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Designing a toxic-element-free Ti-based amorphous alloy with remarkable supercooled liquid region for biomedical application

H.C. Lin [a], P.H. Tsai [a], J.H. Ke [a], J.B. Li [b], J.S.C. Jang [a, b, *], C.H. Huang [c], J.C. Haung [c, **]

[a] Institute of Materials Science and Engineering, National Central University, Taoyuan 32001, Taiwan, ROC
[b] Department of Mechanical Engineering, National Central University, Taoyuan 32001, Taiwan, ROC
[c] Department of Materials and Optoelectronic Materials, National Sun Yat-Sen University, Kaoshoung 80424, Taiwan, ROC

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ABSTRACT

A series of toxic-element-free Ti–Zr–Ta–Si amorphous alloy ribbons have been successfully prepared by melt-spinning. The differential scanning carlorimetry (DSC), X-ray diffraction analysis, bending test and microhardness test are conducted for studying the thermal and mechanical properties. The results show that the $Ti_{42}Zr_{40}Ta_3Si_{15}$ metallic glass ribbon present excellent ductile behavior by the bending testing, without any fracture cracking after bending over 180 degree. In addition, this amorphous alloy possesses a very high glass transition and crystallization temperature of 799 and 898 K, respectively, as well as a very wide supercooled liquid region of 99 K. This amorphous alloy exhibits promising thermal stability during isothermal annealing at the middle temperature of its supercooled region, with more than 3000 s incubation time for isothermal annealing at 823 K (550 °C). This amorphous alloy also shows much lower value of corrosion current density (2.27×10^{-9} A/m^2) than the 304 stainless steel in the 0.3 mass% sodium cloride solutions. This $Ti_{42}Zr_{40}Ta_3Si_{15}$ alloy is believed to be a promising based alloy for fabricating the bulk metallic glass foam by the spacer technique in the application of biomedical implants.

1. Introduction

In recent years, titanium and its alloys (e.g. Ti–6Al–4V and Ti–6Al–7Nb) are often used for the biomedical implant materials in the field of trauma and orthopedic surgery [1–3]. However, they are still subject to unsatisfactory long-termed tribology behavior and may have some health concerns [4,5]. Recently, another novel metallic material category, called the amorphous alloy or metallic glass (MG), for biomedical applications has attracted research attention. Since MGs do not have crystal structural defects such as dislocations, twins or grain boundaries, these materials would possess a homogenous composition with higher strength, higher hardness, lower Young's modulus, larger elastic strain, higher recovery rate (as a result of a higher degree of free volume), and much better corrosion resistance in comparison with typical crystalline alloys [5–15]. Such unique properties make MGs attractive for biomedical applications. Among all the bulk metallic glasses (BMGs), Ti-based BMGs (similar to their crystalline family of the commercial Ti alloys) are regarded as good candidates for bio-implant because of their low density, good biocompatibility and excellent corrosion resistance [3,12]. However, some elements like Be, Ni, Al, or Cu are frequently added in common Ti-based BMG alloy systems in order to improve the glass forming ability (GFA) [6,7,12]. But all of these elements are either toxic or not suitable to contact with human body for a long period [16]. Accordingly, several Be- and Ni-free Ti-based BMGs such as Ti–Zr–Pd–Cu [17], Ti–Zr–Pd–Cu–Nb [18], and Ti–Zr–Pd–Cu–Sn [19] alloys with relatively acceptable GFA have been developed recently, and exhibit reasonable combination of strength and corrosion resistance. In a more serious precaution, the Al or Cu element in the Ti-based amorphous alloys could induce harmful symptoms for human body and would also induce negative effects on the corrosion resistance in the simulated human solution [16,20].

Research reports along the line in developing Ti-based MGs without Be, Ni, Al or Cu have been very limited, for example, the Ti–Zr–Si–Ta [21] and Ti–Zr–Si–Nb [22] amorphous ribbons with good mechanical properties and corrosion resistance as compared

* Corresponding author. Institute of Materials Science and Engineering, National Central University, Taoyuan 32001, Taiwan, ROC. Tel.: +886 3 4267379.
** Corresponding author. Tel.: +886 7 5254063.
E-mail addresses: jscjang@ncu.edu.tw, jscjang@gmail.com (J.S.C. Jang), jacobc@faculty.nsysu.edu.tw (J.C. Haung).

