FABRICATION OF TiZr-BASED BULK METALLIC GLASS FOAM USING HOT-PRESSING AT DIFFERENT TEMPERATURES AND HOLDING TIMES

Nguyen Van Tai[1], Nguyen Hoai Tan[1], Huynh Thanh Thuong[1], Pham Quoc Liet[1], Hoang Minh Thuan[2], Nguyen Van Cuong[1,*]

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ABSTRACT

Biocompatible TiZr-based bulk metallic glass foam (BMGF) plays a critical role for bio-implant application. In this present work, a series of TiZr-based BMGFs were successfully fabricated by using hot pressing method in an inert gas chamber. Amorphous structure and high compactivity of the TiZr-based BMGF were required to retain excellent properties. Temperature and holding time during hot pressing process significantly impact on fabrication of the TiZr based BMGF. Results from differential scanning calorimetry (DSC) and XRD analysis point out that the applied temperatures from 763 to 793K with holding time from 3 to 5 min are suitable for producing the TiZr-based BMGF. As a result, the bulk alloy foam produced at the temperature of 793K and holding time of 5 min still remain amorphous state and display a high-density compact structure after hot pressing. Bright-field TEM image indicates that the TiZr-based BMGFs present a strong bonding-force interface between amorphous metallic glass particles which can make a good condition for generating the foam with higher porosity in further study.

Keywords: *Bulk metallic glass foam; holding time; hot pressing; temperature.*

[1]College of Engineering Technology, Can Tho University, Vietnam

[2]Department of Mechanical Engineering, Hung Yen University of Technology and Education, Vietnam

[*]Email: nvcuong@ctu.edu.vn

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1. INTRODUCTION

Bulk metallic glasses (BMGs) have significantly attracted the attentions for engineering, electronic and biomedical implant applications due to their unique properties, such as large elastic elongation limit, high strength, excellent corrosion and high biocompatibility, in which these properties can be rarely found in crystalline materials [1, 2]. Recently, the TiZr-based BMGs synthesized from multicomponent have resulted in increasing the glass forming ability (GFA). Many researchers had successfully explored some TiZr-based BMGs for biomedical application with addition of Ni and Be such as Ti-Zr-Cu-Ni-Sn [3] and Ti-Zr-Ni-Be [4], or with free-added Ni and Be including Ti-Zr-Cu-Pd [5], Ti-Zr-Cu-Pd-Sn [6] and Ti-Zr-Ta-Si [7]. In order to improve the GFA, some elements like Be, Ni, Cu, or Al are usually selected to add to the TiZr-based alloys; however, these elements are not suitable in human body for a long-time immersion due to toxic release. The TiZr-based glassy alloys without Be, Ni, Cu, or Al elements, just a few publications, have been reported and shown an unsatisfied GFA with extremely high liquidus temperature (T_l is more than 1823K, or 1550°C) and a narrow-supercooled liquid regime (SCL, < 50K). It leads to difficultly prepare a bulk alloy in casting and shaping for the bio-implant.

TiZr-based BMGFs prepared from non-toxic elements have been developed in the TiZr-based alloy system to generate the implantable medical devices. The friendly components of the implant can support to the cell in-growth rate of the tissue. The new tissue cells can infiltrate into the foam, then form excellent logical fixation with the surrounding tissue [8]. In this study, the free-toxic element $Ti_{42}Zr_{35}Ta_3Si_5Co_{12.5}Sn_{2.5}$ glassy alloy with a low liquidus temperature of 1198 K (or 925°C) and a wide SCL regime of 95K was designed to produce metallic glass (MG) powder with the sizes less than 25µm. Then, the TiZr-based BMGFs were fabricated by using hot pressing method at the different temperatures and holding times. Finally, the thermal properties, relative density, structure and bonding-force interface of the prepared BMGFs are analyzed and discussed.

