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The glass forming ability of Cu-rich Cu–Hf binary alloys

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Abstract
We studied the glass forming ability (GFA) of Cu-rich Cu–Hf binary alloys and found that some of the alloys can be prepared as bulk metallic glasses with maximum diameter up to 2 mm by a conventional Cu-mould casting. The best glass former within the compositional range studied is off-eutectic $Cu_{65}Hf_{35}$ alloy, which is markedly different from the prediction from the multicomponent and deep eutectic rules. The GFA, thermal stability, kinetics of the glass transition and crystallization for $Cu_{65}Hf_{35}$ glassy rods were studied. The glass formation mechanism for binary Cu–Hf alloys was investigated from the thermodynamic point of view. It is suggested that the better GFA of off-eutectic $Cu_{65}Hf_{35}$ alloy could be due to its higher value of the parameter γ^*, which is defined as the ratio between the driving force for glass formation and the resistance of glass formation to crystallization.

In recent years, bulk metallic glasses (BMGs) with excellent glass forming ability (GFA) have been developed in many multicomponent alloy systems. As a prominent class of functional and structural materials with unique properties, they have attracted intense interest due to their considerable significance in science and technology [1–9]. To make the best use of these non-crystalline materials, the key problem is to develop BMGs with improved properties and extremely high GFA. Hence, a great deal of effort has been devoted to investigation of the glass forming ability of the alloys [6–9]. It is commonly thought that the formation of metallic glasses is controlled by two factors, i.e., the cooling rate and the composition of the alloys. However, the critical cooling rate, which is the most effective gauge for the GFA of the alloys, is hard to measure experimentally. Therefore, empirical rules for the prediction of element selection and compositional range of glass forming alloys were framed by Johnson [2] and Inoue *et al* [3],

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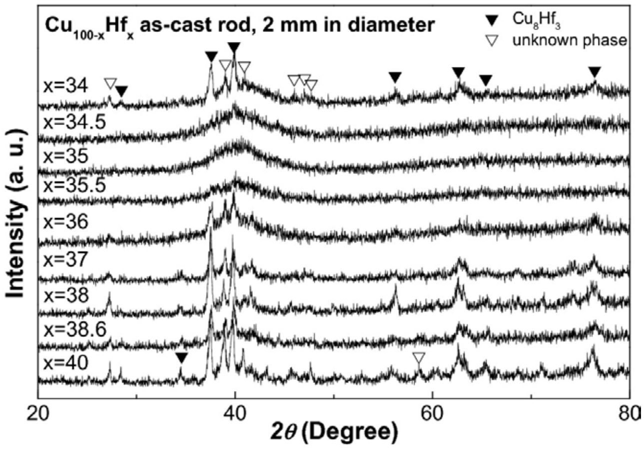

Figure 1. XRD patterns of as-cast $Cu_{100-x}Hf_x$ (x = 34, 34.5, 35, 35.5, 36, 37, 38, 38.6 and 40) rods with the diameter of 2 mm.

as follows: (1) multicomponent alloys with three or more elements; (2) more than 12% atomic radius difference between elements; (3) negative heat of mixing between main elements; (4) the deep eutectic rule resulting from the reduced glass transition criterion. These rules have played an important role as guidelines for the synthesis of BMGs for the last decade.

Binary alloys are usually considered to have lower GFA accordingly due to their lacking complicated structure within the atomic configuration according to the 'confusion principle' [1, 4]. However, recent experimental results have shown that binary Zr–Cu and Ni–Nb alloys can also be vitrified into BMGs [10–13]. And in contradiction to the deep eutectic rule, the better glass formers in Zr–Cu and Ni–Nb binary alloy systems such as $Zr_{35.5}Cu_{64.5}$ [11], $Zr_{50}Cu_{50}$ [12] and $Ni_{62}Nb_{38}$ [13] are off-eutectic. Therefore, the empirical rules for glass formation, that is, multicomponent alloys with composition near the deep eutectic, could be no longer the major concern for designing BMGs.

In this work, we reported that some of the Cu–Hf binary alloys can be prepared as fully glassy rods up to 2 mm in diameter by a conventional Cu-mould casting method. The best glass former within the compositional range studied is off-eutectic $Cu_{65}Hf_{35}$ alloy, which is different from the prediction from the multicomponent and deep eutectic rules. The glass formation mechanism of the binary alloys was studied from the thermodynamic point of view on the basis of Miedema's calculation model.

