Stress-induced martensitic transformation in a Ti$_{45}$Zr$_{38}$Al$_{17}$ cast rod

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Abstract. An ordered B2 intermetallic compound with composition Ti$_{45}$Zr$_{38}$Al$_{17}$ was prepared by copper mold casting. The density of the alloy is 5.078 g/cm$^3$, whereas the Poisson’s ratio and the Young’s modulus are 0.38 and 70 GPa, respectively. Room temperature compression tests show good mechanical properties, namely, a high strength of 1650 MPa combined with a plastic strain of about 19.5 %. These parameters make the material an interesting candidate for biomedical applications like prostheses. Structure investigations reveal that during compression the alloy undergoes a martensitic transformation which proceeds from the parent B2 structure to the orthorhombic B19 structure through an intermediate step involving a hexagonal phase.

1. Introduction

Titanium-based alloys are nowadays widely used as materials for biomedical load-bearing implant applications such as dental, knee, or hip prostheses [1, 2]. The development of new alloys is challenging, since a lot of requirements have to be fulfilled before it can be embedded in the human body. Namely, the materials should be bio-compatible and not cytotoxic, have a low density, high strength, high ductility, and they should have a low elastic modulus adapted to the respective bone [1-3]. Furthermore, they should have a high corrosion resistance and a good fatigue life. Among the advanced structural and functional materials, one strength of Ti-based alloys is that their corrosion resistance is superior to other alloys [4]. Additionally, commercial Ti-based alloys have an ultimate strength ranging between 700 and 1300 MPa and show a plastic strain to failure of 10–25 % [5].

Pure titanium has a relatively high melting point of 1941 K. The phase which is stable at room temperature is the α-phase which crystallizes in a hexagonal close-packed structure (hcp). At 1155 K it transforms into the β-phase which is stable up to the melting point and crystallizes in a body centred cubic structure (bcc). According to this, titanium alloys can be classified in the different groups α, α-β, and β. The transition temperature, and with it the formed phase, is strongly influenced by the alloying elements. Depending on this, the alloying elements are either α-stabilizers (Al, O, N, C, La), β-stabilizers (Mo, V, Nb, Ta, Fe, W, Cr, Si, Co, Mn, H), or neutrals (Zr). For example, the most widely used alloy developed for biomedical applications, Ti-6Al-4V, belongs to the family of α-β alloys [3]. Since these materials show a relatively high Young’s modulus as compared to human bone, the trend in the recent years was to develop β-type materials with good mechanical properties, low toxicity and a low Young’s modulus [2, 6].
In this work, a novel titanium-zirconium-based alloy with composition Ti$_{45}$Zr$_{38}$Al$_{17}$ has been prepared by copper mold casting and the mechanical properties have been evaluated by room temperature compression tests. The composition of the ternary Ti$_{45}$Zr$_{38}$Al$_{17}$ alloy was obtained by replacing Ni with Al in the well-known Ti$_{45}$Zr$_{38}$Ni$_{17}$ quasicrystal-forming alloy [7] with the aim of developing a high-strength Ti-based alloy characterized by low density and low Young’s modulus. Finally, the effect of plastic deformation on phase formation has been studied by investigating samples at different stages of plastic deformation. The formed phases were analyzed using X-ray diffraction and the determined lattice parameters are reported.

2. Experimental

An ingot with nominal composition Ti$_{45}$Zr$_{38}$Al$_{17}$ (purity > 99.9 wt.%) was prepared by arc melting in a titanium-gettered argon atmosphere. The ingot was remelted several times in order to achieve a homogeneous master alloy. From this ingot, cylindrical bulk samples with 3 mm diameter and 100 mm length were prepared by copper mold casting. The density of the samples was evaluated by the Archimedes principle. Cylindrical specimens of 3 mm diameter and 6 mm length were prepared from the as-cast rods and tested with an INSTRON 8562 testing facility under quasistatic loading (strain rate of 5x10$^{-5}$ to 1x10$^{-4}$ s$^{-1}$) at room temperature. Both ends of the specimens were polished to make them parallel to each other prior to the compression test. The elastic constants were evaluated by ultrasonic measurements using an Olympus 5900 PR ultrasonic pulser-receiver. The structure of the samples was characterized by X-ray diffraction (XRD) in transmission mode using a STOE Stadi P diffractometer (Mo K$_\alpha$ radiation, $\lambda$ = 0.07093 nm). The analysis of the diffraction patterns was carried out using the WinPlotR software package [8, 9]. The phase analysis and the determination of the lattice parameters of the as-cast and deformed materials were performed with profile fitting (LeBail fitting). The crystal structures were visualized using the computer program VESTA [10].

