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Original Article

Synthesis and characterization of an open-pore toxic-element-free Ti-based bulk metallic glass foam for bio-implant application


A series of porous toxic-element-free Ti$_{43}$Zr$_{40}$Si$_{15}$Ta$_3$ bulk metallic glass with 13–54 vol.% porosity are produced via powder metallurgy by the space holder method. The amorphous nature, foam morphology, mechanical properties, electrochemical response in simulation body fluid and in-vivo biocompatibility responses are systematically investigated. Results show that these open-cell Ti-based bulk metallic glass foams (BMGFs) exhibit yield strength from 140 to 730 MPa and Young’s moduli from 8 to 53 GPa, matching very well with the mechanical properties of human bone and the estimated data by theoretical models. Compared to the bulk metallic glass (BMG) of the same composition, the high exposed surface area of the produced Ti-based BMGFs exhibited higher current in the cyclic voltammetry (CV) and potential state tests. However, no specific peak corresponding to the oxidation or reduction response of the composition elements is found in the electrochemical test. Moreover, the six-month in-vivo tests in New Zealand white rabbits shows that the good osteo-integration between the newly growth bone and the implanted Ti-based BMGFs, making them promising new candidates for bio-implant applications in avoiding stress shielding or bio-unfriendly symptoms.

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1. Introduction

Titanium (commercial pure Ti, or cp Ti) and its alloys are often used for the biomedical materials for long time [1–3]. However, they may have some health concerns and issue to meet the requirement for long time tribology behavior [4,5]. In recent year, one new metallic material, metallic glass (MG or called amorphous alloy), has attracted great attention on the research of biomedical applications [6–12]. These MGs have a homogenous composition and exhibit high strength, high hardness, larger elastic energy storage, and excellent corrosion resistance as a result of their random or short-range order structures [13–16]. Metallic alloys are the oldest materials and remain the best choice for biomedical implant, especially for the replacement of hard tissue [17–19].

Since the metallic foam materials show high energy absorption capacity and high compressive plastic strain [20]. Therefore, bulk metallic glass foams (BMGFs) have been reported to be one kind of new bio-implant materials more recently, because of their ability to support cell growth, such as the Pd-and Zr-based alloy systems [10,21–24]. Meanwhile, most BMGFs are inherent with much better strengths than conventional metallic foams (e.g., pure tantalum and titanium). In addition, these MGs present very high ration of strength-to-Young’s modulus due to its absence of lattice defects such as dislocations [16]. Whereas, most of MG alloy systems usually contain more or less of the elements of Cu, Be, Ni, and Al to increase its glass forming ability (GFA) [13–16]. Unfortunately, all of these elements have more or less toxicity and are unsuitable to put in the human body for long term [25]. Following the previous argument for the development of Ti-based MGs without adding Be, Ni, Al or Cu elements, only few publications have been reported, such as the MG ribbons of Ti60Zr10Ta15Si15 [7] and Ti60Nb5Zr10Si15 [12] with good mechanical properties and excellent corrosion resistance in comparison with cp Ti. In parallel, Ta has been reported that it can enhance the bone cell in-growth rate for osteology implant. Accordingly, the alloy system of Ti-Zr-Ta-Si seems to be a more preferable metallic glass can be applied on orthopedic implants.