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to commercial pure Ti. It was noted that the Ti–Zr–Si–Ta system with 15 at% of Ta [21] revealed better yield strength of 2390 MPa than the Ti–Zr–Si–Nb system with 15 at% of Nb with a yield strength: of 2200 MPa [22]. Meanwhile, Ta has been well known to enhance cell in-growth rate in human implant. Thus, the Ti–Zr–Si–Ta system appears to be a more preferable MG to be incorporate into implantable medical devices. However, the extremely high liquidus temperature (T_l, more than 1823 K), limited supercooled liquid region (SCL, <50 K), and unsatisfactory GFA of the Ti–Zr–Si–Ta alloy would impose difficulty in casting and shaping into sizable bio-implant devices. Accordingly, in this study, we made efforts in developing a series of new Ti–Zr–Ta–Si amorphous alloys with lower T_l and larger SCL region, more promising for the subsequent fabrication of Ti-based bulk metallic glass foams (BMGFs) by the spacer method of powder metallurgy [23–26].

2. Experimental procedures

Since we have excluded Cu or Ni, the two elements of the small atomic radius about 0.125 nm, which is generally needed to random the crystalline structure of the main element (in the current case the Ti or Ti + Zr, both hexagonal closed packed structure), an appreciable amount of Si with the even smaller atomic radius about 0.11 nm is added to play this role. The Si content is fixed at 15 at%. The pre-alloyed ingots based on the composition of $Ti_xZr_yTa_zSi_{15}$ ($x + y + z = 85$ in at%) were prepared by arc melting of the appropriate mixture of pure elements, such as titanium (99.9 wt% purity), zirconium (99.9 wt% purity), tantalum (99.9 wt% purity), and silicon (99.99% purity), under a Ti-guttered argon atmosphere. Then the alloy ingots were re-melted in an induction furnace under a purified argon atmosphere. After complete melting, the liquid alloys were injected on a water-cooled copper wheel (with tangent speed of 25 m/s and a gap of 0.2 mm between the quartz nozzle and the wheel surface) to form alloy ribbons by an argon back pressure of 4 kgf/mm^2. The ribbons structure was examined by X-ray diffraction (XRD, Bruker D8A), and the thermal properties, such as the glass transition temperature (T_g) and crystallization temperature (T_x), were characterized by differential scanning carlorimetry (DSC, Mettler Toledo DSC1) at a heating rate of 10–40 K/min. The liquidus temperature (T_l) of these ribbons were measured by high temperature differential scanning carlorimetry (HT-DSC, Netsch DSC404) at a heating rate of 10 K/min.

The mechanical flexibility of the ribbons was evaluated by the bending testing by folding a ribbon over 180 degree. After bending over 180 degree, the flexibility of ribbon are rated as B (brittle, the ribbon was fractured completely), SB (slight brittle, the ribbon was fractured partially), and D (ductile, the ribbon was not fractured at all). The hardness measurements for all alloy ribbons were carried out by the indentation method by a micro-hardness tester (Mitutoyo, HM-221) with a load of 30 gf. The fracture surfaces of the deformed specimens are examined by scanning electron microscopy (SEM, Hitachi S-3500). Transmission electron microscopy (TEM, FEI Tecnai G^2 S-Twin at 200 keV) is used to ascertain the amorphous nature of the as-quenched and as-annealed alloy ribbons. TEM samples were sliced from the cross section of the as-quenched and as-annealed alloy ribbons by using the dual beam focused ion beam system (FEI Versa 3D FEG FIB, operated at 30 kV) with special care to minimize the ion damage to samples. The measurements for electrochemical potential dynamic polarization were carried out in a 0.3 mass% NaCl solution and conducted at a scanning rate of 10 mV/min from −0.50 V versus open-circuit potential (OCP), into a more noble direction up to +4.0 V.