Ingots of Cu–Hf binary alloys with different compositions were prepared separately by arc melting of 99.9% (at.%) pure Cu and Hf in a titanium-gettered argon atmosphere. The rods, 2 mm in diameter, were prepared by suction casting under an argon atmosphere. The structure of the samples was characterized by means of XRD using a Rigaku D\ max -2550 diffractometer using Cu Kα radiation. DSC measurements were carried out under a purified argon atmosphere in a Perkin-Elmer DSC-7 at heating rates ranging from 5 to 80 K min^{-1}. The calorimeter was calibrated for temperature and energy at various heating rates with high purity indium and zinc. In order to obtain the melting and liquidus temperatures of the alloys, a high temperature DSC curve was measured under an argon atmosphere in a TA INSTRUMENT SDT-Q600 DSC at a heating rate of 20 K min^{-1}.

Figure 1 shows the XRD patterns of as-cast $Cu_{100-x}Hf_x$ (x = 40, 38.6, 38, 37, 36, 35.5, 35, 34.5 and 34) rods. Crystalline Bragg peaks existed in the patterns for the rods of $Cu_{61.4}Hf_{38.6}$ (eutectic), $Cu_{60}Hf_{40}$, $Cu_{62}Hf_{38}$, $Cu_{63}Hf_{37}$, $Cu_{64}Hf_{36}$ and $Cu_{66}Hf_{34}$, as marked in

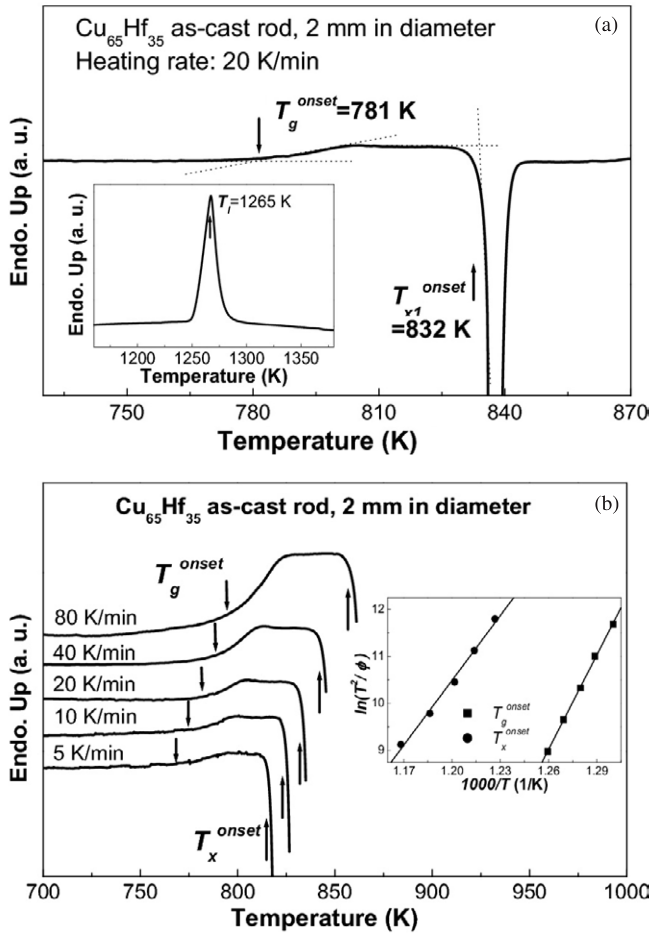

Figure 2. (a) DSC traces of $Cu_{65}Hf_{35}$ as-cast rod for a heating rate of 20 K min^{-1}. The inset shows the HTDSC curve indicating the melting process of $Cu_{65}Hf_{35}$ alloy, and (b) DSC traces of $Cu_{65}Hf_{35}$ BMG for the heating rates of 5, 10, 20, 40 and 80 K min^{-1}. The inset shows the Kissinger plots and their linear fittings for the onset temperatures of the glass transition and primary crystallization.

figure 1, implying lower glass forming ability of the alloys. In contrast, the broadened XRD patterns of off-eutectic $Cu_{64.5}Hf_{35.5}$, $Cu_{65}Hf_{35}$ and $Cu_{65.5}Hf_{34.5}$ samples suggest amorphous nature. But by careful examination, we see that there still exist some small crystalline peaks at about $2\theta = 37.6°$ and $2\theta = 40°$ in the XRD patterns of $Cu_{64.5}Hf_{35.5}$ and $Cu_{65.5}Hf_{34.5}$ samples. Only the $Cu_{65}Hf_{35}$ as-cast rod exhibits the typical broad diffraction maxima of amorphous structure and no obvious crystalline peaks can be found within the XRD resolution limits. Therefore, the $Cu_{65}Hf_{35}$ as-cast rod is fully amorphous. We have studied the GFA of Cu–Hf binary alloys over the whole compositional range and found that $Cu_{65}Hf_{35}$ alloy should be the best glass former.