Nevertheless, the very high liquidus temperature (Tl) more than 1550 °C or 1823 K) would result in unsatisfactory GFA and narrow supercooled liquid regime (SCL, <50 K), making the Ti60Zr10Ta15Si15 alloy difficult in casting and thermoplastic forming into a sizable medical implant. Therefore, based on the alloy composition of Ti60Zr10Ta15Si15, we have developed recently one new more promising Ti42Zr40Si15Ta3 amorphous alloy with a lower liquidus temperature of 1728 K (or 1455 °C), wider SCL regime of 99 K, ductile flexibility, and excellent corrosion resistance [26]. In this study, one of the pore forming techniques, the space holder method of powder metallurgy [10,27,28], was applied in fabricating the Ti-based BMGFs with different fractions of porosity and required open cell sizes. Later in 2016, Nicoara et al. [29] also applied this alloy system to produce powders from melt spun Ti42Zr40Si15Ta3 ribbons, followed by hot press to result in porous pellets with about 14% porosity. The morphology and mechanical aspect of this porous samples were explored, but the critical in-vitro and in-vivo biocompatibility characteristics have never reported yet. Thus, in this study, the amorphous nature, foam morphology, bonding interface, mechanical properties, in-vitro electrochemical properties and in-vivo biocompatibility responses of this Ti42Zr40Si15Ta3 alloy system with porosity up to 54% are characterized and discussed.

2. Materials and experimental procedures

Alloy ingots with composition of Ti42Zr40Si15Ta3 (at.%) were prepared by arc melting the raw materials of high purity Ti, Zr, Ta, and Si under an argon atmosphere. The alloy ingots were turned over and melted for four times in order to make sure a good homogeneous composition. At last, the complete melted metal was injected onto the Cu wheel surface (with water cooling system at 5 °C) to obtain the metallic glass ribbons by melt-spinning [26]. Then, these as-quenched MG ribbons were chopped and ground into powders by mechanical milling in a Spex 8000 Milli (with tungsten carbide vial and balls). In order to avoid the heat accumulation and induce the crystallization of MG ribbon during milling process, the milling process was set as an intermittent program, grind for 10 min and rest for 10 min and constant grinding until the particle diameter reaches the target size. Finally, the MG powders with particle sizes from 63 to 105 μm were sieved and mixed with different volume fractions of NaCl powders (with sizes ranging from 105 to 300 μm) homogeneously, and then hot compressed into the bulk samples under argon atmosphere. NaCl was regard as the space holder in the matrix and was dissolved out into water by ultrasonic agitation. Then, the removed NaCl space becomes the porosity volume. According to our previous results and experiences [10,30,31], the holding time for hot-pressing, compression stress, and temperature were selected to be 5 min, 600 MPa, and 540 °C (within the SCL temperature regime), respectively.

The phase identification and thermal properties (such as glass transition temperature (Tg), onset crystallization temperature (Tc), and liquid temperature (Tl)) of the MG ribbons, MG powders, and resulting BMGFs were investigated systematically by X-ray diffractometry (XRD, Bruker D8A, operated at 40 kV) and differential scanning calorimetry (DSC, Mettler Toledo DSC1 and HT-DSC, Netsch DSC404). The density and porosity of the BMGF samples with a height (12 mm) to diameter (6 mm) were measured by Archimedes test for three time in order to reduce the deviation. In addition, scan electron microscopy (SEM, Hitachi S-3500) was conducted to examine the cross-sectional morphologies of hot-compressed samples and the cross-sectional SEM images were used to statistically estimate the average pore size of the BMGFs. Since the pores were not spherical close pores, the rough pore sizes were calculated by measuring the diameter of the connecting cavity as an approximation. Transmission electron microscopy (TEM, FEI Tecnai G2 S-Twin at 200 kV) were used to characterize the microstructure of the Ti-based BMGFs and to examine the bonding interface between the MG powders. TEM samples were cut from the Ti-based BMGFs by using the focused ion beam system (FEI Versa 3D FEG FIB, operated at 30 kV) with a lower ion current to minimize the ion damage to samples. The Ti-based BMGF samples with a height (12 mm) to diameter (6 mm) ratio of 2:1 are tested under compression at room
temperature with an initial strain rate of $1 \times 10^{-4}$ s$^{-1}$ by using a MTS 810 universal testing machine. The electrochemical cyclic-anodic-polarization test were conducted using a CHI 614 D, CH Instruments Inc., USA. Electrochemical characterization for TiZrSiTa BMGFs were performed in a simulated body fluid (SBF) electrolyte at 310 K. Dense TiZrSiTa BMG sample produced with spin-casting and pure Ti sample were used to compare the electrochemical properties of the foam-like specimen. The electrochemical response was measured in a three-electrode scheme and the exposed surface area of sample was around $4 \times 4 \text{ mm}^2$. It is also noted that only the real exposed area of the BMGFs are much greater than the BMG and Ti. Therefore, the measured electrochemical response of BMGFs should also be greater than the bulk planar samples. The sputtered platinum film with the area of around $5 \times 5 \text{ mm}^2$ was used as the counter electrode, the MG specimens were conducted as the working electrode, and the reference electrode was with a standard Ag/AgCl. The samples were immersed into a 40 ml of commercial Hank's solution at 310 K for cyclic-voltammetry (CV) and the potential state measurements. The typical Hank's solution is consisted of 0.137 M of NaCl, 5.4 mM of KCl, 0.25 mM of Na$_2$HPO$_4$, 0.44 mM of KH$_2$PO$_4$, 1.3 mM of CaCl$_2$, 1.0 mM of MgSO$_4$, and 4.2 mM of NaHCO$_3$. Hank’s solution refers to a chlorine-ion-rich buffer which may induce electrochemical corrosion compared to other simulation body fluid. The CV experiment was carried out with a 0.1 V/s scan rate and range from $-1.0 \text{ V}$ to $+1.0 \text{ V}$. Since the implant materials used in medical environment may contact with the living cells and expose to the membrane potential of 75–80 mV. Therefore, in order to mimic the possible electrochemical reaction between the MG ribbons and cell tissues, a small voltage of 80 mV was applied in the potential state measurement for 30 min.

