Formation of Metallic Glasses in Novel $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ Alloys

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The formation of metallic glasses by rapid solidification has been studied using an equiatomic substitution technique. This paper reports results on a series of $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ glassy alloys with compositions in the range $x = 10\text{--}70\text{ at\%}$ and $y = 10\text{--}30\text{ at\%}$, and with a large supercooled liquid region in the range $\Delta T = T_x - T_g = 40\text{ to }124\text{ K}$ where T_x = crystallization onset temperature and T_g = glass transition temperature. The crystallization of the glassy alloys was studied by a combination of X-ray diffraction and differential scanning calorimetry. For $(\text{Ni}_{50}\text{Cu}_{50})$ -rich alloys with $x = 50\text{--}70\text{ at\%}$, crystallization took place with a single exothermic reaction, and for $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})$ -rich alloys with $x = 20\text{--}40\text{ at\%}$, crystallization took place with a series of exothermic reactions. Increasing the Al content from $y = 10$ to $30\text{ at\%}$ decreased the glass forming ability of the amorphous phase for a wide range of transition metal compositions $x = 40\text{--}70\text{ at\%}$. The most stable amorphous alloy was $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{40}(\text{Ni}_{50}\text{Cu}_{50})_{50}\text{Al}_{10}$ with a crystallization temperature of $T_x = 818\text{ K}$. However the amorphous alloy with the largest supercooled liquid region was $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{60}(\text{Ni}_{50}\text{Cu}_{50})_{20}\text{Al}_{20}$ with a crystallization-glass transition temperature difference of $T_x - T_g = 124\text{ K}$.

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1. Introduction

The conventional strategy for developing metallurgical alloys is to select a main component based on a primary property requirement. Small amounts of alloying additions are then added in order to improve the primary and secondary material properties. This strategy has led to many multi-component alloy systems based on a single main component, with a variety of different alloying additions.

One effect of the conventional strategy for developing metallurgical alloys is that considerable knowledge is accumulated about multicomponent alloys based on one or, sometimes, two main components, but there is very little or no knowledge about alloys containing several main components in approximately equal atomic portions. Information and understanding is highly developed about alloys close to the apexes and edges of the phase diagram, with much less known about alloys in the centre of the phase diagram. This imbalance becomes much more pronounced as the number of components increases and it is therefore clear that conventional alloy development samples only a small fraction of the full range of alloying possibilities.

One method of exploring the wide range of unknown multicomponent alloys is to use equiatomic substitution,¹⁾ i.e. to start from an alloy of interest and then to substitute individual alloy components with multicomponent equiatomic or near-equiatomic mixtures of chemically similar species. Recently many multicomponent metallic glass alloys have been developed successfully by equiatomic substitution.^{2,3)} The purpose of this paper is to describe the formation of metallic glasses in $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ multicomponent alloys developed by equiatomic substitution, based on well-known Zr-based bulk amorphous alloys.^{4,5)}

2. Experimental

Master alloys of composition $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ with late transition metal content

$x = 10\text{--}70\text{ at\%}$ and Al content $y = 10\text{--}30\text{ at\%}$ were prepared by vacuum arc melting with high purity elements (Ti: 99.7%, Zr: 99.5%, Hf, Cu and Al: 99.9% and Ni: 99.95%). Each master alloy was re-melted at least four times to improve chemical homogeneity. Melt-spun ribbons were produced by induction melting 3 g specimens of each alloy in a quartz crucible under Ar, followed by ejection with an Ar overpressure of about $4 \times 10^3\text{ Pa}$ onto a Cu wheel rotating with a surface speed of 40 m/s in an enclosed chamber with an atmosphere of $2 \times 10^4\text{ Pa}$ He. The as-melt-spun ribbons were typically 3–5 mm wide and 20–40 μm thick. Phase identification on as-quenched and heat treated ribbons was performed in a Philips PW 1729 X-ray diffractometer (XRD) using Cu K α radiation scanning from $2\theta = 20\text{--}80^\circ$. Thermal stability was investigated using a TA Instruments 2200 thermal analyser fitted with 2010 differential scanning calorimeter (DSC) by sealing 20 mg specimens of each alloy in Cu pans under high purity Ar and then heating at 20 K/min up to 920 K.

