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Investigation of the thermal and corrosion behavior of a Ti-based bulk metallic glass with composition of $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$

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1. Introduction

Ti-based bulk metallic glasses (BMGs) are of special interest to researchers as a result of their applications in the engineering equipment, the aerospace industry, and the medical industry. These BMGs have properties such as high specific strength, low density, low elastic modulus, and excellent corrosion resistance. The limitation on the size production of Ti-based BMG alloys or low glass-forming ability (GFA), is one of the disadvantages of these materials restricting their engineering applications. Thus, extensive studies have been performed in the two fields of: alloying and the bonding of these materials, in recent years. Ke Fu Yao et al. conducted several studies in the field of design and production of new Ti-based BMGs and succeeded in producing alloys with diameters up to 50 mm and a wide range of super cooled liquid region (SLR). Ke Fu Yao et al. have produced $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$ BMG alloy with a diameter of more than 20 mm and a super cooled liquid region (SLR) of 81 K. It can be one of the common alloys in engineering applications. BMGs have quasi-structure at ambient temperature and tend to change into crystalline states during continuous heating. Thus, it is essential to determine their thermal stability from a technological and scientific point of view. In order to expand the industrial applications of BMGs, it is of special importance to study their corrosion behavior. Hence, the present study deals with the thermal behavior of $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$ BMG alloy and its corrosion behavior in two different solutions, in the as-cast state and during the crystallization stages.

2. Materials and methods

Primary alloy ingots with the composition of $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$ were produced by arc melting of pure elements of Cu, Fe, Be, Zr, and Ti (with high purity of 99.9%) under a high purity argon atmosphere (more than 99.99%) and in the vicinity of molten titanium. BMG block with dimensions of 70×14×8 mm was produced by tilt pour casting method in a copper mold. To study the non-isothermal crystallization behavior of the produced alloy, samples weighing about 2 mgr were cut and subjected to continuous heating at a rate of 10 $K.min^{-1}$ from room temperature to 800 °C (above the melting point of the alloy) under pure argon atmospheres via DSC (Netzsch STA 449 F3). The end temperature of the crystallization peaks was detected at this rate. Then, the samples were continuously heated up to the specified temperatures in a tube furnace at a speed of 10 $K.min^{-1}$ and then quenched in water. After the continuous heat treatment, the structure of the samples was examined by the XRD instrument (Rigaku D/Max-RB model) using Cu-Kα waves. To study the corrosion behavior of the as-cast amorphous alloy and the annealed samples, Potentio state/ Galvano state Autolab instrument (PGSTAT 302 N, Metrohm, Netherlands) was used. For this purpose, the samples were tested in two different solutions of NaCl (with a concentration of 3.5%) and laboratory serum (with a PH close to the human body). Ag/AgCl and Pt electrodes were used as the reference and auxiliary electrodes, respectively.

3. Results and discussions

3.1. Thermal behavior. According to the DSC pattern at 10 $K.min^{-1}$ heating rate (Fig.1a), it can be said that the $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$ BMG alloy is completely crystallized during four exothermic and one endothermic transformation steps, and consequently has a complex crystallization behavior. The XRD pattern of the as-cast alloy and the annealed samples, which are continuously heated up to the various temperatures, is presented in Fig. 1b.

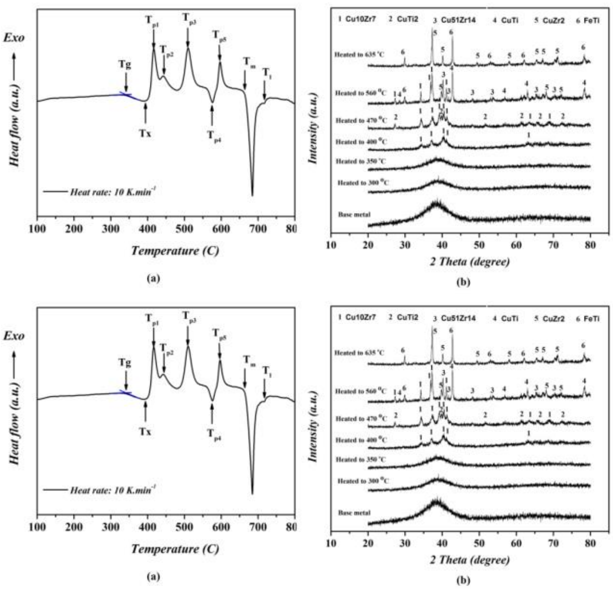

Figure 1. a) DSC pattern of the $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$ BMG alloy at 10 $K.min^{-1}$ heating rate. b) XRD patterns of the as- cast $(Ti_{41}Zr_{25}Be_{28}Fe_{6})_{93}Cu_{7}$ BMG alloy and it′ s non-isothermal annealed samples.

