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Surface modification of Zr-based bulk amorphous alloys by using ion irradiation

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ABSTRACT

Surfaces of the $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}M_2$ (M = Er and Gd) bulk amorphous alloys were modified by irradiation with energetic singly charged argon (Ar^+) ions. Samples of both the alloys were irradiated with 2.17×10^{17} argon ions of 10 keV energy. As cast and ion irradiated samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Mechanical properties like Vicker's hardness, nanohardness, elastic modulus and elastic recovery were measured. Considerable increase in elastic modulus and hardness was observed because of ion irradiation in these alloys. The ion irradiated samples of the $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Er_2$ alloy showed better properties as compared to $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Gd_2$ alloy. $CuZr_2$ phase was detected in ion irradiated alloys by XRD and confirmed by EDS. The range of Ar^+ ions was found to be approximately 9.3 ± 5.4 nm in both alloys.

1. Introduction

Bulk metallic glasses (BMGs) are new class of materials which have unique properties [1] and numerous applications [1,2]. Iqbal et al. [3–5] reported production of bulk amorphous alloys with promising mechanical and thermal properties. Wang [6] reviewed in detail the effect of minor alloying additions to improve properties of amorphous materials. The properties of the BMGs can be improved using various techniques such as laser melting [7], electron beam melting [8], electron beam irradiation [9], ion implantation [10,11], laser irradiation [12], proton irradiation [13] and ion irradiation [14]. The irradiation affects the microstructure and mechanical properties and induces phase transition. Study of crystallization behavior of an alloy is important from the thermal stability point of view during applications. Crystallization can occur due to temperature effects or irradiation when the alloy is in use. The crystallization of amorphous phases occurs not only by thermal annealing but also by electron irradiation, focused ion beam, electron pulsing and high mechanical pressure [9]. In case of amorphous alloys certain phases can be produced within the amorphous matrix by ion irradiation that can enhance the surface properties without affecting the amorphous structure. Iqbal et al. [14] have studied ion irradiation of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy and noticed improvement in mechanical properties of the irradiated areas of the alloy. Later on, Carter et al. [15] have verified these results on the same alloy using the techniques of X-ray diffraction (XRD) and transmission electron microscopy (TEM). However, Nagata et al. [16] did not observe precipitation of crystalline phases after ion irradiation. Yang et al. [17] and Tao et al. [18] have studied the effect of Co ion implantation on the surface structure and properties of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG and observed formation of ZrO_2 phase as well as increase in hardness. It was also reported that Co implantation changed single stage crystallization to double stage crystallization. Zhang et al. [19] reported significant variation in mechanical properties by controlling residual stresses and surface treatments. The results showed that as cast, abraded and peened samples have clear cut difference in plasticity. In the present study, the effect of ion irradiation on microstructure and mechanical properties of the two $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}M_2$ alloys is reported.

2. Experimental

Bulk amorphous ingots with compositions $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Er_2$ (designated as alloy A) and $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Gd_2$ (designated as alloy B) were synthesized by Cu mold casting technique using 2-4N pure metals. The details of the ion-beam system used for present study are given elsewhere [20]. The beam diameter at the surface of sample was 3 mm. Fine polished samples of size 5 mm × 5 mm × 2.5 mm was kept perpendicular to the ion beam direction during irradiation. The samples of each alloy were irradiated with 1.44×10^{17} and 2.17×10^{17} Ar^+ ions of 10 keV energy. The pressure in the target chamber was maintained at about 10^{-5} Pa. The ions were produced in a magnetically confined hollow cathode duoplasmatron, focused with an Einzel lens and mass analyzed with the help of ExB velocity filter. The projected range of Ar^+ ions in these samples was calculated using computer code SRIM (stopping and ranges of ions in metals) [21]. The microstructure of as cast and the ion irradiated samples of both the alloys were examined in the scanning electron microscope (SEM) and analyzed by energy dispersive spectroscopy (EDS) attached with it. Structural analysis was performed