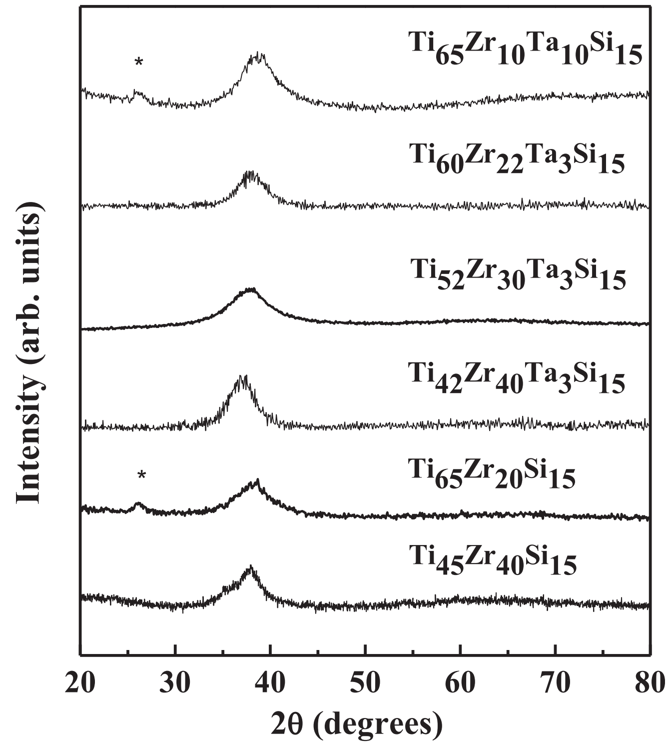

Fig. 1. XRD patterns of the as-quenched $Ti_xZr_yTa_zSi_{15}$ ($x + y + z = 85$, in at%) alloy ribbons. The small broad peak with * marker at about 27 degree can be indexed corresponding to the (003) diffraction peak of Ti_4O_7 phase.

3. Results and discussion

The XRD patterns obtained from the as-quenched $Ti_xZr_yTa_zSi_{15}$ ($x + y + z = 85$, in at%) alloy ribbons show a broad wide peak in the range of 30°–50° except for the alloys with high Ti content, such as $Ti_{65}Zr_{10}Ta_{10}Si_{15}$ and $Ti_{65}Zr_{20}Si_{15}$ alloys, which containing another small broad peak, as shown in Fig. 1. The small broad peak located around 27° is identified corresponding to the (013) diffraction peak of Ti_4O_7 phase. Since these two high Ti content alloys have very high liquidus temperature (over 1500 °C) and need to use the casting temperature over 1600 °C during the melt-spinning process. Therefore, these two Ti-based alloy melts are suggested reacting with the quartz tube and form Ti_4O_7 phase during the casting process. In general, all of these $Ti_xZr_yTa_zSi_{15}$ alloys in this study can be cast into amorphous ribbons by melt-spinning process.

The HT-DSC results (not shown) indicate that T_l decreases significantly by decreasing the Ta content from 10 at% to 3 at% as shown in Table 1. The lowest liquidus temperature of 1455 °C (1728 K) occurs for the alloy composition of $Ti_{42}Zr_{40}Ta_3Si_{15}$. In

Table 1
Thermal parameters of the as-quenched $Ti_xZr_yTa_zSi_{15}$ ($x + y + z = 85$, in at%) alloy ribbons. The index γ is defined by $T_x/(T_g + T_l)$ [26], γ_m by $(2T_x\text{-}T_g)/T_l$ [27], and T_{rg} by T_g/T_l.

Composition	T_g (K)	T_x (K)	T_l (K)	ΔT_x (K)	T_{rg}	γ	γ_m	Note
$Ti_{65}Zr_{10}Ta_{10}Si_{15}$	708	800	1813	92	0.39	0.32	0.49	Am
$Ti_{60}Zr_{22}Ta_3Si_{15}$	825	888	1768	63	0.47	0.34	0.54	Am
$Ti_{52}Zr_{30}Ta_3Si_{15}$	843	921	1744	78	0.48	0.36	0.57	Am
$Ti_{42}Zr_{40}Ta_3Si_{15}$	799	898	1728	99	0.46	0.36	0.55	Am
$Ti_{65}Zr_{20}Si_{15}$	870	958	1786	88	0.49	0.36	0.59	Am
$Ti_{45}Zr_{40}Si_{15}$	775	881	1753	106	0.44	0.35	0.56	Am

Note: heat rate of DSC is 20 K/min. Am: amorphous; Am/Cryst: partially amorphous.