Formation and Biocompatibility of Ni-Free Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$
Bulk Metallic Glass

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A Ni-free bulk metallic glass (BMG) of Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ with a diameter of 3 mm was successfully prepared by copper mold casting. The structure and thermal stability of the BMG were studied by x-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). It is found that the BMG is apparently of a single amorphous structure and exhibits a wide supercooled liquid region of 101°C. A static-state compression revealed that the BMG possesses a superior fracture strength of 1709 MP and extended plastic strain of 9.5%. The corrosion resistance of the BMG was examined by electrochemical polarization in phosphate buffered solution, which demonstrates that the BMG also exhibits an excellent corrosion resistance. Finally, the potential cytotoxicity of the Ni-free BMG was evaluated through cell culture followed by 3-(4,5-Dimethylthiazol-2-y1)-2,5-diphenyltetrazolium bromide (MTT) assay and scanning electron microscope (SEM) observation. It is shown that the BMG exhibits a high cell viability and proliferation activity, and NIH/3T3 cells can closely adhere and well extend on the surfaces of the BMG alloy. The results indicate that the Ni-free Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ BMG developed in the present work is promising for biomedical applications. [doi:10.2320/matertrans.MJ200730]

1. Introduction

Zr-based bulk metallic glasses (BMGs) has attracted an increasing attention in the last decade because of the combination of superior strength (above 1.5 GPa), high elastic strain limit (around 2.0%), relatively low Young’s modulus (50 ~ 100 GPa) and excellent corrosion resistance.\cite{1,2,3} The properties together with easy forming ability show excellent glass forming ability and quite satisfactory liquid region of 101°C. A static-state compression revealed that the BMG possesses a superior fracture strength of 1709 MP and extended plastic strain of 9.5%. The corrosion resistance of the BMG was examined by electrochemical polarization in phosphate buffered solution, which demonstrates that the BMG also exhibits an excellent corrosion resistance. Finally, the potential cytotoxicity of the Ni-free BMG was evaluated through cell culture followed by 3-(4,5-Dimethylthiazol-2-y1)-2,5-diphenyltetrazolium bromide (MTT) assay and scanning electron microscope (SEM) observation. It is shown that the BMG exhibits a high cell viability and proliferation activity, and NIH/3T3 cells can closely adhere and well extend on the surfaces of the BMG alloy. The results indicate that the Ni-free Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ BMG developed in the present work is promising for biomedical applications. [doi:10.2320/matertrans.MJ200730]

2. Experimental

Alloy ingots with nominal composition of Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ was prepared from elemental metals (purity $>$ 99.9%) by arc-melting under a Ti gettered Ar atmosphere. In order to make composition homogenous, a two-step melting process was carried: First, the raw elements of Zr and Nb, which possess the highest melting temperatures in the system, were melted together to get a homogenous Zr-Nb solid solution; Then, the binary alloy ingot were re-melted with remaining metals (i.e., Cu, Fe and Al) to obtain a master alloy with a desired composition. From the master alloy, a sample rod with a diameter of 3 mm and length of 50 mm was finally produced by copper mould casting.

The amorphous feature of as-cast alloy was verified by x-ray diffraction (XRD), $\chi'$ Pert PRO) with CuK$_\alpha$ radiation and transmission electron microscopy (JEM-2010). Thermal stability and melting behavior of the glassy rod was examined using a differential scanning calorimetry (DSC, Perkin-Elmer 7) and differential thermal analyzer (DTA, Perkin-Elmer 7) at a heating rate of 20°C/min under a constant flow of argon. A quasi-static uniaxial compression test was carried out at

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room temperature by using a MTS machine operated under displacement control at a strain rate of $1 \times 10^{-4}$ s$^{-1}$. Samples with a length of 6 mm and diameter of 3 mm with aspect ratio of 2:1 were cut from the rod for the test.

Electrochemical polarization was conducted in a three-electrode cell using a platinum counter electrode and a saturated calomel reference electrode (SCE). The whole cell was kept at 37°C throughout the test. The electrolyte used in the present study is phosphate buffered solution (PBS, PH=7.4), whose compositions are composed of 8 g/L NaCl, 0.2 g/L KCl, 0.14 g/L NaH$_2$PO$_4$ and 0.2 g/L KH$_2$PO$_4$. The potentiodynamic polarization curve of the BMG was recorded at a potential sweep rate of 1 mV/s when the open-circuit potential became almost steady after immersion in PBS for at least 20 min. 316 L stainless steel and Ti-6Al-4V alloy were measured in the same condition for comparison.

The potential cytotoxicity of the BMG was evaluated through cell culture for one week followed by 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. In this process, NIH/3T3 cells (embryonic mouse fibroblast cell line) were first seeded at a density of 1.44 x 10$^5$ cells/mL on the polished and sterilized alloy slices with a size of 5 mm x 3 mm x 1.5 mm in a 96-well plate, and then cultured in Dulbecco’s modified Eagle’s medium (DMEM; Gibco), supplemented with 10% fetal bovine serum (FBS) in a 37°C, humidified, 5%CO$_2$/95% air environment. The culture medium was changed every 3 days. After 7 days, the BMG specimens were taken out for MTT assay. Three specimens were tested simultaneously for dependability. The cytotoxicity test of Ti-6Al-4V alloy was also performed under the same condition for comparison and a blank test (i.e., cells were cultured in wells without alloy samples) was taken as a control. The morphology of cells grown on the samples was examined by scanning electron microscopy (SEM, Philips Quanta 200).

