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Evolution of microstructure and non-equilibrium phases in electron beam treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy

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Abstract

Electron beam (EB) is becoming very popular for the modification of the surfaces as it involves localized melting and fast cooling which helps in achieving the non-equilibrium phases as well as fine microstructure. Surface modification of Zr-based amorphous alloy $Zr_{55}Cu_{30}Al_{10}Ni_5$ has been carried out by EB melting. Differential scanning calorimetry (DSC) was employed to determine the supercooled liquid region and activation energy of crystallization. The as-cast and modified surfaces of amorphous alloy at different beam conditions were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques. Various phases like $NiZr_2$, $CuZr_2$ and $Cu_{10}Zr_7$ were identified which resulted in the enhancement of hardness of the modified alloy surface.

Keywords: Bulk metallic glasses; Surface hardening; Electron beam; Glass-forming ability

1. Introduction

Bulk metallic glasses (BMGs) have attracted an increasing attention in the past decade because of their importance in both fundamental science and engineering applications [1,2]. However, a single phase of BMG usually displays limited plasticity at room temperature, i.e., normally less than 2% in compression and nearly zero in tension, thus, limiting the range of their commercial applications. Attempts have been made to improve ductility as well as hardness by making composite materials consisting of a crystalline reinforcing phase in metallic glass matrix. A number of techniques so far have been developed for the fabrication of BMG matrix composites. For instance, the precipitation of nanocrystals through the partial devitrification of BMGs [3], the addition of foreign particles or fibers into the melt prior to casting [4–6], and the precipitation of a dendritic [7] or spherical [8] ductile crystalline phase from the melt. The formation of BMG composites and the effect of reinforcing phase on the mechanical properties of the amorphous matrix have been extensively studied in recent years [9–11]. However, little work has been done on the surface modification of BMG by forming BMG matrix composite (having crystalline phases embedded in an amorphous matrix on the surface). EB surface melting technique has gained applications in nuclear, chemical and aerospace industries due to its large penetration depth and high cooling rate. The main reason is that the resulting supercooling of the localized area helps in achieving the non-equilibrium phases as well as fine microstructure [12].

It is a well-known fact that homogeneous distribution of nanocrystals/precipitates in the amorphous matrix enhances the tensile strength as compared to the corresponding single-phase bulk amorphous alloys [13–15]. Due to the high hardness of the composite surface/alloy the wear and tear of the components used in the moving parts will be reduced and the life of the components will be enhanced. In the present study, $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG alloy surface was melted by EB to introduce the non-equilibrium crystalline phases in the amorphous matrix to form composite surface. The microstructure of EB melted $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG was investigated using SEM and the compositional analysis was done by EDS. Non-equilibrium

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Table 1
EB melting parameters

Sample no.	Current (mA)	Voltage (kV)	Pulse time (s)	Beam diameter (mm)	Working distance (mm)	Vacuum (Torr)	Power (W)
1	10	20	0.9	2	160	10^{-5}	200
2	15	20	0.9	2	160	10^{-5}	300
3	20	40	0.9	2	160	10^{-5}	800

phases formed as a result of partial devitrificated surface layer during rapid solidification were identified by XRD and finally hardness of EB modified surface was measured.

2. Experimental

The alloy buttons with the composition of $Zr_{55}Cu_{30}Al_{10}Ni_5$ were cast in an arc furnace cooled with water, by melting the mixture of elements having 2N purity in Ti gettered atmosphere of high purity Ar at pressure of 4.5×10^{-4} Pa. The mixture was melted several times to get the chemical homogeneity. Cylindrical rods of 4 mm diameter and 40 mm length were synthesized in an induction furnace under Ar atmosphere using pressure up to 2×10^{-3} Pa by Cu mould casting. This rod was cut into four pieces having diameter 4 mm and length 4 mm each by slow speed cutter. Low temperature DSC was carried out using the Perkin-Elmer DSC 7/Pyris-1 at heating rate of 10, 20, 30 and 40 K/min to evaluate thermal parameters for crystallization. High temperature DSC was conducted at 40 K/min to determine the melting and liquidus temperatures using NETZSCH DSC 404C. In order to modify the surface, three samples were exposed to EB under different conditions listed in Table 1. Samples were examined under SEM and analysis was done using EDS. XRD was conducted, by Rigaku D/Max-2500 diffractometer using Cu Kα_1 radiation (λ = 1.54056 Å) to identify the crystalline phases in the EB melted samples. Vicker's microhardness was measured using Matsuzawa Seiki DMH-2 microhardness tester under load of 0.98 N.