2. EXPERIMENTAL METHODS

High purity elements of Ti (99.9% wt.%), Zr (99.9% wt.%), Si (99.9% wt.%), Ta (99.9% wt.%), Co (99.9% wt.%) and Sn (99.9% wt.%) were used to fabricate the alloy ingots of $Ti_{42}Zr_{35}Si_5Ta_3Co_{12.5}Sn_{2.5}$ (in atomic percentage) by arc melting of the appropriate mixture under a Ti-gettered argon atmosphere. The alloy ingots were re-melted for four times by turning-over melting to form a homogenous mixture. Next, TiZr-based MG powder with particle size less than 25µm were produced by inert gas atomization technology. Then, the foams were fabricated by using the MG powder at the different temperatures of 763, 773, 783, 793 and 798K (the temperature of the supercooled liquid region) with various holding times, as summarized in Table 1. The compressive stress for hot pressing was selected at 300MPa via our previous results and experiences [9].

The porosity of the TiZr-based BMGF was determined by using the Archimedes law, and confirmed with statistical averaging calculation over six measurements. The volume of the perfect bulk glassy alloy only contains the volume of MG powder while the hot-pressed samples have the volume of MG powder and voids due to uncomplex compactness during hot pressing. The MG ribbon with thickness of 0.5mm was assumed as a fully dense structure, in which the density of the MG ribbon is similar to that of the perfect bulk glassy alloy. The volume of the hot-pressed sample was calculated by mass deviation of the sample in air and in water, as in Equation (1). The density of the hot-pressed samples was calculated via its mass and volume. Then, the real porosity was determined as a ratio between the volume of voids and the volume of the perfect TiZr-based BMG, as shown in Equation (2).

$$V_1 = \frac{m_1 - m_2}{D'};\ V_2 = \frac{m_1}{D}; D_1 = \frac{m_1}{V_1} \quad (1)$$

$$\text{Real porosity } (\%) = \frac{V_1 - V_2}{V_2} * 100 \quad (2)$$

where V_1 and V_2 are volume of the hot-pressed sample, and volume of the perfect TiZr-based BMG, respectively; m_1 and m_2 are the weight of the sample in air and water, respectively; D', D and D_1 are density of water, MG ribbon and the hot-pressed sample, respectively.

Table 1. List of parameters used to fabricate the TiZr-based BMGF

Sample	Comp. Stress (MPa)	Applied Temp. (K)	Holding time (min)	Porosity (vol.%)	Density (g/cm^3)
F1	300	763	3	14.47	5.312
F2	300	773	3	11.85	5.437
F3	300	783	3	9.19	5.569
F4	300	793	3	7.69	5.647
F5	300	793	4	5.33	5.773
F6	300	793	5	2.02	5.961
F7	300	793	6	1.98	5.963
F8	300	798	5	1.75	5.977

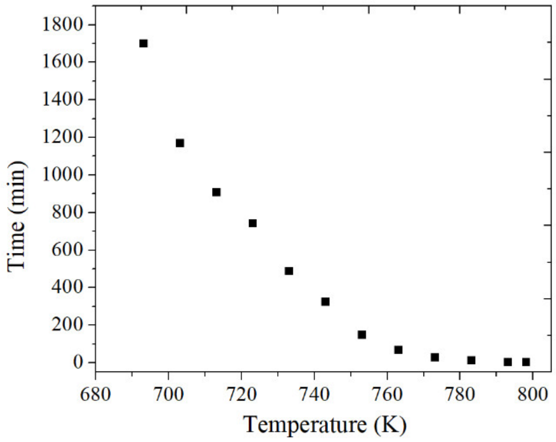
Differential scanning carlorimetry (DSC, Mettler Toledo DSC1) at a constant heating rate of 40K/min under an argon atmosphere was used to determine the thermal properties. The amorphous structure of MG powder, and the TiZr-based BMGFs fabricated at the different temperatures and holding times was characterized by X-ray diffractometry (XRD, Bruker D8A, operated at 40kV). In addition, the bonding-force interface between the MG particles in the foam was examined by transmission electron microscopy (TEM, FEI Tecnai G2 S-Twin at 200keV). The SEIKO SMI 3050 dual focused ion beam (FIB, FEI Versa 3D FEG FIB, operated at 30kV) system was selected to fabricate the cross-section TEM coil for TEM examination.