### 3. Results and Discussion

Figure 1a shows the XRD pattern of the Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ alloy rods prepared. A broad diffraction hump without any appreciable crystalline peaks in the XRD pattern indicates that the as-cast sample is basically amorphous. The amorphous feature was further verified by TEM (see Fig. 1(b)), as indicated by a featureless contrast in the bright field image and a diffused diffraction ring in the corresponding selected area diffraction pattern. Figure 2(a) shows DSC curve of the BMG at a heating rate of 20°C/min. It can be seen that the BMG exhibits a distinct glass transition followed by a wide supercooled liquid region before crystallization. The glass transition temperature ($T_g$), the onset temperature of crystallization ($T_x$) are determined to be 350°C, 451°C, respectively. This yields a supercooled liquid region ($\Delta T = T_x - T_g$) of 101°C. This value is much larger than that of the alloys developed by Jin et al. ($\Delta T = 73$–63°C)\textsuperscript{11} and that of Zr$_{60}$Nb$_5$Cu$_{22}$sPd$_5$Al$_{15}$ BMG reported in our previous work ($\Delta T = 37$°C).\textsuperscript{14} In addition, the BMG follows a multi-process of crystallization similar to the crystallization pathway that was found in Zr$_{60}$Nb$_5$Cu$_{22}$sPd$_5$Al$_{15}$ BMG, in which quasicrystals were initially formed.\textsuperscript{14} Fig. 2(b) shows the DTA curve of Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ BMG heated up to 1100°C. The BMG exhibits three endothermic events with the onset melting temperature of 829°C and liquidus temperature of 941°C. This yields a reduced glass transition temperature ($T_{rg} = T_g$/$T_l$) of about 0.37, which is much smaller than the values of $T_{rg}$ for most of Zr-based BMGs. Nevertheless, Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ system can be easily cast into bulk glass with a diameter of 3 mm, implying that $T_{rg}$ may not be an effective measure to evaluate the glass forming ability for the present system. The multiprocess melting processes indicate that the alloy is far from the eutectic composition.

Figure 3(a) shows the stress-strain ($\sigma$–$\epsilon$) curve of Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ BMG obtained under compressive loading at a strain rate of $1 \times 10^{-4}$ s$^{-1}$. The BMG exhibits very good mechanical properties with yield strength ($\sigma_y$) of 1393 MPa, fracture strength ($\sigma_f$) of 1709 MPa and fracture strain of 11.4%. Interestingly, a considerably large plastic strain as high as 9.5% is obtained although the BMG is apparently of a single amorphous structure (see Fig. 1). In addition, an elastic strain of 1.9% with a relatively low elastic modulus of about 73 GPa can be obtained from the test. The modulus is more close to that of human bone (20–30 GPa) in comparison to 316 L stainless steel (~200 GPa) and Ti-6Al-4V alloy (110 ~ 125 GPa). To be noted that the serrations in the elastic deformation part (Fig. 3) is probably from the noise of MTS machine. The noise usually exists when using...
very low strain rate. However, it does not affect the deformation behavior of the sample. Figure 3(b) shows the morphology of the side surface of the sample after fracture. A huge number of jagged and bifurcated shear bands can be observed in the sample. Since the plastic deformation achieved by bulk metallic glasses is confined almost entirely to the narrow regions near the shear bands, the high density and extended distribution of shear bands in the sample are probably the origin for the good plasticity.

Figure 4 shows the polarization curve of the BMG in PBS open to air at 37°C. The results for 316 L stainless steel and Ti-6Al-4V tested under the same condition are also presented for comparison. It can be seen that the BMG exhibits a spontaneous passivation with a wide stable passive region before pitting occurred. In comparison with 316 L stainless steel and Ti-6Al-4V alloy, the BMG shows evidently a lower passive current density, suggesting that the passive film formed on the BMG surface is more protective than on other two alloys. Moreover, the pitting potential of the BMG is much higher than that of 316 L stainless steel.

Figure 5(a) shows the results of MTT assays for Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ BMG and Ti-6Al-4V alloy after cell culture for 7 days. The BMG shows a closely similar absorbance to Ti-6Al-4V alloy, indicating that the BMG has high cell viability and proliferation activity. To directly observe the morphology of cells on the BMG surface after cell culture, some specimens were subjected to SEM observation after standard bio-treatments. Figure 5(b) shows clearly that NIH/3T3 cells closely adhered and well extended on the surface of Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ BMG. This indicates that the BMG developed in this work exhibits an excellent biocompatibility.

4. Conclusions

A Ni-free BMG of Zr$_{60}$Nb$_5$Cu$_{20}$Fe$_5$Al$_{10}$ has been developed in this work. The BMG exhibits a superior strength of 1709 MPa, extended plastic strain of 9.5% and relative low elastic modulus of 73 GPa. The BMG also shows an excellent corrosion resistance in phosphate buffered solution as indicated by a low passive current density and wide passive region in electrochemical polarization. Cytotoxicity test
suggests that the BMG have a very good biocompatibility, comparable to Ti6Al4V. The present results demonstrate that Zr$_{60}$Nb$_{5}$Cu$_{20}$Fe$_{5}$Al$_{10}$ BMG developed in the work is promising for biomedical applications.

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