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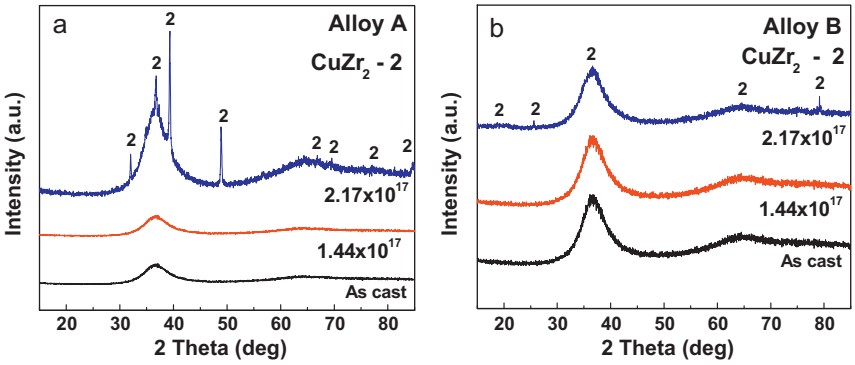

Fig. 1. (a, b) XRD patterns of as cast and irradiated samples of alloy A (a) and alloy B (b) exposed with 1.44×10^{17} and 2.17×10^{17} ions, respectively.

by D/Max -2500 Rigaku X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å). Vicker's hardness of the as cast and ion irradiated samples was measured by MVK-H3 Mitutoya hardness tester. Nanohardness and elastic modulus were measured by MTS Nanoindenter XP.

3. Results and discussion

The XRD patterns of the as cast samples of alloy A and alloy B are shown in Fig. 1(a) and (b), respectively, which contain broad bands indicating amorphous nature of the alloys. Physical examination of as cast samples showed excellent metallic luster indicating amorphous structure. SEM examination of both samples revealed featureless surface which also confirms the amorphous nature of the alloys. The alloy A and alloy B remain amorphous up to the irradiation of 1.4×10^{17} ions, as XRD patterns of both the alloys still show broad brands as shown in Fig. 1(a) and (b). The XRD patterns of both alloys, irradiated with 2.17×10^{17} ions are also shown in Fig. 1(a) and (b). Sharp diffraction peaks exist in the XRD patterns of both alloys along with broad bands. It is evident that crystalline phases resulted in the amorphous matrix. The $CuZr_2$ phase was identified in the XRD patterns. The number and intensity of the diffraction peaks in alloy A is higher than alloy B which indicates that amount of crystallization in alloy A is greater than alloy B. This indicates that crystallization occurred in the alloy A, while major portion of alloy B remained amorphous. In the present systems, Zr and Cu atoms are in majority, therefore, $CuZr_2$ phase is produced as a result of the movement of atoms due to ion irradiation. The $CuZr_2$ course precipitates were also confirmed by EDS. The EDS analysis also revealed smaller size precipitates that were rich in Ni and Zr, and their composition corresponds to $NiZr_2$. The $NiZr_2$ phase was not detected by XRD due to its low volume fraction. Most probably the primary phase $NiZr_2$ (Laves phase) nucleated at the start of the irradiation because heat of mixing (ΔH_{mix}) of Ni–Zr pair (−49 kJ/mol) is lower than all other pairs of the constituents of the alloy [22]. The second reason is the smallest size of Ni [23] and the largest size of Zr atoms. As the irradiation continues, majority of metastable $NiZr_2$ precipitates continuously transformed into $CuZr_2$ phase. Nucleation of precipitates by ion irradiation in the present alloys is inline with the previous studies [14,15].

Hardness measurements were conducted on the as cast and ion irradiated samples and the results are summarized in Table 1. The average Vicker's hardness (H_V) of as cast samples of alloy A and alloy B was 400 and 396, respectively. The hardness of the irradiated samples for alloy A and alloy B was found to be 485 and 476, respectively, which indicates an increase of 20% in H_V due to irradiation. The nanohardness H of as cast alloy A and alloy B was approximately 6.2 GPa and 5.6 GPa. While increase in nanohardness of irradiated samples was approximately 20%. The elastic moduli of as cast alloy A and alloy B were found to be 93 GPa and 89.4 GPa, respectively. The increase in hardness and elastic moduli is due to nucleation of crystalline phases and precipitation hardening [24]. SEM viewgraph at low magnification of the alloy A sample irradiated with 2.17×10^{17} ions is shown in Fig. 2(a), where the central circular region is the ion irradiated area. Precipitates were observed in both irradiated alloy samples as shown in Fig. 2(b) and (c). Three-sided Berkovich indent produced during nanohardness test on a sample of alloy A is shown in Fig. 2(d). Absence of diagonal cracks in indents indicates presence of ductility in the alloys.

