Extra-high oxygen addition as a new strengthening strategy to overcome strength/ductility trade-off in fully biocompatible hexagonal titanium alloys.

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Abstract

A new titanium alloy family was developed aiming at creating a fully biocompatible alternative to titanium alloys currently on the dental implants market. Despite their hexagonal close-packed (HCP) single-phase structure, these Ti-Zr-O materials display an extremely interesting combination of properties. Zirconium is shown to be involved through a double contribution: on the one hand, a moderate but noticeable solid solution strengthening effect and on the other hand, a strong grain refinement. Therefore, the combination of both effects results in a beneficial strengthening of Ti-Zr-O alloys. However, the main remarkable aspect remains the outstanding hardening generated by extra high oxygen addition, occurring without any drop of ductility. The evolution of the dislocation network according to the oxygen content has been investigated to understand the underlying mechanisms in these Ti-Zr-O alloys, allowing to overcome the classical strength/ductility trade-off in commercial titanium alloys. Finally, the different perspectives of these findings in the field of biomedical and more generally in the field of titanium alloys are discussed.

Introduction

Thanks to an excellent combination of properties such as biocompatibility or corrosion resistance, the use of titanium in dental implants has become predominant in modern dentistry. However, the Ti-6Al-4V (TA6V), one of the most used alloys in this field, is more and more contested on the assumption that vanadium may display long-term detrimental cytotoxic effects [1-2], and that aluminium could play a role in the appearance of neurodegenerative diseases as Alzheimer in treated patients [3]. The current study aims to present a new fully biocompatible titanium alloy family specially designed for dental applications.

Among the most biocompatible metals, zirconium provides the advantages of being also one of the most resistant with respect to corrosion [4] and of being miscible in any proportion with titanium [5]. Hence, solid solution strengthening could be obtained while preserving the ductile HCP phase of titanium. It should be noted that the zirconium should not exceed 10 wt% to maintain the Young's modulus as low as possible and thus promote osseointegration [6]. Nevertheless, the strength of such a matrix is not expected to be high enough to reach the values of reference materials such as TA6V. Therefore, the strengthening of the Ti-Zr binary is brought by the introduction of interstitials such as oxygen: cost-effective, light and presenting no risk for healthcare. Although oxygen has been blamed, for decades, for its severe embrittling effect on titanium [7–10], several research works have since showed that this approach could be successful [11–13]. Still, the use of oxygen as an alloying element is quite innovative and opens an interesting insight for the titanium industry.

In this study, the microstructure and tensile properties of this new alloy family has been investigated with a special attention given to the role of oxygen on active deformation mechanisms.

Material and experiments

Ti-Zr-O buttons of 200g were fabricated by TIMET UK from pure titanium and zirconium sponges, and oxygen was added in a controlled way through a solid-state process (i.e. using powder particles of TiO₂) during the melting. Ingots were then hot-rolled and annealed at 650°C for 30 minutes. Nominal compositions and actual interstitials contents assessed by gas analyses are listed in Table 1 (C, H and Fe contents were found to be less than 60ppm). As-received ingots were cold-rolled down to 0.6mm sheets with a reduction level of 40% or 85% depending on their cold-workability (as shown in table 1).

Table 1: Summary of studied alloys. The analysed interstitials contents and the thickness reduction applied by cold-rolling are specified for each composition.

Alloys Designation (Contents in wt%)	Interstitial Elements (Content in wt%)		Thicness Reduction by cold-rolling (%)
	O	N	
Ti - 4.5Zr - 0.15O	0.147	0.004	85
Ti - 4.5Zr - 0.25O	0.242	0.003	85
Ti - 4.5Zr - 0.4O	0.374	0.010	85
Ti - 4.5Zr - 0.6O	0.561	0.003	40
Ti - 4.5Zr - 0.8O	0.835	0.003	40
Ti - 0.4O	0.392	0.007	40
Ti - 9Zr - 0.4O	0.389	0.008	40

The metal sheets were subsequently recrystallized in pre-heated molten carbonate baths at 750°C for 600s and water quenched. Electron Backscatter Diffraction (EBSD) studies were carried out in a ZEISS GEMINI field emission gun scanning electron microscope (FEG-SEM) operating at 20kV. Prior to EBSD observations, samples were electropolished using a solution of 59% 2-butoxyethanol, 33% CH₃OH, 6% HClO₄ and 2% HCl. Flat tensile specimens were machined along the rolling direction and then tested with an INSTRON 5966 tensile machine at room temperature at a strain rate of 10⁻³s⁻¹. A 10 mm gauge length extensometer was used for direct strain measurement. Slices of the tensile samples were taken parallel to the tensile axis and mechanically polished up to 100µm of thickness. Thin foil specimens were prepared with a twin-jet electropolishing apparatus using a solution of methanol, butan-2-ol and perchloric acid (10 : 6 : 1 volume ratio), at 19 V and with a temperature between -25 and -13°C. The thin foils were examined with a JEOL 2000EX electron microscope operating at 200 kV.

Results and discussion

Microstructure's sensitivity to alloying elements

The evolution of EBSD mapping of recrystallised samples according to zirconium content is displayed along the rolling direction (RD) on figure 1. All alloys exhibit a single HCP phase composed of equiaxed grains. The microstructure is highly textured and present the expected orientation for α titanium submitted to cold rolling followed by recrystallization treatment along RD [14]. However, the grain size is revealed to be very sensitive to the alloy composition (figure 1.d).