For in-vivo tests, 6 male New Zealand white rabbits with the weight around 2.5–3.5 kg were purchased from the Taiwan Livestock Research Institute (Taiwan, Taiwan). According to Taiwan required ethical standards, the rabbits should be kept on a good living condition, such as farmed in a temperature-controlled room ($298 \pm 1 \text{ K}$) and a 12:12 light-dark cycle (dark on at PM 06:00). One hour before the surgical operation, the rabbits should be IM injected with the Atropin (0.3 mg/kg) for analgesia and the Cefazolin (1 gm/kg) for anti-bacterial. Surgical programs were anesthetized by the anesthetizing mixture Ketamine (40 mg/Kg, Ketalar) with Xylazine (10 mg/kg). The BMGF samples were prepared into the small plates with dimension around $3 \text{ mm} \times 3 \text{ mm} \times 0.5 \text{ mm}$. The surgical positions are located at the epiphyses growth plate of each right leg. The medical saw was made the rabbit empty out his right leg bone (hole size $3 \times 3 \times 0.5 \text{ mm}$), and the wounds were then stitched by surgical sutures. The X-rays images of rabbits on the surgery legs was measured with 4.2 kV and the exposure time 3.5 s (HP 9178 A and HP 9816S; Hewlett-Packard, Fort Collins, CO, USA). The rabbits were recovered carefully and finally sacrificed after 6 months tenure. Before the observation of microcomputed tomography ($\mu$-CT), the retrieved legs with implantation were soaked in a 10% formalin. And then all proximal tibias were examined by $\mu$-CT after the tissues were removed. The frequency of collection data was at 0.5° per rotation step through 180° and with a scanning range of 34 × 17 mm. The voxel size was isotropic and fixed at 8.7 μm [32]. Furthermore, the C-reactive protein (CRP) assay was carried out to check whether any inflammation reaction would occur by Union Clinical Laboratory of Kaohsiung Medical University.