3. Results and Discussion

Figure 1(a) shows XRD traces from as-quenched ribbons of the multicomponent alloys $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ with $x = 20\text{--}70\text{ at\%}$ and a low Al content of $y = 10\text{ at\%}$. These traces all exhibit a broad diffraction peak from $2\theta \sim 35\text{--}45^\circ$ indicating the formation of an amorphous phase over a wide late transition metal composition range of $x = 20\text{--}70\text{ at\%}$. Figure 1(b) shows XRD traces from as-quenched ribbons of the multicomponent alloys with $x = 10\text{--}50\text{ at\%}$ and a higher Al content of $y = 20\text{ at\%}$. These traces again exhibit a broad diffraction peak indicating the formation of an amorphous phase, but over a narrower late transition metal composition range of $x = 10\text{--}40\text{ at\%}$. The XRD trace for $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{30}(\text{Ni}_{50}\text{Cu}_{50})_{50}\text{Al}_{20}$ i.e. $x = 50\text{ at\%}$ and $y = 20\text{ at\%}$ shows the presence of a bcc crystalline phase. Figure 1(c) shows XRD traces from as-quenched ribbons of the multicomponent alloys with $x = 10\text{--}50\text{ at\%}$ and an even higher Al content of

Fig. 1 XRD traces from $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ multicomponent alloys with (a) $x = 20\text{--}70\text{ at\%}$ and $y = 10\text{ at\%}$, (b) $x = 10\text{--}50\text{ at\%}$ and $y = 20\text{ at\%}$, and (c) $x = 10\text{--}50\text{ at\%}$ and $y = 30\text{ at\%}$.

$y = 30\text{ at\%}$. These traces again exhibit a broad diffraction peak indicating the formation of an amorphous phase, but over an even narrower late transition metal composition range of $x = 10\text{--}20\text{ at\%}$. The XRD traces for $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{30}(\text{Ni}_{50}\text{Cu}_{50})_{40}\text{Al}_{30}$ and $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{20}(\text{Ni}_{50}\text{Cu}_{50})_{50}\text{Al}_{30}$ *i.e.* $x = 40\text{--}50\text{ at\%}$ and $y = 30\text{ at\%}$ are similar to the bcc crystalline phase formed in $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{30}(\text{Ni}_{50}\text{Cu}_{50})_{50}\text{Al}_{20}$, however the XRD trace for $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{40}(\text{Ni}_{50}\text{Cu}_{50})_{30}\text{Al}_{30}$ *i.e.* $x = 30\text{ at\%}$ and $y = 30\text{ at\%}$ is different and the peaks can be indexed as corresponding to a Laves phase. Comparing Figs. 1(a)–(c) shows that increasing the Al content from 10 to 20 and then 30 at% progressively narrows the composition range for glass formation. Equilibrium phase diagrams⁶ show that low

levels of Al dissolve into solid and liquid Ti, Zr, Hf, Ni and Cu, reducing the melting point and increasing the stability of the liquid. However, high levels lead to the formation of intermetallic compounds TiAl , Zr_3Al , Hf_3Al , Ni_3Al and Cu_3Al , increasing the melting point and decreasing the stability of the liquid. This indicates why the glass forming ability of $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ alloys is sensitive to Al.

Figure 2(a) shows DSC traces from as-quenched ribbons of the multicomponent alloys $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ alloys with $x = 20\text{--}70\text{ at\%}$ and a low Al content of $y = 10\text{ at\%}$. There are several exothermic crystallization reactions over the composition range $x = 20\text{--}40\text{ at\%}$ *i.e.* for early transition metal rich alloys, with the onset temperatures of the first and second exothermic peak both increasing with increasing late transition metal content x . In comparison, there is a single sharp exothermic crystallization reaction for the composition range $x = 50\text{--}70\text{ at\%}$, *i.e.* for late transition metal rich alloys, with the onset temperature decreasing with increasing late transition metal content x . Figure 2(b) shows DSC traces from as-quenched ribbons of the multicomponent alloys with $x = 10\text{--}50\text{ at\%}$ and a higher

Fig. 2 DSC traces from $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ multicomponent alloys with (a) $x = 20\text{--}70\text{ at\%}$ and $y = 10\text{ at\%}$, and (b) $x = 10\text{--}50\text{ at\%}$ and $y = 20\text{ at\%}$.