3. RESULTS AND DISCUSSION

3.1. Effect of temperature and holding time on fabrication of TiZr-based BMGF

TiZr-based MG powder was used to fabricate the TiZr-based BMGF by using hot pressing technique. The temperatures were carefully chosen in the supercooled liquid region to maintain amorphous structure after hot pressing. The amorphous MG powder possess three transition regions in the continuing heating process including (1) glass transition; (2) a supercooled liquid region; (3) and then crystallizes into a crystallization phase. The glass transition temperature (T_g) of the amorphous alloys was known as the transition temperature between the glassy stage and the liquid stage to suppress the crystallization transformation [10]. At the high temperature, the amorphous alloys are sensitive for transformation from the amorphous structure to the crystalline phase. Figure 1a shows the incubation times of the TiZr-based MG powder via conducting the isothermal annealing experiments. The incubation time for the isothermal annealing was the time that the temperature became constant to the beginning of crystallization. It significantly decreased as the isothermal temperature increased and approached T_x. As the temperature increases from 691 to 753K, the incubation time decreases sharply from 1700 to 150 min. Then, the incubation time continuously reduces when the temperature increases gradually to 763K. As the temperature increases in range from 763 to 793K, the incubation time continuously decrease but change insignificantly in comparison with the previous temperatures. These results proved that the crystallization transformation of the TiZr-based MG powder was sensitive to the isothermal temperature, especially when the temperature was higher than 763K. At the temperature of 793K, the incubation time is around 6 min.

Fig. 1b shows the thermal property of MG powder after the isothermal annealing at the different temperatures and holding times. For the MG powder annealed at 793K in 5 min, the Tg point locates around 761K, corresponding to the first peak on the DSC trace, and the Tx point is around 852K. It indicates that the isothermal annealed MG powder still remain the amorphous structure. The glass forming ability (GFA) of the amorphous alloy as well as its critical size was assessed via calculating ΔTx (supercooled liquid region, Tx-Tg) and γ (Tx/(Tg +Tl). A wide range of the supercooled liquid region (above 50K) combining with a high value of γ (larger than 0.4) can provide the high GFA, and be possible to fabricate the sample with the attainable maximum sizes. Thus, the widely supercooled liquid region (91K) of the MG powder annealed at 793K in 5 min can be accepted to generate the amorphous BMGF. As the holding time increases to 6 min, Tx peak of the annealed MG powder disappears on the DCS curve. It means that there is a transformation from the amorphous structure to the crystalline phase during the isothermal annealing process. In parallel, the crystalline transformation also occurs as the MG powder was heated to 798K and kept in 5 min. Therefore, the temperature from 763 to 793K, and the holding time from 3 to 5 min were suggested for further fabrication of the TiZr-based BMGF to remain the amorphous structure after hot pressing.



a)

