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ORIGINAL ARTICLE

Glass forming ability and crystallization kinetics in $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) bulk glassy alloys

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Abstract : In the present work, the formation of amorphous phase as primary phase was found in $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) glassy alloys. Wedge shaped bulk samples, with thickness form 2 mm up to 5mm, were prepared by copper mould casting technique. Ribbons of the same composition, with 30 μm thickness, were prepared by melt spinning technique. The thermal stability and structural properties were evaluated by differential scanning calorimetry (DSC) and X-ray diffraction (XRD), respectively. The effect of high temperature on the isothermal crystallization of $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) bulk metallic glass rod with a diameter of 2 mm was investigated by HTX-ray diffraction. It was found that the crystallization behaviour of $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) bulk metallic glass strongly depends on the annealing temperature. The different crystallization behaviour is believed to be due to the different structures that the metallic glass possesses at different temperatures.

Keywords : Bulk metallic glasses; Ribbons; DSC; XRD method; HTX-ray diffraction; Crystallization behavior.

INTRODUCTION

Among the numbers of developed bulk metallic glasses (BMGs) recently, Zr-based BMG was considered to be one of the most promising materials and has attracted much attention due to its exceptional properties[1-3], such as a high strength, high hardness, high elastic strain up to 2%, good wear resistances[4,5], and near perfect as cast surfaces, exceptional glass-forming ability (GFA) with a critical cooling rate as low as 1 K/s. However, these excellent properties can be altered when the as-quenched structure is not fully amorphous and the glass forming ability still remains an important characteristic in order to produce such a class of materials in industrial environment. Crystallization studies of metallic glasses are interesting from many points of view[6,7].

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The results of such studies are helpful in understanding the mechanism and kinetics of phase transformation into the equilibrium state. Very recently, we have found the formation of an icosahedral phase in Zr-based alloys containing V, Nb and Ta[8]. The aim of the present work is to study the behaviour of glass formation of the $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) prepared by the melt-spinning process, in the ribbon shape, and then injected into a copper mould to prepare alloy rods of about 2 mm in diameter.

Crystallization kinetics has been presented as function of annealing temperature of bulk metallic glasses $Zr_{59}Cu_{18}Ni_8Al_{10}$ with and without Nb, Ti and Ta addition. The isothermal crystallization was investigated by in situ high temperature X-rays diffraction.

EXPERIMENTAL

Ingots of $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP% Nb, Ti and Ta) master alloys were prepared from commercial-grade materials by arc-melting furnace under Ar atmosphere. In order to study the effect the Nb, Ti and Ta on GFA, the liquid alloys were quenched in a copper mold. Bulk samples preparation has been performed in a commercial casting machine used for the jewellery industry. It consists in an upper chamber, in which the induction coil and the crucible are placed, and a lower one, which contains the copper mold. Both chambers can be evacuated until 10^{-1} mbar and subsequently filled with pure Ar. For comparison, ribbons of 5 mm width and about 30 µm thickness were prepared using a single-roller melt spinner at a wheel speed of 24 m/s. All the ribbons and cylinders were investigated by differential scanning calorimetry (DSC) using a constant heating rate of 10 °C/mn. The structural properties of the samples were examined by X-ray diffraction (XRD) with Cu Kα (λ = 1.54056 Å) radiation.

RESULTS AND DISCUSSION

In order to confirm the glassy state of the samples, further X-ray diffraction measurements were performed. Figure 1 shows XRD pattern of the cast $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) rods with a diameter of 2 mm, together with the XRD pattern of the melt-spun glassy alloy ribbons. Only a broad peak is seen around a diffraction angle of 40°, 39° and 39°for the bulk sample and ribbon for $Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$, $Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ and $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$, respectively, no