The loading and unloading curves (P–h curves) for the ion irradiated alloys are given in Fig. 3(a) and (b). Here "P" represents the applied load (in mN) and "h" is the penetration depth (in nm) of the nanoindenter into the sample. The elastic recovery (h_f/h_{max}) and percentage elastic recovery of displacement on unloading $\%R = ((h_{max} - h_f)/h_{max}) \times 100\%$ are two important parameters where h_f is the final indentation depth and h_{max} is the maximum penetration depth of the indenter [25]. The nanoindentation parameters are given in Table 1. Pop-in and pop-out marks were previously observed in $Zr_{55}Cu_{30}Al_{10}Ni_5$ irradiated alloy [14] but were not observed in these alloys. The elastic recovery is found to be 0.753 ± 0.014, while the percentage elastic recovery ($\%R$) ranges between 24.75 ± 1.35 for the present alloys. The alloy A has better mechanical properties than alloy B. The possible reason is that Er has lower atomic size (0.17558 nm) than Gd (0.18013 nm). Gd atoms produced more disorder than Er atoms per unit volume in the base alloy. It is a fact that atomic packing density of alloy B is higher than alloy A. We believed that ion irradiation is mainly responsible for the nucleation of crystalline phases in the amorphous matrix and causes enhancement of surface properties. The irradiated samples behave like composite materials. Penetration

Table 1
Mechanical properties and nanohardness parameters of the as cast and irradiated samples of two alloys.

Alloy designation	Nature of sample	H_V	H (GPa)	E (GPa)	H/E	h_f (nm)	h_{max} (nm)	h_f/h_{max}	$\%R$
Alloy A	As-cast	400	6.2	93.0	0.067	245	320	0.766	23.4
	Irradiated	485	7.5	113.1	0.066	209	278	0.752	24.8
Alloy B	As-cast	396	5.6	89.4	0.062	241	318	0.758	24.2
	Irradiated	476	6.6	108.7	0.061	201	272	0.739	26.1

