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

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A B S T R A C T
A series of toxic-element-free Ti–Zr–Ta–Si amorphous alloy ribbons have been successfully prepared by melt-spinning. The differential scanning calorimetry (DSC), X-ray diffraction analysis, bending test and microhardness test are conducted for studying the thermal and mechanical properties. The results show that the Ti42Zr40Ta3Si15 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/m2) than the 304 stainless steel in the 0.3 mass% sodium chloride solutions. This Ti42Zr40Ta3Si15 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.

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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
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 incorporated 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 (BMGs) 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 present 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_{x}Zr_{y}Ta_{z}Si_{l} (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/mm². 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_c), were characterized by differential scanning calorimetry (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 calorimetry (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 G² 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.

3. Results and discussion

The XRD patterns obtained from the as-quenched Ti_{x}Zr_{y}Ta_{z}Si_{l} (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_{30}Si_{15} and Ti_{65}Zr_{20}Ta_{30}Si_{15} alloys, which contain 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 TiO₂ 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 TiO₂ phase during the casting process. In general, all of these Ti_{x}Zr_{y}Ta_{z}Si_{l} 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_{3}Si_{15}. In

![Fig. 1. XRD patterns of the as-quenched Ti_{x}Zr_{y}Ta_{z}Si_{l} (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 TiO₂ phase.](image)
addition, the DSC scans of all as-quenched Ti_{x}Zr_{y}Ta_{z}Si_{15} alloy ribbons exhibit a minor small hump followed by a large exothermic peak due to crystallization, as shown in Fig. 2. In order to identify the true supercooled liquid region, the Ti_{x}Zr_{y}Ta_{z}Si_{15} alloy ribbon was vacuum annealed for 5 min at the temperature of the small hump (namely 530 °C) and at temperature after the large exothermic peak (namely 700 °C), respectively. Then the annealed samples were characterized by XRD. Only the sample annealed at 700 °C shows a typical crystalline XRD pattern and the sample annealed at 530 °C still presents a broaden XRD pattern in the range of 30°–50°, as shown in Fig. 3. This indicates that the amorphous nature is still kept after annealed over the temperature of the first small hump but before the large exothermic peak. In parallel, the results of TEM analysis on the Ti_{x}Zr_{y}Ta_{z}Si_{15} alloy ribbon under the as-quenched and the annealed (at 530 °C) condition also support that the amorphous state is still remained after annealing at 530 °C, as illustrated in Fig. 4.

In order to reconfirm the SCL region, the as-quenched Ti_{x}Zr_{y}Ta_{z}Si_{15} alloy ribbons were isothermally annealed at various temperatures within the SCL region (namely 550, 560, 575 and 580 °C) to clarify its incubation time and crystallization behavior. Fig. 5 shows the heat flow as a function of annealing time for the Ti_{x}Zr_{y}Ta_{z}Si_{15} alloy ribbons. The typical exothermic heat flow of crystallization can be clearly seen at each annealing temperature. A quite long incubation time period more than 3000 s can be obtained upon the isothermal annealing at 550 °C. Therefore, the \( T_{g} \) and \( T_{x} \) can be presumably defined at the onset temperature of the first small hump and at the onset temperature just before the large exothermic peak, respectively. The overall thermal properties of the Ti_{x}Zr_{y}Ta_{z}Si_{15} amorphous alloys are listed in Table 1. Nevertheless, all of these Ti_{x}Zr_{y}Ta_{z}Si_{15} alloys present similar lower values of GFA index (\( \gamma_{m} \) [27] values are typically ranging from 0.34 to 0.36) or \( \gamma_{m} \) [28] values are typically ranging from 0.54 to 0.59) in comparison with that of Ti_{x}Zr_{y}Cu_{z}Si_{14} alloy [17]. For Zr- or Cu-based BMGs (with the smaller atomic-size elements such as Cu or Ni) capable to be cast into sizable rods over 10 mm in diameter, the value of \( \gamma_{m} \) need to be about 0.40 and 0.65 or above, respectively. The GFA index in Table 1 would imply that the current Ti-based alloys would be difficult to be cast into large rods. It follows that the sintering of amorphous MG powders would be more feasible for preparing the bulk metallic glass foams, as reported elsewhere [29]. But on the other hand, the current alloys all possess quite large SCL region in Table 1, and Ti_{x}Zr_{y}Ta_{z}Si_{15} even exhibits an SCL \( \Delta T_{f} \) of 99 K. Such a wide SCL temperature range would benefit significantly for the subsequent thermoplastic forming process for bio-implant devices.

