Materials Science and Engineering C 51 (2015) 148–152

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Microstructure and mechanical properties of Ti–Zr–Cr biomedical alloys

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ARTICLE INFO

Article history:
Received 29 December 2014
Received in revised form 6 February 2015
Accepted 23 February 2015
Available online 24 February 2015

Keywords:
Microstructure
Titanium alloy
Mechanical properties
Biomaterials

ABSTRACT

The Ti–15Zr–*x*Cr ($0 \le x \le 10$, wt.%) alloys were investigated to develop new biomedical materials. It was found that the phase constitutions and mechanical properties strongly depended on the Cr content. The Ti–15Zr alloy was comprised of α′ phase and a small fraction of β phase was detected with adding 1 wt.% Cr. With addition of 5 wt.% or more, the β phase was completely retained. In addition, the ω phase was detected in the Ti–15Zr–5Cr alloy and Ti–15Zr–7Cr alloy which exhibited the highest compressive Young's modulus and the lowest ductility. On the other hand, all the Ti–15Zr–*x*Cr alloys without ω phase exhibited high microhardness, high yield strength and superior ductility. Furthermore, the elastic energy of Ti–15Zr–10Cr alloy (5.89 MJ/m^3) with only β phase and that of Ti–15Zr–3Cr alloy (4.04 MJ/m^3) with α′ phase and small fraction of β phase was higher than the elastic energy of c.p. Ti (1.25 MJ/m^3). This study demonstrated that Ti–15Zr–3Cr alloy and Ti–15Zr–10Cr alloy with superior mechanical properties are potential materials for biomedical applications.

1. Introduction

Titanium and its alloys are prized metals for biomedical applications mainly because of their amazing combination of strength, toughness, ductility and corrosion resistance [1,2]. The commercially pure Ti (c.p. Ti) with a low strength is currently used as dental implant while the Ti–6Al–4V alloy with a high strength is widely used as orthopedic implant [1]. However, the release of V ion into the human body induces cytotoxic effects and might cause long-term health problems [3,4]. Therefore, many efforts have been devoted to develop V-free Ti alloys, such as Ti–Zr [5,6], Ti–Mo [7,8], Ti–Ta [9], Ti–Nb [10–12] and Ti–Cr alloys [13–15].

Besides the stable phases in Ti alloys, many metastable phases which are α′, α″, ω and β′ phases, can be formed due to the insufficient cooling time during fabrication. The mechanical properties of Ti alloys are sensitive to their phase constitutions because the mechanical properties of different phases are various [1,12,16,17]. Among all the alloying element, Zr is a promising candidate that exhibits acceptable mechanical strength, low ionic cytotoxicity in vitro, excellent biocompatibility in vivo, a good resistance to corrosion and superior osteocompatibility [4,15,18,19]. Therefore, Zr is considered as alloying element in mostly new-developed Ti alloys for biomedical applications, such as in Ti–29Nb–13Ta–4.6Zr [20,21], Ti–24Nb–4Zr–8Sn [22] and Ti–3Zr–2Sn–3Mo–25Nb alloys [23]. On the other hand, Cr, which has excellent corrosion resistance, is a strong β stabilizer [24]. In addition, Cr is proved to control the anodic activity of Ti alloys and increase the tendency of Ti to passivate that increases the corrosion resistance of Ti alloys [4,25]. Although Cr is toxic and elicits an allergic response, the toxicity and allergenicity of Cr are mainly attributed to Cr ions rather than the metal [26,27] and the release of Cr ions could be prevented by the self-repairable titanium oxide layer formed on the Ti alloy surface. Therefore, toxic and allergic problems related to Cr in the present study are ignorable and Cr is also a promising alloying element to be added into Ti base alloys for biomedical applications.

A recent work has shown that Ti–10Zr–*x*Cr alloys exhibiting high hardness and bending strength, but too high Young's modulus [24,28]. For biomedical Ti alloys, the high strength to bear heavy loading and low Young's modulus to avoid the stress shielding are required. Therefore, a further investigation on Ti–Zr–Cr alloys to develop new alloys with lower Young's modulus for biomedical applications is necessary. Since the addition of Zr into Ti alloys increases the stability of β phase [29] but did not enhance the Young's modulus of β phase [30], it is expected that the Ti–15Zr–*x*Cr alloys have the potential to exhibit higher stress bearing ability and lower Young's modulus than Ti–10Zr–*x*Cr alloys.

