Structure of Ti-46Al Alloys. Rare Met. Mater. Eng. 2012, 41, 570–574, doi:10.1016/S1875-5372(12)60038-1.

40. Louguine-Luzgin, D.V. High-Strength Ti-Based Alloys Containing Fe as One of the Main Alloying Elements. Mater. Trans. 2018, 59, 1537–1544, doi:10.2320/matertrans.M2018114.

41. Nishikiori, S.; Takahash, S.; Satou, S.; Tanaka, T.; Matsuo, T. Microstructure and creep strength of fully-lamellar TiAl alloys containing beta-phase. Mater. Sci. Eng. A 2002, 329–331, 802-809, doi:10.1016/S0921-5093(01)01638-0.

42. Palm, M.; Lacaze, J. Assessment of the Al-Fe–Ti system. Intermetallics 2016, 14, 1291–1303, doi:10.1016/j.intermet.2005.11.026.

43. Mazdiyasni, S.; Miracle, D.B.; Dimiduk, D. M.; Mendiratta, M.G.; Subramanian, P.R. High temperature phase equilibria of the lip composition in the Ti-Ni, Ti-Fe and Ti-Cu systems. Scripta Metall. 1989, 23, 327–331, doi:10.1016/0304-8853(89)90376-1.

44. Liu, J.; Li, F.; Liu, C.; Wang, H.; Ren, B.; Yang, K.; Zhang, E. Effect of Cu content on the antibacterial activity of titanium–copper sintered alloys. Mater. Sci. Eng. C 2014, 35, 392–400, doi:10.1016/j.msec.2013.11.028.

45. Kikuchi, M.; Takada, Y.; Kiyosue, S.; Yoda, M.; Wolfu, M.; Cai, Z.; Okuno, O.; Okabe, T. Mechanical properties and microstructures of cast Ti-Cu alloys. Dent. Mater. 2003, 19, 174–181, doi:10.1016/S0109-5641(02)00227-1.

46. Ohkubo, C.; Shimura, I.; Aoki, T.; Hanatani, S.; Hosoi, T.; Hattori, M.; Oda, Y.; Okabe, T. Wear resistance of experimental Ti–Cu alloys. Biomaterials 2003, 24, 3377–3381, doi:10.1016/S0142-9612(03)00157-1.

47. Takahashi, M.; Kikuchi, M.; Takada, Y. Mechanical properties and microstructure of dental cast Ti–Ag and Ti–Cu alloy. Dent. Mater. J. 2002, 21, 270–280, doi:10.4012/dmj.21.270.

48. Zhang, E.; Zheng, L.; Liu, J.; Bai, B.; Liu, C. Influence of Cu content on the cell biocompatibility of Ti–Cu sintered alloys. Mater. Sci. Eng. C 2015, 46, 148–157, doi:10.1016/j.msec.2014.10.021.

49. Wan, Y. X.; Xiong, G. Y.; Liang, H.; Raman, S.; He, F.; Huang, Y. Modification of medical metals by ion implantation of copper. Appl. Surf. Sci. 2007, 253, 9426–9429, doi:10.1016/j.apsusc.2007.06.031.

50. Tian, X.B.; Wang, Z.M.; Yang, S.Q.; Luo, Z.J.; Fu, R.K.Y.; Chu, P.K. Antibacterial copper containing titanium nitride films produced by dual magnetron sputtering. Surf. Coat. Technol. 2007, 201, 8606–8609, doi:10.1016/j.surfcoat.2006.09.322.

51. Shelekhov, E.V.; Sviridova, T.A. Programs for X-ray analysis of polycrystals. Met. Sci. Heat Treat. 2000, 42, 309–313, doi:10.1007/BF02471306.

52. Brandes, E.A.; Brook, G.B.; (Eds.). Equilibrium Diagrams; In Smithells Metals Reference Book, 7th ed.; Reed Educational and Professional Publishing Ltd.: Oxford, UK, 1992.