The mechanical response of the melt spun ribbons is characterized by Vickers’s microhardness and bending testing. The microhardness readings are presented in Table 2. Except the Ti_{x}Zr_{y}Ta_{z}Si_{15} alloy, the microhardness readings of the rest alloys exhibit a decreasing trend with decreasing the Ti/Zr atomic ration. Basically, the hardness ranges from 550 to 850 H_{v}, all greater than the ~200–300 H_{v} for the commercial Ti alloys. The current hardness level can be classified as sufficient surface hardness for practical biomedical uses. As for the bending, three representative SEM images of the fracture ribbons after bending over 180 degree are illustrated in Fig. 6. The fracture surfaces of the Ti_{x}Zr_{y}Ta_{z}Si_{15} and Ti_{y}Zr_{z}Si_{15} alloy ribbons present the similar brittle (termed B in Table 2) morphology with sharp and flat cleavage facets; the typical image is shown in Fig. 6(a). In comparison, the fracture surface of the Ti_{x}Zr_{y}Ta_{z}Si_{15} and Ti_{y}Zr_{z}Si_{15} alloy ribbons shows only slightly brittle (termed SB in Table 2) morphology with partial cleavage facets, many shear bands crossed over the fracture surface leaving the vein-like pattern on the fracture surface, as shown in Fig. 6(b). On the contrary, the Ti_{x}Zr_{y}Ta_{z}Si_{15} and Ti_{y}Zr_{z}Si_{15} alloy ribbons exhibit the best flexibility and ductile (termed D in Table 2) fracture behavior. No obvious fracture crack could be found with only many shear band traces on the bended area of
these two alloy ribbons after bending over 180 degree, as shown in Fig. 6(c). In general, the brittle alloy ribbons would possess the higher hardness (such as the Ti65Zr20Si15 and Ti60Zr22Ta3Si15 alloys), and the softer alloy ribbons (such as the Ti42Zr40Ta3Si15 alloy) would exhibit the best flexibility without fracture over bending testing.

Based on the above evaluation tests in terms of various thermal and mechanical responses, the Ti42Zr40Ta3Si15 alloy appears to possess the lowest Tl of 1728 K (or 1455 °C, easy to cast), large SCL region of 99 K (easy to form into complicated shape by thermoplastic forming), and the best ductile flexibility in the Ti_xZr_yTa_zSi_15 alloy system. All of these characteristics are promising for subsequent fabrication into Ti-based bulk metallic glass foams by the spacer method via thermoplastic forming process [24–26].

Therefore, we conduct the electrochemical corrosion resistance evaluation for this very alloy. The major element for inducing the serious corrosion behavior in either NaCl or simulated body fluid (SBF) is the high ionic strength chloride (Cl). There have been some previous studies, showing the high Cl-containing product on the corroded regions [30,31]. Therefore, we immersed the Ti-based glassy alloy under extreme Cl-containing corrosive media, 3.5% NaCl solution for evaluating the corrosion resistance between the 304 SS and Ti-based glassy alloys. The results of the potentiodynamic polarization test in the 3.5 mass% NaCl solutions of the Ti42Zr40Ta3Si15 amorphous alloy and 304 stainless steel (SS) are presented in Fig. 7. The results show that the values of the corrosion voltage (E_corr) readings for the Ti42Zr40Ta3Si15 amorphous alloy and 304 SS are about 2.2 and –0.032 V, respectively. Ti42Zr40Ta3Si15 can sustain a much higher voltage before corrosion reaction. Also, the corrosion current density (I_corr) for the Ti42Zr40Ta3Si15 amorphous alloy and 304 SS estimated by the Tafel slope method are about 2.27 × 10^-9 A/cm^2 and 3.98 × 10^-7 A/cm^2, respectively. The comparison of the polarization curves indicates that the Ti42Zr40Ta3Si15 amorphous alloy exhibits a wider passive region than 304 SS, the passive region (E_pit – E_corr) of the Ti42Zr40 Ta3Si15 amorphous alloy can be up to about 1.25 V. This implies that with a small corrosion current density (I_corr) and a higher pitting potential (E_pit) in 3.5 mass% NaCl solutions, the Ti42Zr40 Ta3Si15 amorphous alloy exhibits much better corrosion resistance than 304 SS. In addition, a summarized comparison of the corrosion response of the Ti42Zr40Ta3Si15 MG, Ti–6Al–4V, and 304 SS under Hank’s SBF solution and 3.5 mass % NaCl solutions also show a good agreement with present results, as shown in Table 3. Without defects such as grain boundaries on the surface, the amorphous structure of the Ti42Zr40Ta3Si15 amorphous alloy results in a more homogeneous passive film after anodic polarization.

### Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hardness (Hv)</th>
<th>Bending behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti65Zr20Ta3Si15</td>
<td>610 ± 12</td>
<td>D</td>
</tr>
<tr>
<td>Ti60Zr22Ta3Si15</td>
<td>679 ± 5</td>
<td>B</td>
</tr>
<tr>
<td>Ti65Zr20Ta3Si15</td>
<td>624 ± 17</td>
<td>SB</td>
</tr>
<tr>
<td>Ti42Zr40Ta3Si15</td>
<td>560 ± 12</td>
<td>D</td>
</tr>
<tr>
<td>Ti52Zr30Ta3Si15</td>
<td>848 ± 7</td>
<td>B</td>
</tr>
<tr>
<td>Ti65Zr20Si15</td>
<td>604 ± 5</td>
<td>SB</td>
</tr>
</tbody>
</table>

Note: D: ductile; SB: slight brittle; B: brittle.
4. Conclusion

Based on the results of XRD, TEM, DSC, microhardness, bending and corrosion evaluations, the current toxic-element-free Ti$_{42}$Zr$_{40}$Ta$_{3}$Si$_{15}$ amorphous alloy is demonstrated to possess low liquidus temperature of 1728 K (or 1455 °C), wide SCL region of 99 K, promising thermal stability during isothermal annealing at its SCL region, high hardness of 560 H$\nu$, ductile flexibility and apparently upgraded corrosion resistance. The overall electrochemical corrosion performance of the metallic glass is considered to be either compatible or superior to the commercial Ti$_6$Al$_4$V or 304 SS. This suggests that the Ti$_{42}$Zr$_{40}$Ta$_3$Si$_{15}$ amorphous alloy is a promising material for producing the Ti-based BMGF by the spacer method of powder metallurgy and can be applied for the biomedical implants.

References