The $Cu_{10}Zr_{7}$ intermetallic phase (the product of the first crystallization step) was observed in the XRD pattern of the sample under continuous heating up to 400 °C. $Cu_{10}Zr_{7}$ and $CuTi_{2}$ phases were identified as stable phases in the diffraction pattern of the annealed sample when non-isothermally heated up to the final temperature of the

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second crystallization peak (470 °C). Considering the overlap of the first and second crystallization peaks, it can be said that the $CuTi_2$ phase nucleates during the growth of the $Cu_{10}Zr_7$ phase. The $Cu_{10}Zr_7$, CuTi, $Cu_{51}Zr_{14}$ compounds and Laves phase with the composition of $CuZr_2$ are observed in the XRD pattern of the sample heated up to 560 °C. Considering the two recent XRD patterns, it is indicated that the intermetallic $Cu_{51}Zr_{14}$ phase is the product of the third step of crystallization. FeTi and $CuZr_2$ are the stable phases at the sample which is continuously heated up to the crystallization end temperature (635 °C). Therefore, during the middle endothermic transformation stage, $Cu_{10}Zr_7$ and $Cu_{51}Zr_{14}$ were converted to the Laves stable phase with the composition of $CuZr_2$.

3.2. Corrosion behavior

The corrosion behavior of the as-cast amorphous alloy and the annealed samples was investigated in two laboratory serum solution and 3.5% NaCl solution. Fig. 2 a-b shows the TOEFL corrosion curve of these samples in two different solutions. As shown in Fig. 2 a-b and Table 1, the trend of changes in the TOEFL curve and the results of the corrosion in the two solutions are almost identical. For the studied alloy in the initial state and the annealed conditions, the current density and corrosion rate in 3.5% NaCl solution is more than the serum solution.

In the $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{93}Cu_7$ BMG, the corrosion current density in 3.5% NaCl solution is 0.4 $\mu A/cm^2$ and the corrosion rate is 0.004 mm/year, which is approximately equal to the corrosion current density and corrosion rate of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ and $Ti_{45}Zr_5Cu_{45}Ni_5$ BMG alloys. It should be noted that the corrosion current density in AISI 316L steel with a wide application in the medical industry has been reported to be 1.316 $\mu A/cm^2$. Therefore, the present BMG alloy has much higher corrosion resistance. In the serum solution, the as-cast $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{93}Cu_7$ BMG alloy showed a corrosion current density of 0.138 $\mu A/cm^2$ and a corrosion rate of 0.0013 mm/year. Since it does not contain the allergen elements, i.e. Al, Ni, it can be used in the medical applications such as dental implants in humans.

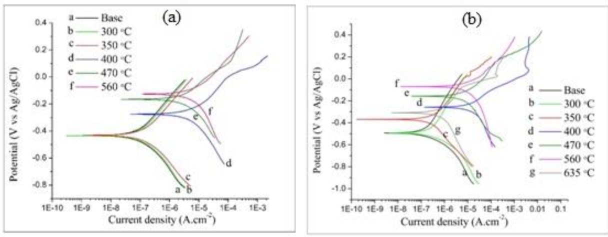

Figure 2. The TOEFL curves of the as-cast amorphous alloy and the annealed samples at, a) Serum solution with a PH near human body, b) 3.5% NaCl solution.

The data obtained from TOEFL curves including mean corrosion current density ($mA.cm^{-2}$) and mean corrosion velocity (mm/year) are tabulated at Table 1.

4. Conclusion

In the present study, a Ti-based bulk metallic glass with the composition of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{93}Cu_7$ was successfully produced and its thermal behavior was studied. This alloy has a complex thermal behavior with five pre-melting crystallization steps. Then, the formed phases in each stage of crystallization were identified with continuous heating of the alloy until the end of the desired crystallization stage. The corrosion behavior of the as-cast BMG alloy, the BMG alloy samples after heating up to a temperature in the structural relaxation region, heating up to a temperature in the super cooled liquid region (SLR), and after heating up to the end temperature of each crystallization stage was then studied. $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{93}Cu_7$ alloy with a diameter of more than 20 mm, super cooled liquid region (SLR) of 81 K, and a corrosion rate of 0.004 mm/year in 3.5% NaCl solution and 0.0013 mm/year in medical serum, is an appropriate choice for engineering and medical applications.

Table 1. Mean current density and mean corrosion velocity of the as-cast amorphous alloy and the annealed samples which are obtained from TOEFL curves at serum solution and 3.5% NaCl solution.

Sampl e/data	***Serum solution***							***3.5 % NaCl solution***						
	As-cast	**300 °C**	**350 °C**	**400 °C**	**470 °C**	**560 °C**	**635 °C**	**As-cast**	**300 °C**	**350 °C**	**400 °C**	**470 °C**	**560 °C**	**635 °C**
Corrosion current density ($nA.cm^{-2}$)	138	118	107	6512	5548	5816	---	428	450	500	7432	5102	5506	2159
Corrosion density (mm/year)	0.0013	0.0011	0.0010	0.0622	0.0529	0.0555	---	$4*10^{-3}$	$4.3*10^{-3}$	$4.8*10^{-3}$	$7.09*10^{-2}$	$4.98*10^{-2}$	$5.36*10^{-2}$	$2.06*10^{-2}$