### 3. Results and discussion

#### 3.1. Basic characteristics

Fig. 1 shows the representative XRD patterns obtained from the Ti$_{42}$Zr$_{40}$Si$_{15}$Ta$_3$ MG powders and BMGFs with different porosity volume fractions. All samples exhibit a typical amorphous nature with a broad hump over 2θ around 30–50° and no apparent crystalline peak could be resolved. This indicates that the Ti-based BMGFs would remain its amorphous structure after hot pressing within its SCL temperature regime. The glass nature of the Ti$_{42}$Zr$_{40}$Si$_{15}$Ta$_3$ MG was traced by DSC and the results are listed in Table 1. The wide SCL region of 99 K is confirmed, but the GFA index, $\gamma = [T_{g}/(T_{x+T_{g}})]$ and $\gamma_m = [(T_{x} - T_{g})/T_{x}]$ (where $T_g$ is the glass transition temperature and $T_x$ the crystallization temperature) [33,34] values of 0.36 and 0.55 (needing to be over 0.4 and 0.6, respectively) are still not high enough to produce sizable bulk MGs. Thus, the MG powder sintering method appears to prepare larger specimens necessarily.

#### Table 1 – Representative thermal properties, in termed of glass transition temperature $T_g$, crystallization temperature $T_x$, liquidus temperature $T_l$, supercooled region ($\Delta T_s$), GFA index of $\gamma$ and $\gamma_m$, as well as the mechanical properties, in terms of elastic modulus E and nano-hardness H. The deviations of all the data are less than 10%.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_g$</th>
<th>$T_x$</th>
<th>$T_l$</th>
<th>$\Delta T_s$</th>
<th>$\gamma$</th>
<th>$\gamma_m$</th>
<th>E</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Ti</td>
<td>–</td>
<td>–</td>
<td>1668</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>135</td>
<td>2.5</td>
</tr>
<tr>
<td>Ti$<em>{42}$Zr$</em>{40}$Si$_{15}$Ta$_3$</td>
<td>526</td>
<td>625</td>
<td>1455</td>
<td>99</td>
<td>0.36</td>
<td>0.55</td>
<td>90</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Fig. 1 – XRD patterns of the Ti$_{42}$Zr$_{40}$Si$_{15}$Ta$_3$ MG powder and BMGFs with different fractions of porosity.
Using the pre-set processing parameters determined in our previous study [10], a series of porous specimens with volume fractions of pre-set NaCl spacer from 13 to 54 vol% were prepared by hot-pressing (compressed at 540 °C and 600 MPa for 300 s). The porosity fractions of the resulting BMGFs were measured to be 14%, 35%, 48%, and 54%. The cross-sectional morphologies of some representative porous specimens with different porosity fractions are presented in Fig. 2. The cross-sectional appearance of the sample with 54% porosity in Fig. 2(a) demonstrates the high uniformity of pore size and distribution. The pore sizes of all porous samples are in the range of 520 ± 130 μm, as evident from the cross-sectional SEM images in Fig. 2(b)–(d). This pore size is close to the ideal size (~300-600 μm) for bone cell growth. Meanwhile, the cross-section SEM images of these MG porous specimens reveal well bonded cell walls, no obvious interface between the bonded amorphous powders, as shown in Fig. 2.

Fig. 3(a) shows the typical compression stress-strain curves of the TiZrSiTa BMGFs with different real porosities ratio from 13% to 54%. The Young’s modulus and yield stress (close to the maximum plateau stress) both decrease with increasing porosity, varying from 53.1 down to 8.6 GPa for the modulus and from 729 down to 144 MPa for the yield strength, as listed in Table 2. In comparison with the human bone (depending on the position in outer harder region or inner softer regime), Young’s modulus of 1–25 GPa and yield strength of 50–270 MPa [35], the mechanical properties of hot-pressed BMGFs, with a higher porosity of 48% and 54% can match well with the mechanical properties of human bone, avoiding the risk of stress shielding effect.