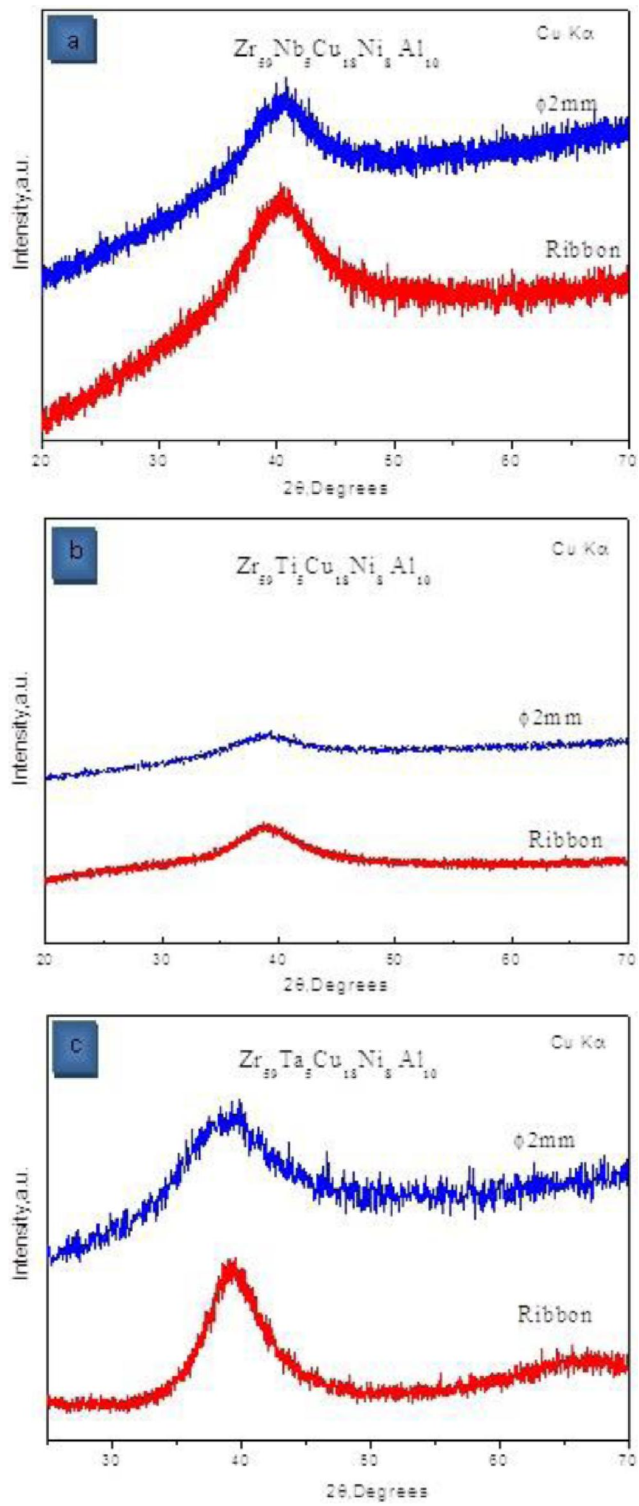

Figure 1 : XRD pattern of the cast rod with a diameter of 2 mm, together with the XRD pattern of the melt-spun glassy alloy ribbon, (a) $Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$ (b) $Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ (c) $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$

detectable sharp diffraction peak indicating crystalline structure can be observed. These are typical XRD patterns of amorphous structures, confirming that both samples possess amorphous structures.

The critical cooling rate for glass formation, *R*c, is an important characteristic parameter for predicting the ease or difficulty of glass formability. It is defined as the minimum cooling rate necessary to keep the melt amorphous without detectable crystallization upon solidification. A slower *R*c indicates a greater glass-forming ability of an alloy system.

Figure 2 shows the constant-rate heating (10°C/mn) DSC curves of $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Ta, Ti and Nb) analysis was carried out for melt-spun ribbons and as-cast cylinders. In the temperature range investigated, all the curves are characterized by two exothermic peaks, revealing a multi-step crystallization path that does not depend on the way of preparation. The analysis of the thermal stability data, summarized in TABLE 1, reveals striking similarities between the as-cast cylinders and the melt-spun ribbon.

TABLE 1 : Thermal properties of as-cast rods and ribbons for $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Ta, Ti and Nb) alloys (continuous heating at10 °C/mn).

Alloy	T_g (°C)	T_{x1} (°C)	T_{x2} (°C)	ΔT_x (°C)
$Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$ (Ribbon)	337	386	479	49
$Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$ (RodΦ2mm)	336	385	478	49
$Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ (Ribbon)	363	405	451	42
$Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ (RodΦ2mm)	362	403	453	41
$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ (Ribbon)	343	402	431	59
$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ (RodΦ2mm)	342	400	430	58

The DSC curves indicate a small difference in glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid region ($\Delta T_x = T_x - T_g$) of the $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta) glassy alloys the melt-spun ribbon and as-cast cylinders, for the as cast of 2 mm diameter cylinder and the ribbons alloys presents no pronounced difference in glass transition temperature *T*g, temperature crystallization T_{x1} and T_{x2} for these alloys $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Nb, Ti and Ta).