53. Bowen, A.W. Omega phase embrittlement in aged Ti-15%Mo. Scr. Met. 1971, 5, 709–716, doi:10.1016/0036-9748(71)90258-4.

54. Wang, Y.B.; Zhao, Y.H.; Lian, Q.; Liao, X.Z.; Valiev, R.Z.; Ringer, S.P.; Zhu, Y.T.; Lavernia, E.J. Grain size and reversible beta-to-omega phase transformation in a Ti alloy. Scr. Mater. 2010, 63, 613–616, doi:10.1016/j.scriptamat.2010.05.045.

55. Gonzalez, M.; Pena, J.; Gil, F.J.; Manero, J.M. Low modulus Ti-Nb-Hf alloy for biomedical applications. Mater. Sci. Eng. C 2014, 42, 691–695, doi:10.1016/j.msec.2014.06.010.

56. Mishra, R.; Balasubramaniam, R. Effect of nanocrystalline grain size on the electrochemical and corrosion behavior of nickel. Corr. Sci. 2004, 46, 3019–3029, doi:10.1016/j.corsci.2004.04.007.

57. American Society for Testing, Materials. In Annual Book of ASTM Standard; ASTM: Philadelphia, PA, USA, 1978; Volume 817.

58. Schistz, J.; Di Tolla, F.D.; Jacobsen, K.W. Softening of nanocrystalline metals at very small grain sizes. Nature 1998, 391, 561–563, doi:10.1038/35328.

59. Hao, Y.L.; Li, S.J.; Sun, Y.; Zheng, C.Y.; Hu, Q.M.; Yang, R. Super-elastic titanium alloy with unstable plastic deformation. Appl. Phys. Lett. 2005, 87, 091906, doi:10.1063/1.2037192.

60. Mello, M.G.; Taipina, M.O.; Rabelo, G.; Cremasco, A.; Caram, R. Production and characterization of TiO2 nanotubes on Ti-Nb-Mo-Sn system for biomedical applications. Surf. Coat. Technol. 2017, 326, 126–133, doi:10.1016/j.surfcoat.2017.07.027.
61. De Mello, M.G.; Salvador, C.F.; Cremasco, A.; Caram, R. The effect of Sn addition on phase stability and phase evolution during aging heat treatment in Ti–Mo alloys employed as biomaterials. *Mater. Charact.* **2015**, *110*, 5–13, doi:10.1016/j.matchar.2015.10.005.

62. Moraes, P.E.L.; Contieri, R.J.; Lopes, E.S.N.; Robin, A.; Caram, R. Effects of Sn addition on the microstructure, mechanical properties and corrosion behavior of Ti–Nb–Sn alloys. *Mater. Charact.* **2014**, *96*, 273–281, doi:10.1016/j.matchar.2014.08.014.

63. Tsao, L.C. Effect of Sn addition on the corrosion behavior of Ti–7Cu–Sn cast alloys for biomedical applications. *Mater. Sci. Eng. C* **2015**, *46*, 246–252, doi:10.1016/j.msec.2014.10.037.

64. Niinomi, M. Recent metallic materials for biomedical applications. *Metall. Mater. Trans. A* **2002**, *33*, 477–486, doi:10.1007/s11661-002-0109-2.

65. Gosheger, G.; Hardes, J.; Ahrens, H.; Streitburger, A.; Buerger, H.; Erren, M.; Gunsel, A.; Kemperd, F.H.; Winkelmann, W.; Eiff, C. Silver-coated megaendoprostheses in a rabbit model-analysis of the infection rate and toxicological side effects. *Biomaterials* **2004**, *25*, 5547–5556, doi:10.1016/j.biomaterials.2004.01.008.

66. Hardes, J.; Ahrens, H.; Gebert, C.; Streitbuerger, A.; Buerger, H.; Erren, M.; Gunsel, A.; Wedemeyer, C.; Saxler, G.; Winkelmann, W.; et al. Lack of toxicological side-effects in silver-coated megaprosthesis in humans. *Biomaterials* **2007**, *28*, 2869–2875, doi:10.1016/j.biomaterials.2007.02.033.

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