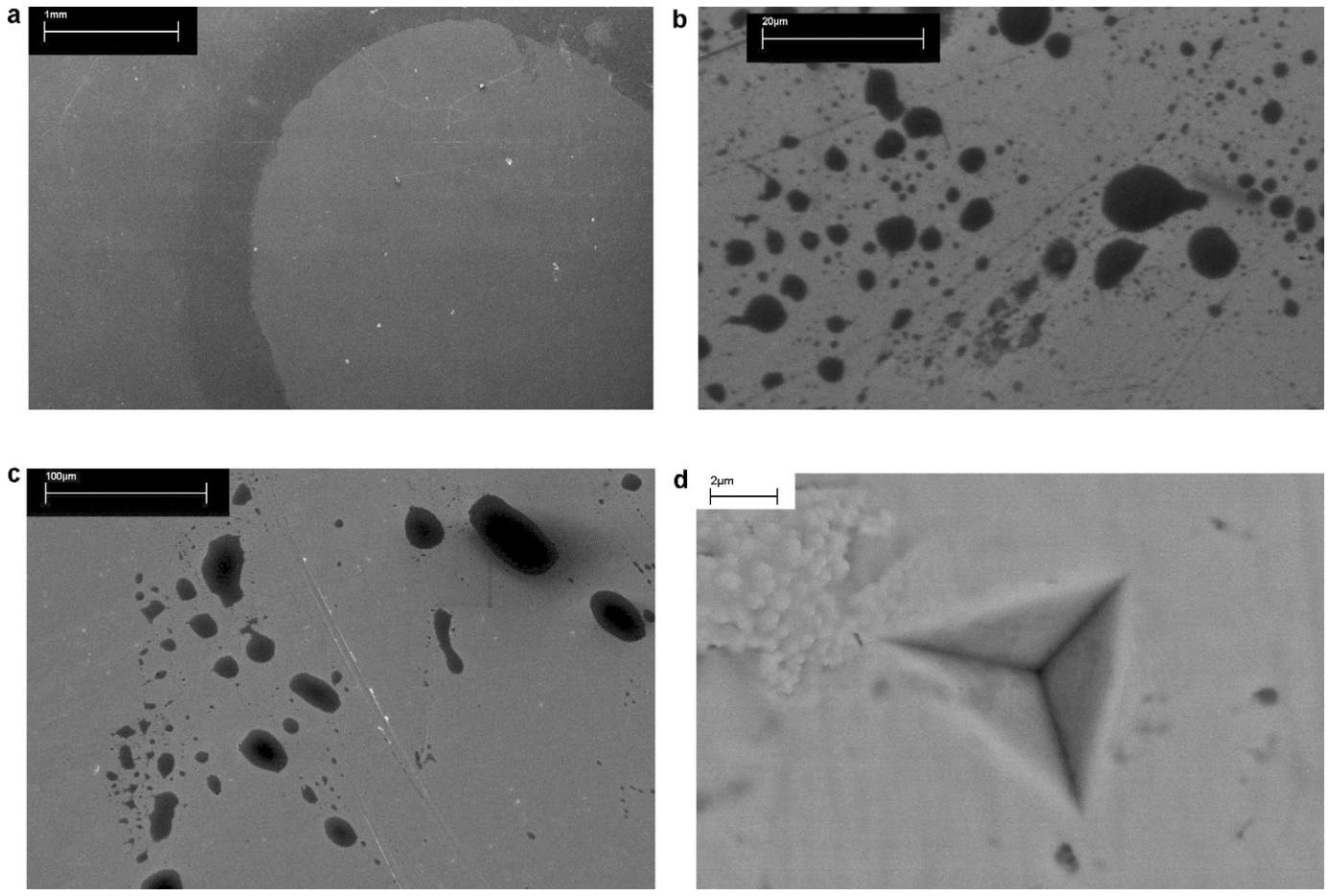

Fig. 2. (a–d) SEM viewgraphs of samples irradiated with 2.17×10^{17} ions: full view of the alloy A sample (a) precipitation in alloy A (b), alloy B (c) and three sided Berkovich indent on alloy A (d).

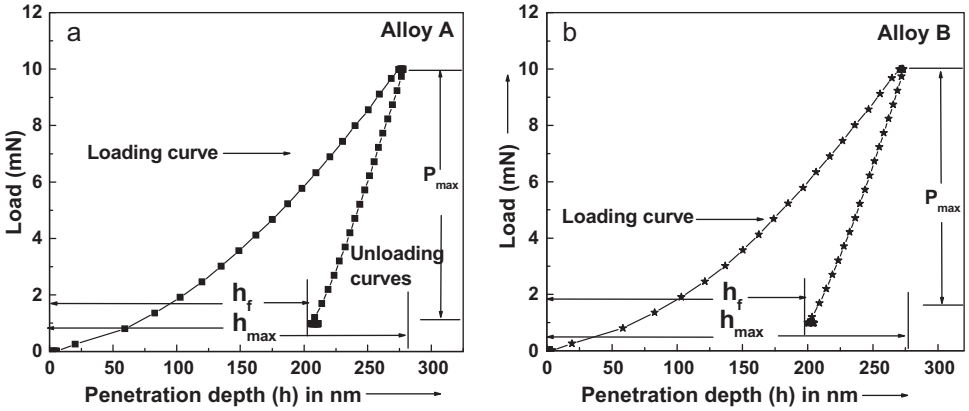

Fig. 3. (a, b) *P–h* curves of the samples irradiated with 2.17×10^{17} ions of the alloy A (a) and the alloy B (b).

depth of 10 keV argon ions in these alloys is 9.3 ± 5.4 nm indicating that the damage is a surface phenomenon.

4. Conclusions

Bulk amorphous $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Er$ and $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Gd$ alloys were irradiated with the Ar^+ ions. The Vicker's hardness, nanohardness and elastic modulus of exposed areas were improved considerably. The ion irradiated samples of the $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Er_2$ alloy showed better mechanical properties as compared to the $[Zr_{0.65}Cu_{0.18}Ni_{0.09}Al_{0.08}]_{98}Gd_2$ alloy. The XRD and EDS analysis confirmed presence of $CuZr_2$ phase in the amorphous matrix of both the irradiated alloys. The range of Ar^+ ions was found to be approximately 9.3 ± 5.4 nm in both the alloys. Due to shallow range of the ions, observed changes are limited to the surfaces.

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