During the heating the sample loses energy, sound volume joined the curve of the state superfused towards, then when temperature rises, crystallization intervenes and it joined curve of the crystallized state.

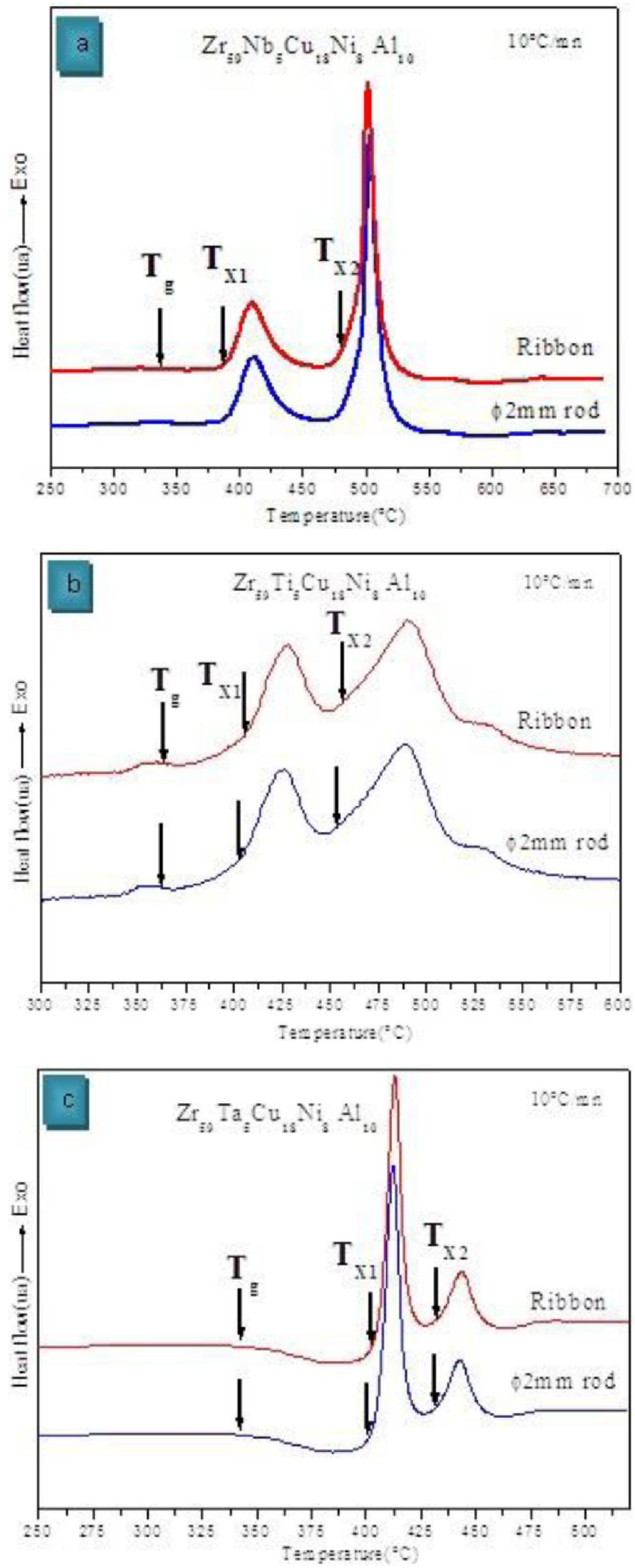

Figure 2 : DSC curves of the cast rod with a diameter of 2 mm and of the melt-spun glassy alloy ribbon. Tg, Tx, indicate to glass transition and temperatures crystallization melting respectively, (a) $Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$ (b) $Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ (c)$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$.