A series of Ti–15Zr–*x*Cr alloys were prepared and subjected to mechanical property evolutions in this study. The purpose is to develop new Ti alloys to satisfy high requirements of high hardness, high strength and low Young's modulus in biomedical applications, such as dental implant and hard tissue replacements.

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http://dx.doi.org/10.1016/j.msec.2015.02.028
0928-4931/

2. Experimental procedure

The ingots of c.p. Ti and Ti–15Zr–*x*Cr alloys with nominal composition (in wt.%) of Ti–15Zr, Ti–15Zr–1Cr, Ti–15Zr–3Cr, Ti–15Zr–5Cr, Ti–15Zr–7Cr, Ti–15Zr–10Cr were prepared by using arc melting on a water-cooled copper hearth in a high-purity argon gas atmosphere. The raw materials were pure sponge titanium (>99.9 wt.%), pure zirconium (>99.9 wt.%), and pure chromium (>99.9 wt.%). These ingots were re-melted at least eight times to ensure the chemical homogeneity. Specimens for all measurements were cut from the ingots. After removing the damaged surface by mechanical polishing with SiC paper to 2000#, the electropolishing was carried out in a solution of 6% perchloric acid, 35% butanol, and 59% methanol at ~230 K.

The phase constitutions of all the alloys were characterized via X-ray diffraction (XRD) at room temperature with Cu Ka radiation operated at 45 kV and 40 mA and the microstructure of all the alloys was examined by using an optical microscope. For optical microscope observation, the polished specimens were etched in an aqueous solution of hydrofluoric acid (HF, 10 vol.%) and nitric acid (HNO_3, 20 vol.%).

The mechanical properties like microhardness, Young's modulus, yield strength and ductility were determined by Vickers hardness and compressive test. The microhardness measurement of polished specimens was carried out using Vickers hardness tester (MMT-3; Matsuzawa, Tokyo, Japan) at 500 g for 10 s and the compressive test was conducted at room temperature in air at an initial strain rate of $1.67 \times 10^{-3}\ s^{-1}$ using the Instron servohydraulic dynamic testing system. The dimension of the compression specimen was 5 mm × 5 mm × 10 mm. In addition, a strain gage was applied to measure the compressive Young's modulus.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the XRD patterns of c.p. Ti and Ti–15Zr–*x*Cr ($0 \le x \le 10$) alloys, indicating that the phase constitutions of Ti–15Zr–*x*Cr alloys are sensitive to the Cr content. The c.p. Ti and Ti–15Zr alloy only contained α phase and α′ phase (Fig. 1), respectively [5]. There is no indication that β phase peaks or any intermediate phases were included in Ti–15Zr alloy because Ti–Zr binary system shows a completely solid solution for both high temperature β phase and low-temperature α phase. In contrast with the Ti–15Zr alloy, since the alloying element Cr acted as a β stabilizer, a small amount of β phase was retained with only 1 wt.%. Cr addition. This is different with that obtained in Ti–10Zr–Cr alloys by Ho et al. [24]. This variation is ascribed to the change of Zr content in the present alloy system. It is suggested that Zr stabilized β phase in the β-type Ti alloys [29], although it is usually considered as neutral element. With the increase of Cr content, the volume fraction of β phase increased, which was proved by the increased intensity of the peaks of β phase in the Cr containing alloys. By introducing more than 5% Cr, the peaks from α′ phase disappeared on the XRD patterns, but the peaks from β phase was observed in the alloys, suggesting β phase was entirely retained with a body-centered cubic crystal structure.