Figure 1: EBSD mapping of Ti-X%Zr-0.4%O with X=0, 4.5 or 9 ((a), (b), (c) respectively) in recrystallised state and along RD. (d) represents the grain size evolution according to Zr content. (b) is representative of Ti-4.5%Zr-Y%O microstructure (Y=0.15 to 0.8)

Hence, a ratio of 1:6 can be noticed with the addition of Zr, leading to a reduction of the average grain size from 30 to 5 μm. Still, further increase in Zr content does not lead to significant grain size decrease. This phenomenon was evidenced by Matayshi & al [15] in Ti-Zr alloys and seems to arise from a zirconium segregation at the grain boundaries (GB). This “solute drag effect” would lead to GB pinning and prevent grain coarsening even during heat treatment at high temperature.

The figure 1.b is representative of the microstructure of all Ti-4.5%Zr-X%O alloys (with X = 0.15-0.8%). It is worth noting that the grain size and the texture stay unchanged with O addition, regardless the thickness reduction applied. Eventually, in accordance with the known solubility limit of oxygen in HCP titanium [10,15,16], no other phase is evidenced on recrystallized states, even in oxygen-rich materials.

Contributions of the alloying elements to the tensile properties

The uniaxial tensile behaviour of the Ti-Zr-O alloys is plotted on figure 2.a and 2.b according to zirconium and oxygen contents, respectively. At first sight, it can be noticed that both exhibit enhanced yield strength and mechanical resistance with increasing alloying element content. The yield stress evolution with respect to substitutional concentration is found to increase of about 33MPa per 1wt%Zr addition. This increase is believed to originate from two major factors. The first one is the Hall-Petch effect as a result of the grain size reduction from 30 to 3 μm due to some “solute-drag effect”. Nevertheless, Medvedev *et al.* [18] assessed that such a grain size decrease in Ti-Zr alloys could not be responsible for a rise of the yield strength of more than 80MPa. Thus, the solid solution effect shall account as a complementary contribution to the observed strengthening. However, those two effects are accompanied by a slight deterioration in ductility at higher zirconium content, as stated in the literature [18-19]. This trend justified maintaining Zr content as low as 4.5wt% for the other Ti-Zr-O alloys for optimized strength/ductility combination.

Figure 2: Evolution of tensile properties of TiZrO alloys according to Zr content (a) (wt%O fixed at 0.4) and according to O content (b) (wt% Zr fixed at 4.5). Materials were tested at room temperature at a strain rate of $10^{-3}s^{-1}$.

As expected, the strengthening effect of oxygen is shown to be much higher compared to the one of zirconium. Indeed, with a drastic yield strength increase of around 100MPa for 0.1wt%O (consistent with the values stated in the literature for O addition in pure Ti [12-13]), the hardening potential of the interstitial element is thirty times stronger than zirconium in TiZrO alloys. Surprisingly, and in contrast with Ti-O based systems, unrepresentative ductility loss has been witnessed, despite extra-high oxygen contents up to 0.8wt%. As a result, a promising combination of mechanical properties can be reached in the Ti-4.5Zr-0.8O alloy, displaying a UTS value of 1075MPa combined with a total elongation of 28% at fracture. It may be noted that this level of ductility has been hardly obtained, in “high-strength” titanium alloys (over 1000 MPa in UTS), neither by precipitation nor by pre-deformation treatments approaches.

Analysis of the dislocation network

In order to explain the unexpected combination of properties in the oxygen-rich alloys, TEM analysis are conducted on strained samples to study the evolution of the dislocation network in relation with interstitial content (figure 3).

Figure 3: TEM observations of dislocation networks of Ti-4.5%Zr-X%O alloys, X=0.15, 0.4, 0.6 and 0.8 (respectively (a), (b), (c), and (d)). Slices were taken in 3%-strained tensile samples, parallel to the tensile axis.

Regardless of the oxygen concentration, screw dislocations control plastic deformation in Ti-Zr-O alloys at room temperature. In low oxygen content materials (figure 1.a), the dislocation network seems entangled, whereas in oxygen-rich alloys (figure 1.d), plastic deformation is no more homogeneous. Furthermore, solute oxygen enhances the pinning effect and the density of debris seems to increase with the interstitial addition, which witnesses the presence of extensive cross slip. In other words, as oxygen content increases, an evolution can be observed from entangled to lined up dislocations, with dislocations becoming straight and hardly aligned along their screw direction. Such behaviour has already been reported [20-21] but with lower oxygen level. Indeed, the appearance of bands is also highlighted, in the most oxygen-rich alloy (figure 1.d), in which dislocations are confined. However, this type of strain localization at microscale should lead to a facilitated material damage during straining, which is not observed. Further investigations will be conducted to apprehend this apparent contradiction between macro- and microscale behaviours.

Conclusion

In summary, a new Ti-Zr-O alloy family has been designed in order to offer a fully biocompatible alternative for current dental implant materials (Ti-6Al-4V, particularly). The Ashby chart, displaying mechanical strength versus elongation at fracture, over the different titanium alloys families (figure 4), clearly shows that the combination of properties of Ti-Zr-O alloys is unprecedented, especially among the single-phase α titanium alloys. All this conducted to a patent deposit on November 2017 on the Ti-Zr-O family composition [23].

Figure 4: Property map of titanium alloys with location of TiZrO Alloys.

The previous experimental observations may promote the “O based solid solution strengthening approach” opening new tracks in the design strategies, as these preliminary results showed its potential remarkable efficiency for strength/ductility trade-off optimization. The comprehension of the underlying mechanisms supporting these properties is still ongoing.

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