Fig. 3 Supercooled liquid region $\Delta T = T_x - T_g$ where T_x = crystallisation onset temperature and T_g = glass transition temperature versus late transition metal content x at% for the amorphous phase in $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ multicomponent alloys. (solid squares: $y = 10$ at%, and solid circles: $y = 20$ at%)

Al content of $y = 20$ at%. Once again there are several exothermic crystallization reactions for the composition range $x = 10$ – 40 at%, *i.e.* for early transition metal rich alloys, with the onset temperatures of the first and second exothermic peaks again both increasing with increasing late transition metal content x . The alloy with the highest late transition metal content, $x = 50$ at% and $y = 20$ at% is only partially amorphous in the as-quenched state, as shown in Fig. 1(b), but again crystallizes with a single, sharp exothermic crystallization reaction.

Figure 3 shows the variation of supercooled liquid region ($\Delta T = T_x - T_g$ where T_x = crystallization onset temperature and T_g = glass transition temperature) versus alloy composition. Alloys with compositions in the range $x = 20$ – 60 at% and with a low Al content of $y = 10$ at% show an approximately constant supercooled liquid region in the range 50 to 70 K. In comparison, alloys with compositions in the range $x = 10$ – 40 at% and with a higher Al content of $y = 20$ at% show a supercooled liquid region which is much more variable and sensitive to composition. The largest supercooled liquid region $\Delta T = 124$ K is shown by the alloy $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{60}(\text{Ni}_{50}\text{Cu}_{50})_{20}\text{Al}_{20}$ *i.e.* with $x = 20$ at% and $y = 20$ at%. This strong variation in ΔT around the alloy with composition $x = 20$ at% and $y = 20$ at% appears to be associated with the competition between different phases such as MgZn_2 type phase with hexagonal structure, Zr_2Cu type phase with tetragonal structure and Ti_2Ni type phase with cubic structure observed after high temperature heat treatment, which is reported in more detail elsewhere.^{7,8)} It is notable that the relationship between alloy composition and ΔT in previous researches^{9–11)} varies more less strongly than reported here.

Figure 4 shows a pseudo-ternary phase diagram for all the as-quenched $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ multicomponent alloys studied. Open, closed and shaded circles indicate crystalline, amorphous and partially amorphous alloy compositions respectively. The phase diagram shows clearly how the glass forming ability decreases with increasing Al content. It also shows that early transition metal, $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})$ -rich alloys have a better glass-forming ability than late transition metal $(\text{Ni}_{50}\text{Cu}_{50})$ -rich alloys.

Fig. 4 Pseudo-ternary phase diagram showing as-quenched amorphous alloy region in $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ multicomponent alloys with $x = 20$ – 70 at% and $y = 10$ – 30 at%; Open, closed and shaded circles indicate crystalline, amorphous and partially amorphous alloy compositions respectively.

4. Conclusion

New multicomponent $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{100-x-y}(\text{Ni}_{50}\text{Cu}_{50})_x\text{Al}_y$ alloys can be developed by the equiatomic substitution technique. The most stable amorphous alloy in this series of alloys is $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{40}(\text{Ni}_{50}\text{Cu}_{50})_{50}\text{Al}_{10}$ with a crystallization temperature of $T_x = 818$ K. The amorphous alloys all have a supercooled liquid region $\Delta T > 40$ K ($\Delta T = T_x - T_g$ where T_x = crystallization onset temperature and T_g = glass transition temperature), and the alloy with the largest supercooled liquid region is $(\text{Ti}_{33}\text{Zr}_{33}\text{Hf}_{33})_{60}(\text{Ni}_{50}\text{Cu}_{50})_{20}\text{Al}_{20}$ with $\Delta T = 124$ K.

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