The yield stress and Young’s modulus of a porous metal typically depend on its porosity ratio and relative density, as proposed by Gibson and Ashby [36,37]. In their function, the structure of the porous material can be simplified to consist of periodically arranged units for an open-cell porous material. It is assumed that the deformation of the porous material is dominated by the bending of beams or struts under compres-

### Table 2 – Summary of mechanical properties of the BMG foams fabricated under the condition of 105–63 μm MG powder, 524 ± 130 μm spacer powder, and 600 MPa hot-pressing stress at 540 °C for 300 s.

<table>
<thead>
<tr>
<th>Porosity</th>
<th>E (GPa)</th>
<th>σ (MPa)</th>
<th>E/ES</th>
<th>σ/σy</th>
<th>ρ/ρ0</th>
<th>(ρ/ρ0)1/3</th>
<th>(ρ/ρ0)2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>90.0</td>
<td>2655</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>14%</td>
<td>53.1</td>
<td>729</td>
<td>0.40</td>
<td>0.27</td>
<td>0.86</td>
<td>0.80</td>
<td>0.74</td>
</tr>
<tr>
<td>35%</td>
<td>21.1</td>
<td>320</td>
<td>0.16</td>
<td>0.12</td>
<td>0.65</td>
<td>0.52</td>
<td>0.42</td>
</tr>
<tr>
<td>48%</td>
<td>12.9</td>
<td>216</td>
<td>0.10</td>
<td>0.08</td>
<td>0.52</td>
<td>0.37</td>
<td>0.27</td>
</tr>
<tr>
<td>54%</td>
<td>8.6</td>
<td>144</td>
<td>0.06</td>
<td>0.05</td>
<td>0.46</td>
<td>0.31</td>
<td>0.21</td>
</tr>
</tbody>
</table>

E: Young’s modulus (GPa), σ: yield stress (MPa).
sion. The relationships between the relative density, elastic modulus, and yield stress are given by

\[
\frac{E}{E_o} = C_1 (\rho / \rho_o)^{n_1},
\]

\[
\frac{\sigma_{pl}}{\sigma_s} = C_2 (\rho / \rho_o)^{n_2},
\]

where \( E \) is the elastic modulus of the porous material, \( E_o \) is the elastic modulus of the wall material (i.e., Ti_{42}Zr_{40}Si_{15}Ta_{3}), \( \rho \) is the BMGF density, \( \rho_o \) is the density of the wall material, \( \sigma_{pl} \) is the plateau stress of the porous material, \( \sigma_s \) is the yield strength of the wall material, and \( C_1, C_2, n_1 \) and \( n_2 \) are constants. The complex dependence of \( C_1, C_2, n_1 \) and \( n_2 \) on structure is considered to relationship with the bonding strength of the cell walls. Experimental measurements indicate that it should be approximately equal to \( C_1 = 1, C_2 = 0.3, n_1 = 2 \) and \( n_2 = 1.5 \) for open-cell porous structure, and \( C_1 = 0.35, C_2 = 0.3, n_1 = 1, n_2 = 1 \) for close cell porous structure by the Gibson and Ashby model. The higher bonding strength would lead to a higher \( C_1 \) or \( C_2 \) value. For the Ti-based BMGFs, is \( \sim 133 \) GPa, \( \sigma_s \sim 2.6 \) GPa, and \( \rho_o \) is 6.3 g/cm³. The calculated data are all compiled in Table 2. Fig. 3(b) and (c) present the yield stress and Young's modulus of the BMGFs as function of relative density, in terms of \( (\rho / \rho_o)^{1.5} \) and \( (\rho / \rho_o)^2 \), respectively. The dependent on both the modulus and stress can be well predicted by the Gibson and Ashby model [36,37]. The fit line for the elastic modulus gives the relationship \( E/E_o \sim 0.59 (\rho / \rho_o)^2 \), with the fitting \( R^2 \) reaches the value of 0.957. Meanwhile, The fit line for the yield stress yields \( \sigma_{pl}/\sigma_s \sim 0.37 (\rho / \rho_o)^{1.5} \), with the fitting \( R^2 \) reaches the value of 0.932. Based on the fit line, the required modulus or strength can be predicted. For example, if the Ti-based BMGF needs to possess a lower modulus about 5 GPa and a lower strength about 120 MPa, the fit line predicts that the foam should possess a density about 1.6 g/cm³ and a porosity volume fraction of \( \sim 75\% \).