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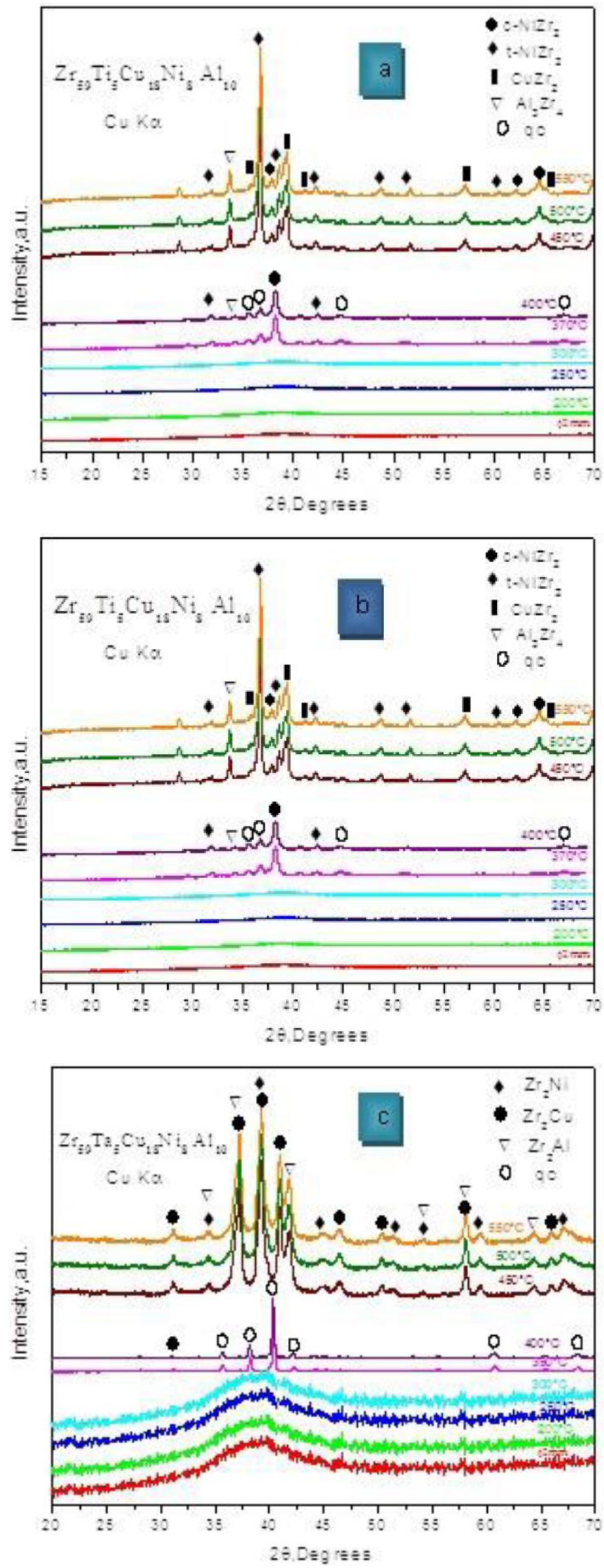

Figure 3 : XRD scans of annealed samples with and without addition Nb,Ti and Ta indicating by (a) $Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$ (b) $Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ (c)$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$.

The structural evolution during heating was investigated by XRD. The diffraction patterns of rod form with diameter of 2 mm at prepared through water-cooled copper mold casting heated to different temperatures are shown in Figure 3 of $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ with or without Nb, Ti and Ta addition at different annealing temperature. The rod form with diameter of 2 mm broad maxima characteristic for amorphous materials and no trace of crystalline phases, indicating that they are in the amorphous state for temperatures between 200°C and 350°C for $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Ta, Ti and Nb) The phase formation reflects at the TP%350°C and 400°C for $Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$, $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$, respectively and TP%370°C, 400°C for $Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$. Obviously, the first step of devitrification is mostly linked with the formation of quasicrystalline phase, in the figures 3(a, b and c). Concerning XRD patterns of the bulk samples in $Zr_{59}Nb_5Cu_{18}Ni_8Al_{10}$ Figure 3(a) at 450 °C are identified the crystalline phases after complete crystallization of the as-cast 2 mm include Zr_2Cu and Zr_2Ni. Appeared phases are essentially cubic $NiZr_2$, tetragonal $NiZr_2$, tetragonal $CuZr_2$, and hexagonal Al_3Zr_4 at 450 °C for $Zr_{59}Ti_5Cu_{18}Ni_8Al_{10}$ in Figure 3(b). Figure 3(c) shows the pattern reveals the formation of the Zr_2Cu, Zr_2Ni and Zr_2Al phase at 450 °C for $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$. Further study shows that there is similar tendency of the microstructure as the holding time increases from 3 to 9 min at 450 C.

CONCLUSIONS

In conclusion, a series of bulk metallic glasses with different compositions of $Zr_{59}Cu_{18}Ni_8Al_{10}X_5$ (XP%Ta, Ti and Nb) were annealed at various temperature by in situ High temperature X-rays diffraction have been studied. It can be seen that all samples were completely crystallized at 450°C.

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