Figure 2(a) shows the DSC trace of $Cu_{65}Hf_{35}$ rods at a heating rate of 20 K min^{-1}. A marked endothermic behaviour before crystallization demonstrates a distinct glass transition with the onset temperature (T_g^{onset}) at about 781 K. The sharp exothermic reaction occurs following the glass transition associated with the transformations from the supercooled liquid

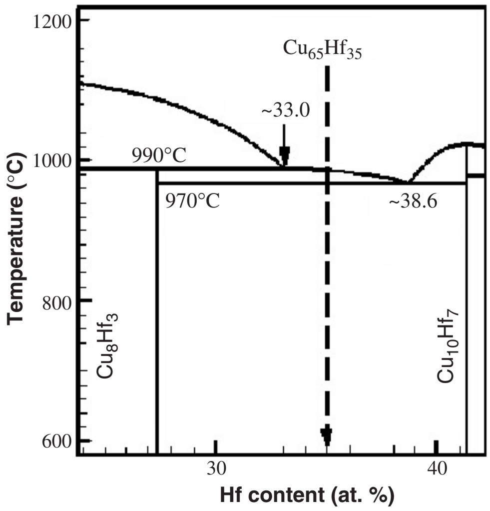

Figure 3. Part of the Cu–Hf phase diagram [16]. The best glass former found in this work is marked.

state to the equilibrium crystalline intermetallic phases. The onset temperature for the crystallization (T_{x1}^{onset}) is about 832 K. The melting process of $Cu_{65}Hf_{35}$ alloy is shown in the inset of figure 2(a) and the peak temperature obtained from the high temperature DSC curve is about 1265 K. The peak temperature could be regarded as the liquidus temperature (T_l) and its value is roughly in accordance with the value of T_l obtained from the Cu–Hf binary phase diagram [14]. Therefore, the reduced glass transition temperature T_{rg} $(=T_g/T_l)$, the supercooled liquid region ΔT_x $(=T_{x1} - T_g)$ and the parameter γ $(=\frac{T_{x1}}{T_g+T_l})$, which are usually employed to reflect the GFA of the alloys [3, 7–9], are about 0.62, 51 K and 0.407. They all indicate a better GFA of $Cu_{65}Hf_{35}$ alloy.

In order to investigate the glass transition and crystallization behaviours as well as the thermal stability of $Cu_{65}Hf_{35}$ BMG in more detail, DSC measurements were carried out at the heating rates (ϕ) of 5, 10, 20, 40 and 80 K min^{-1}, as shown in figure 2(b). The inset of figure 2(b) shows Kissinger's linear relationship between $\ln(T^2/\phi)$ and $1/T$ for the onset temperatures of the glass transition and crystallization [15, 16]. Thus the effective activation energy for glass transition (E_g) and crystallizations (E_x) of $Cu_{65}Hf_{35}$ as-cast rod can be obtained from Kissinger equations as about 5.77 and 3.96 eV respectively. The high value of E_g, which is similar to that of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG, suggests high thermal stability of $Cu_{65}Hf_{35}$ as well as the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ amorphous alloys [16].

The better GFA of off-eutectic alloys has evoked tremendous interest recently. A phase selection diagram is proposed for explaining the phenomena and it is suggested that the better glass former could be on the side with the steeper liquidus slope [11]. However, the analysis can only provide a direction for good glass formers, rather than a specific alloy composition. Furthermore, the better glass former among Cu–Hf binary alloys, i.e. $Cu_{65}Hf_{35}$, is on the side with the smoother liquidus slope [14], as shown clearly in figure 3.