These relationships can be well predicted by this model, and the \( C_1 \) and \( C_2 \) proportional coefficients are also close to other Ti-based open-cell materials. However, this Ti-based BMGFs present slightly lower values for both the yield stress and Young's modulus in comparison with the Zr-based BMGFs [10]. This might be attributed to the attenuation of interface between MG particles. A clear crystallization zone was found locating along the interface between MG particles as illustrated in Fig. 4(b). This crystallization zone was identified to contain the ultrafine TiO₂ crystalline phase with size of 10–20 nm, as shown in Fig. 4(c), which is suggested that the surface of Ti-based MG particles were oxidized by the residue oxygen and to form the TiO₂ crystalline phase along the interface during the hot-pressing.

Fig. 3 – (a) Compression stress-strain curves of the BMGFs with different porosities of 13–54%. (b) and (c) are the relative Young's modulus and yield stress as function of the relative BMGF density, respectively, based on the Gibson and Ashby model. The fitting \( R^2 \) for (b) is 0.957 and for (c) is 0.932.
Fig. 4 – (a) Cross-sectional SEM image of Ti$_{42}$Zr$_{40}$Si$_{15}$Ta$_{3}$ BMGF sample with 54 vol% porosity. (b) bright-field TEM image of Ti$_{42}$Zr$_{40}$Si$_{15}$Ta$_{3}$ BMGF sample which taken from the bonding interface where indicated by one white line in Fig. 4(a), (c) selected area diffraction pattern which taken from the area indicated by the arrow in Fig. 4(b), (d) high resolution TEM image which enlarged from the area indicated by the arrow in Fig. 4(b).

Results showed that the TiZrSiTa BMG and pure Ti exhibited stable electrochemical properties since no significant current was observed for these two samples. Alternatively, the measured current response of the TiZrSiTa BMGF was about 2-order larger than that of the reference pure Ti and the dense TiZrSiTa BMG. The big charge current of TiZrSiTa BMGF was caused by the greater exposed area of the open-cell structure. It is also noted that there was no significant redox peaks observed in the CV scan for TiZrSiTa BMGF sample, indicating the low-electrochemical activity of the produced foam-like sample.

Alternatively, the bio-implant may suffer the electrochemical corrosion owing to the potential difference across the membrane potential of cell. The values of membrane potential are typically ranging from 40 to 80 mV, depending on the concentration of the Na$^+$ and K$^+$ of a cell. In order to mimic the real biological surrounding in the body, the samples were immersed into the Hank’s solution with an applied potential of 80 mV. Fig. 6 displays the measured amperometric i-t curves showing comparison of the cyclic voltammetry responses of TiZrSiTa BMG, TiZrSiTa BMGFs and pure Ti in the Hank’s solution. Similarly, the TiZrSiTa BMG and the pure Ti samples showed low current responses in the Hank’s solution. However, the TiZrSiTa BMGF exhibited high current response.

3.2. Biocompatibility in vitro electrochemical testing

Fig. 5 presents the comparison of the cyclic voltammetry responses of TiZrSiTa BMG, TiZrSiTa BMGFs and pure Ti in the Hank’s solution, where pure Ti was used as the reference.
3.3. In-vivo testing