3. Results and discussion

The Ti$_{45}$Zr$_{38}$Al$_{17}$ rod displays remarkable mechanical properties. The Poisson’s ratio and the Young’s modulus, estimated by ultrasonic measurements, are 0.38 and 70 GPa, respectively. The Young’s modulus of the current alloy is remarkably lower than that of Ti-based alloys currently used as structural biomaterials in bone-replacing applications, such as Ti-6Al-4V (about 110 GPa [2]). This is a critical aspect for bone-replacing implants which require low elastic stiffness approximating as far as possible that of the surrounding bone tissue [11], which is about 15-25 GPa [2]. A typical room temperature uni-axial compression true stress-true strain curve of the tests under quasistatic loading for the Ti$_{45}$Zr$_{38}$Al$_{17}$ alloy is shown in figure 1. The specimen exhibits an elastic regime of 1.85% before yielding, which occurs at about 1350 MPa (0.2% offset). After yielding the stress increases with increasing strain reaching an ultimate compression strength (UCS) of about 1650 MPa. The stress

![Figure 1. Compressive stress-strain curves of the as-cast Ti$_{45}$Zr$_{38}$Al$_{17}$ rod. The circles indicate the points 1-3 at which samples for X-ray diffraction were prepared.](image-url)
then slightly decreases with further increasing strain up to fracture, which occurs at a stress of about 1500 MPa and at 19.5 % strain. Such properties are comparable to those of recently developed Ti-based [12, 13] which show a yield strength varying between 1000 and 1800 MPa combined with plastic strain of 5-20 %. However, the current alloy is characterized by a lower density (5.078 g/cm$^3$) with respect to other Ti-based alloys (> 5.35 g/cm$^3$) [13] giving rise to a higher strength/density ratio.

The diffraction pattern of the as-cast sample is shown in figure 2. The as-cast material crystallizes in the B2 (CsCl) structure type with spacegroup Pm-3m. Therefore, the Ti$_{45}$Zr$_{38}$Al$_{17}$ rod belongs to the family of β-Titanium alloys. The lattice parameter is $a = 0.338377(8)$ nm, as determined by profile analysis. The three elements titanium, zirconium and aluminium are distributed on two crystallographic sites, namely the 1a and 1b sites.

In order to study the effect of the plastic deformation on phase formation, the structure of samples at different stages of plastic deformation were analyzed using X-ray diffraction: (i) deformed to 10 % strain (point 2 in figure 1) and (ii) deformed to 19.5 % (point 3 in figure 1), the latter one corresponding to the fracture strain. The diffraction pattern of the sample deformed up to 10 % strain (figure 2) shows additional reflections to the initial B2 phase. All the peaks observed in the diffraction pattern can be explained when an hcp structural model with the spacegroup P6$_3$/mmc is assumed. The lattice parameters of this hexagonal phase are: $a = 0.590037(2)$ nm and $c = 0.481426(5)$ nm. It was reported that the composition Ti$_2$ZrAl also crystallizes in the hexagonal Structure P6$_3$/mmc [14]. This structure is a superstructure of α-titanium with doubled lattice parameters $a$ and $b$. The diffraction pattern of the material deformed up to fracture (19.5 %) can be indexed with a B19 (AuCd) structure type with the orthorhombic spacegroup Pmma. Additionally to the reflections of the B19 phase, the reflections of the initial B2 phase are still present. This indicates that only a part of the material transforms during deformation. All reflections can be explained assuming these two phases. The determined lattice parameters for the B19 phase are: $a = 0.3128(1)$ nm, $b = 0.4832(2)$ nm, and $c = 0.5139(2)$ nm.

A martensitic transformation of a B2 to a B19 structure is well known for titanium-based shape memory alloys. In that case, the material directly transforms from B2 to B19 by a shear/shuffle of the B2 (1 1 0) plane along the B2 [1 -1 0] direction [15]. In the case of the plastic deformation of the Ti$_{45}$Zr$_{38}$Al$_{17}$-alloy in this study, the transition seems to include a further step, namely the P6$_3$/mmc phase. The crystal structures of the three phases observed during plastic deformation are illustrated in figure 3.
Figure 3. Crystal structures of the three phases observed for the as-cast material, as well as for the 10 % and 19.5 % deformed Ti₄₅Zr₃₈Al₁₇ alloy, respectively. The initial B2 type structure is still present at the different degrees of deformation.

4. Summary
The investigation of the structural transformations occurring during plastic deformation of the titanium-based Ti₄₅Zr₃₈Al₁₇ alloy has shown an interesting two-step like behaviour. The initial B2 type intermetallic compound first transforms to a hexagonal phase, which is similar to the equilibrium phase of Ti₂ZrAl, and then to a B19-type orthorhombic phase upon fracture. For all investigated phases the lattice parameters have been determined. These are the first insights into the plastical transformation mechanism for this material that is interesting from the viewpoint of mechanical properties which were also investigated. A low density of 5.078 g/cm³ as well as a Poisson’s ratio and a Young’s modulus of 0.38 and 70 GPa, respectively, have been determined. These are combined with a high strength of 1650 MPa and a plastic strain of nearly 20 % making the material a promising candidate for biomedical applications.

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