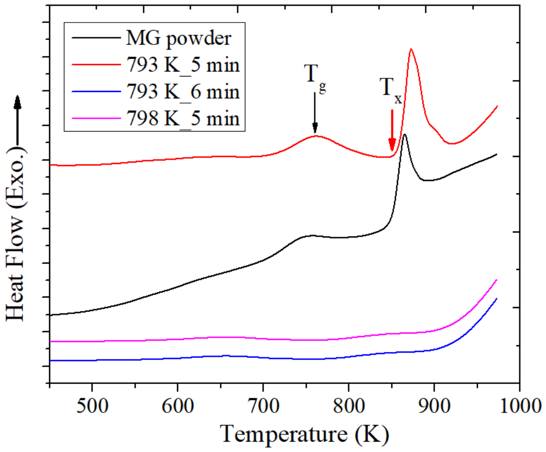


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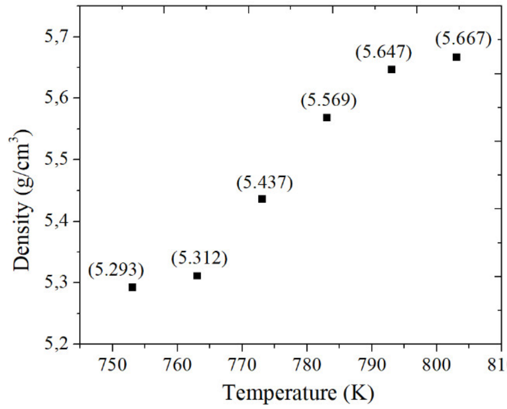
Fig. 1. (a) Incubation time of MG powder under different isothermal annealing experiments; (b) DSC traces of MG powder after the isothermal annealing at the various temperatures and holding times

The TiZr-based BMGFs were hot-pressed in the supercooled liquid region, therefore, the dense degree of the sample directly related to the applied temperature in hot pressing. The ions move more faster as the temperature increases, and these ions are more frequent collisions under a compressive pressure, leading to decrease the free-spaces in the hot-pressed sample. The density of the hot-pressed samples was employed to access the dense degree, in which the bonding-force interface of the hot-pressed samples depends on the dense degree. The ribbon density (approximately 6.081g/cm^3) was set as a reference density to assess the dense degree of the hot-pressed samples. Fig. 2 the relationship between the temperature, holding time and density for the hot-pressed samples. The density increased gradually from 5.293 to 5.647g/cm^3 as the temperature increased from 753 to 793K. The density increased rapidly as the operation temperature increased to be more than 773K (500°C). The increase in density indicated that the free volume fraction inside the hot-pressed samples decreased significantly. The porosity of the samples reduces from 14.47% to 7.69% as the temperature increases from 763 to 793K. At the higher temperatures, the strength of the atomic activity increase, resulting in formation of a thermodynamic quasi-steady state under a compressive stress. Thus, the MG particles is easier to connect together and annihilate the free-space to form a compact structure.



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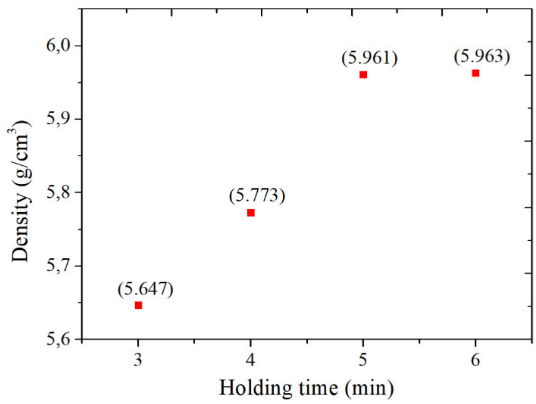


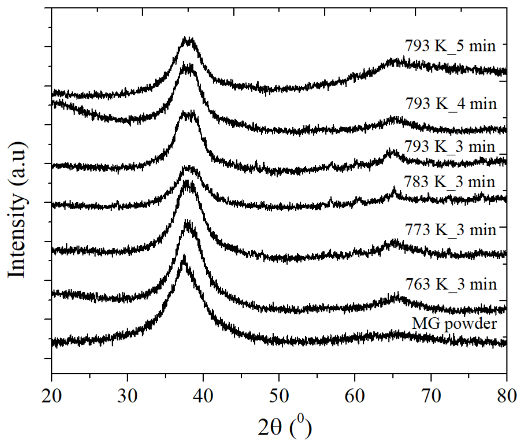
b)

Fig. 2. Effect of temperature (a) and holding time (b) on dense level of TiZr-based BMGF

Meanwhile, holding time in hot pressing also affect the dense degree of the hot-pressed sample. To assess the effect of holding time on TiZr-based BMGF fabrication, a constant pressure of 300 MPa and the temperature of 793 K were used for hot pressing. As in Fig. 2b, the density of the TiZr-based BMGFs increased gradually with holding time. The sample with the density of 5.961g/cm^3 (the porosity is around 2.02%) can be obtained with holding time at 5 min for hot pressing. Thermal energy could be transferred to all the amorphous MG particles. Moreover, with sufficient holding time, the MG particles were compressed to form a compact structure during hot pressing. There are 3 possible stages occur during hot pressing in the supercooled liquid region.