The porous of TiZrSiTa BMGF was implanted into the rabbit’s right tibia for six months of implantation test in the animal center of Kaohsiung Medical University. The implantation operations of the rabbits were carried out without infection after the surgical operations. The rabbits were recovery well and fed with an intensive care. CRP value was used to monitor the inflammatory reaction of the rabbit every month after the surgery. A low measured CRP value (lower than 0.1 mg/dL) for the rabbits during the 6 month recovery was obtained, implied that it had no obvious inflammation reaction caused by the porous of TiZrSiTa BMGF implantations. Fig. 7 shows the x-ray and micro CT scan images showing the bone fusion condition surrounding of the implanted porous BMGF. It is clear that the open-cell structure for the porous of TiZrSiTa BMGF was complete and the symptoms of the rabbits recovered well after six months of implantation. The x-ray image (Fig. 7a) shows that there was no significant interface between the implanted MG and the bone tissue, indicating a nice fusion for the implanted BMGF. Moreover, no radiolucent line around the porous of TiZrSiTa BMGF was observed in the micro CT image (Fig. 7b), indicating that there was no local inflammation such that inflammation caused osteolysis was prevented.

In addition, 3D µ-CT were used to further evaluate the bone ingrowth/ongrowth property on the implanted porous MG. Fig. 8c shows the sagittal plane (X-Z plane) and transverse plane (X-Y plane) of the BMGF implant site. The high-density cortical bone (compact bond) showed dark-orange color while the low-density cancellous bone (sponge bond) showed light-yellow color. The intermediate between the cortical bone and the cancellous bone showed orange color and the implanted MG specimens showed black color. The µ-CT images revealed that the newly grown tissue grew around the porous of TiZrSiTa BMGF and the osteotomy sites healed well. The density of the newly grown bone tissue near-by the BMGF interfaces is similar to the density of the sponge bone near the cortical bone, indicating that the porous of TiZrSiTa BMGF exhibited nice osteo-induction property. The in-vivo test showed that the porous of TiZrSiTa BMGF own good osteo-integration property after 6 months of implantation. However, micro-CT scan could not provide the detail bone ingrowth information inside the porous structure of the BMGF since x-ray was blocking by the metal structure of porous BMGF. Therefore, the implant site was mounted with epoxy resin and then cut with diamond

![Graph of the comparison of the i-t curves for the TiZrSiTa BMGFs, TiZrTaSi BMG and pure Ti with the applied low-voltage (80 mV) in the Hank's solution.](image)

![Fig. 7 – (a) X-ray image, (b) 3D micro-CT image and (c) the corresponding images showing the surrounding bone density near the TiZrSiTa BMGFs implant after six months of implantation.](image)
saw for detail histology observations. Fig. 8 shows optical and SEM images of the cross section views of the implanted porous BMGF and the closed-up views of the ingrowth bone for Ti42Zr40Si15Ta3 after six months of implantation. The red arrow indicate new ingrowth bone tissue. It is clear that the newly grown bone grew into the produced TiZrSiTa BMGF and showed nice osteo-integration between the newly grown bone and the porous BMGF, confirming the high potential for the produced porous TiZrSiTa BMGF in long-term implantation applications.

4. Conclusion

This paper presents a newly developed open-cell toxic element-free Ti42Zr40Si15Ta3 bulk metallic glass foams for bio-implantation applications. The TiZrSiTa BMGFs with various porosities were fabricated by a powder metallurgy in a space holder. The mechanical properties, material properties, electrochemical response and the in-vivo biocompatibility were experimentally investigated. The measured Young’s moduli and yield strength ranging of the BMGFs were ranging from 8 to 53 GPa and from 140 to 730 MPa, which could well match the mechanical properties of human bone. Results also indicated that the developed BMGFs exhibited high porosity for cell ingrowth and nice electrochemical stability for reducing ion release. A six-month in-vivo test by implanting the BMGF into rabbit tibia was performed. The micro-CT scan and histology observations confirmed that the newly grown bone usefully grew into the porous structures of the TiZrSiTa BMGF and resulted in a good osteointegration result. The foam-like Ti42Zr40Si15Ta3 metallic glass developed in the present study has shown its good bone ingrowth and bone integration capabilities, confirming that it is a promising material for bio-implant applications.

Conflicts of interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version. This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue. The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2020.02.079.

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