3. Results and discussion

XRD pattern of the as-cast sample is shown in Fig. 1(a) and a broad band is observed from 35° to 45°, which indicates the amorphous nature of the alloy. Thermal stability and glass-forming ability (GFA) are important parameters that are measured by performing DSC. Fig. 2(a) shows the low temperature DSC plots of the alloy at different heating rates. All DSC traces have a single exothermic peak which shows that single stage crystallization reaction is taking place in the alloy. DSC with heating rate of 40 K/min exhibits a significant endothermic reaction characteristic of T_g at 696 K, determined by tangent method. The alloy also shows an extended supercooled liquid region of 74 K at heating rate of 40 K/min before the onset of crystallization temperature T_x. Different thermal parameters derived from DSC curves are listed in Table 2.

The activation energy for crystallization of an alloy is an important kinetic parameter related to the thermal stability of amorphous phase. Based on the results of the exothermic peak (T_p) shifts in DSC measurements conducted at different heating rates, the value of activation energy was calculated from

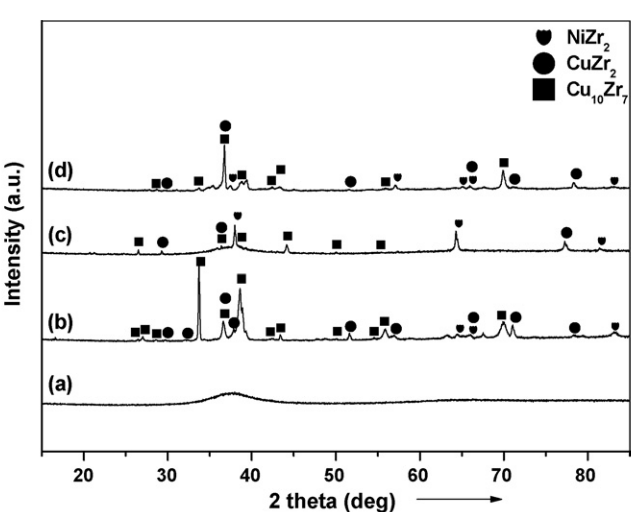

Fig. 1. XRD patterns of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy at different conditions: as-cast sample (a), sample 1 (b), sample 2 (c) and sample 3 (d).

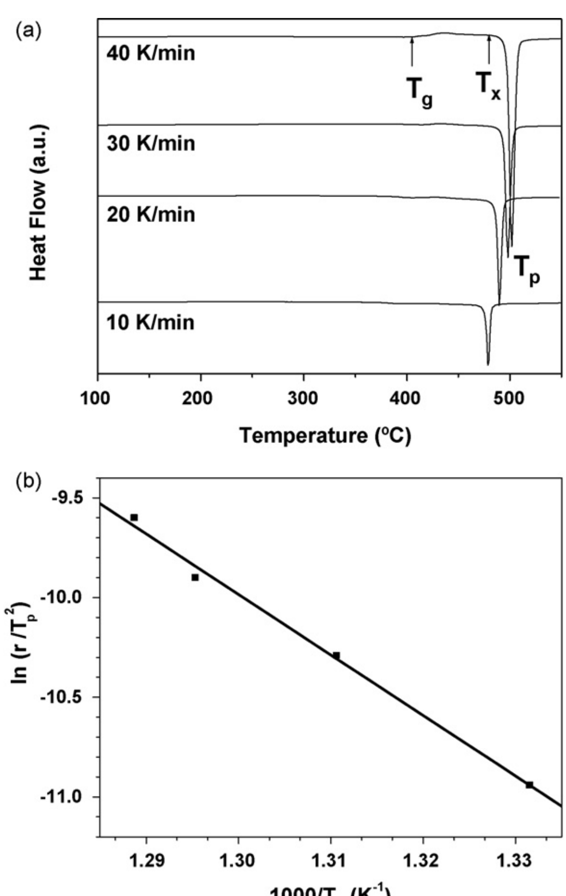

Fig. 2. (a) Low temperature DSC curves of as-cast $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy at different heating rates and (b) plot of $\ln(r/T_p^2)$ vs. $1000/T_p$.