Elastic deformation firstly occurs until the flow stress reach to the peak, and appears the stress overshoot phenomenon. It is attributed to the amount of free volume come from the delayed activation of the shear transition. Then, plastic deformation including softening phenomenon occurs due to rapid decrease of the flow stress leading to appear a relatively stable stress plateau. The shear transition activated by the high stress can be ascribed to be a main reason for the rapid generation of free volume, resulting strain softening. Finally, the flow stress is stable in horizontal direction after deformation, in which the overshoot or processing softening phenomenon in stress cannot seemly observed. Therefore, a high compression temperature together with sufficient holding time can create a suitable condition to eliminate the free volume fraction, and result in increasing the density of the sample. The temperature at 798K and holding time in 6 min were also applied to evaluate the dense degree of the hot-pressed samples. Unfortunately, a fraction of the amorphous structure of the hot-pressed sample transformed to the crystalline structure, as seen in Fig. 1b.

3.2. Structural characterization of TiZr-based BMGF



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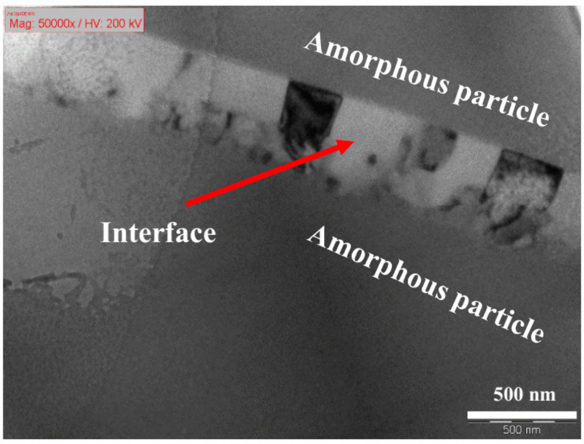

b)

Fig. 3. (a) XRD patterns of MG powder and TiZr-based BMGFs produced at the different temperatures and holding times; (b) Bright-field TEM image of interface between the amorphous alloy particles

XRD patterns, as shown in Fig. 3a, present two distinct normal broad humps within the 2θ ranges of 30° - 50° and 60° - 70°, indicating that the TiZr-based BMGFs hot-pressed at the different temperatures and holding times retain their amorphous characteristic. Multiple humps in the XRD patterns of an amorphous material can be ascribed to the material's transformation to a more disordered state. This implies that the selected parameter combination including the temperature from 763 to 793K and holding time from 3 to 5 min is suitable for hot pressing to avoid the transformation from the amorphous structure to the crystalline phase. Amorphous alloys have higher tensile strength and lower elastic modulus in comparison with crystalline alloys of the same composition. Amorphous alloys also indicate higher anti-corrosion than crystalline alloys. Thus, the hot-pressed TiZr-based BMGFs with amorphous structure are require to keep excellent mechanical properties and electrochemical behaviors. Besides, Fig. 3b shows the bright-field TEM image of the interface between the amorphous alloy particles of the TiZr-based BMGF with a porosity of 2.02%. A strong bonding-force interface formed between the amorphous alloy particles in the sample can be obtained after hot pressing.

4. CONCLUSIONS

Temperature and holding time significantly influence on the fabrication of TiZr-based BMGF. The dense level of the hot-pressed sample, and transformation behavior between the original amorphous structure and the crystalline phase depend directly on the temperature and holding time. The hot-pressed samples with a compact structure and amorphous MG particles exhibiting a satisfactory compact connecting ability can be obtained as the temperature of 793K and holding time of 5 min were used. The density of this sample was 5.961g/cm^3 (its porosity was approximately 2.02%), which was close to the ribbon density (6.081g/cm^3). Thus, the temperature at 793K and holding time in 5 min were suitable conditional parameters for producing the TiZr-based BMGF to retain the amorphous structure and to obtain a suitably compact structure.

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