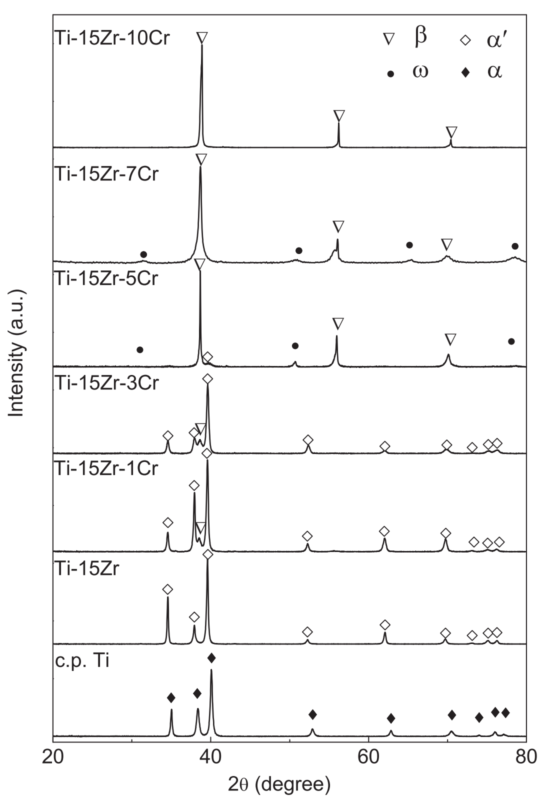

Fig. 1. XRD patterns of c.p. Ti and Ti–15Zr–*x*Cr alloys at a scan rate of 2°/min.

Fig. 1 also shows peaks of ω phase in Ti–15Zr–5Cr and Ti–15Zr–7Cr alloys. ω phase, which formed in metastable β Ti alloys [31,32], drastically affects the mechanical properties and increases the Young's modulus although it is a nanostructured phase [20,25,33]. Therefore, it is important to check the ω phase formation or not by a lower scanning speed. However, the ω phase was only detected in Ti–15Zr–5Cr and Ti–15Zr–7Cr alloys although a very low scanning rate, 0.2°/min, was performed. This means the ω phase only forms in Ti–15Zr–5Cr and Ti–15Zr–7Cr alloys.

Fig. 2 shows optical micrographs of Ti–15Zr–*x*Cr alloys. Comparing to c.p. Ti (optical micrograph not shown here), the coarse acicular martensitic structures appeared in Ti–15Zr alloy (Fig. 2a) as a result of martensitic transformation start temperature decreased with 15% Zr addition [5]. With the addition of Cr content, the martensitic structures were refined gradually (Fig. 2 b and c) and the retained β phase was observed (Fig. 2c). On the other hand, β phase became dominant when Cr addition is more than 5% or more (Fig. 2d–f). These results agree with the XRD results though the ω phase is too small to be observed by an optical microscope.

3.2. Mechanical properties

Fig. 3 shows microhardness values of c.p. Ti and the Ti–15Zr–*x*Cr alloys. The microhardness of Ti–15Zr alloy was higher than that of c.p. Ti due to the solution strengthening [5]. The microhardness values of all the Ti–15Zr–*x*Cr alloys (214–519 HV) were significantly higher than that of c.p. Ti (177 HV). Additionally, the Cr element effectively increase the microhardness values in the Ti–15Zr base alloys because of solution strengthening, precipitation strengthening, etc. When 1 wt.% and 3 wt.% Cr were added into Ti–15Zr alloy, the microhardness slightly increased to 254 and 316 HV, respectively. This is caused by the solution strengthening of Cr in α′ phase Ti–15Zr alloy. These results are in agreement with the microhardness of Ti–10Zr–Cr alloys [28]. Furthermore, Ti–15Zr–5Cr and Ti–15Zr–7Cr alloys had significantly higher microhardness values among all the Ti–15Zr base alloys, which is mainly a result of the hardening effect of ω phase. It was reported that ω phase had the highest hardness among all of the stable phases and metastable phases in Ti alloys and drastically increases the hardness of Ti alloy [34]. On the other hand, the microhardness of Ti–15Zr–10Cr alloy decreased to 307 HV due to the disappearance of ω phase, but it was still 1.7 times greater than that of c.p. Ti. This value is also greater than that of Ti–10Zr–10Cr alloy (about 260 HV) [28], which is responsible to the solution strengthening caused by adding Zr.

Fig. 4 shows the room temperature compressive stress–strain curves of c.p. Ti and the Ti–15Zr–*x*Cr alloys. It is exhibited that the alloying element Cr has an important impact on the yield strength, plastic strain and compressive Young's modulus of these alloys. All the compositions except Ti–15Zr–5Cr alloy (brittle fracture) and Ti–15Zr–7Cr alloy (2% plastic strain) exhibit more than 35% plastic strain. At least 40%