Thermodynamic analysis could be useful in evaluating the composition of the good glass former in more detail. Previous work mostly focuses on the mixing enthalpy (ΔH) and mismatch entropy (S_σ) of metallic glasses [17, 18]. However, because glass formation is always a process of competition between supercooled liquid and the resulting crystalline phase, the

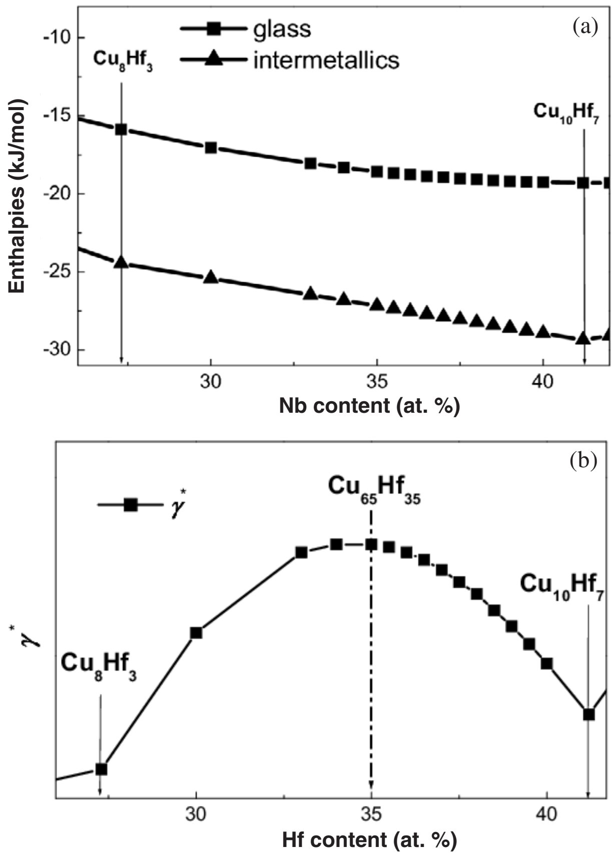

Figure 4. (a) Calculated formation enthalpies for metallic glasses and intermetallic compounds of Cu–Hf binary alloys with the composition ranging from Cu_8Hf_3 to $Cu_{10}Hf_7$. (b) The dependence of parameter γ^* on the Hf concentration in Cu–Hf binary alloys.

influence of the formation enthalpy of crystalline phases on the synthesis of metallic glasses should not be neglected. Lu and Liu have demonstrated that the GFA of the alloys depends not only on the liquidus and glass transition temperature, but also on the stability of the competing crystalline phases [7, 8]. Therefore, consideration of the formation of crystalline phases, as well as that of the amorphous phase, could be very important for evaluating the glass formation ability of the alloys. More recently, we have defined a new parameter, γ^*, for approaching the GFA of the alloys thermodynamically [13]. Since the contribution from entropies is much smaller as compared with that from the formation enthalpy of solid compounds (lower than 5% according to Inoue's criteria) [17–19], we can neglect the entropy contribution and express the new parameter for glass formation, γ^*, in terms of formation enthalpies alone:

$$\gamma^* = \frac{-\Delta H^{\mathrm{amor}}}{\Delta H^{\mathrm{amor}} - \Delta H^{\mathrm{inter}}}$$

where ΔH^{amor} and $\Delta H^{\mathrm{inter}}$ are the formation enthalpies of glasses and intermetallic compounds respectively. $-\Delta H^{\mathrm{amor}}$ could be considered as the driving force for glass formation, while the difference between the driving force for glass and the intermetallic compound ($\Delta H^{\mathrm{amor}} - \Delta H^{\mathrm{inter}}$) represents the resistance for glass formation to crystallization. ΔH^{amor} and $\Delta H^{\mathrm{inter}}$ for

Cu–Hf binary alloys with the composition ranging from Cu_8Hf_3 to $Cu_{10}Hf_7$ are calculated using Miedema's model [20–22], as shown in figure 4(a). The values of the parameter γ^* for Cu–Hf binary alloys within the compositional range are shown in figure 4(b). As a thermodynamic factor concerning the effect of both driving force and resistance, synthetically, on the GFA of the alloys, parameter γ^* indicates that alloys with composition from $Cu_{64}Hf_{36}$ to $Cu_{65}Hf_{35}$ could be the better glass formers. The modelling result is roughly in accordance with the experimental data in the present work. Actually, we have successfully predicted the better glass formers in Cu–Zr and Ni–Nb [13] binary alloys according to parameter γ^*. It should be noted that the formation of metastable intermediate phase could dramatically influence the calculated results and the GFA of the alloys. Fortunately, no intermediate phases have been found according to our XRD and DSC results. Therefore, parameter γ^* could be used as a useful guideline to identify the best glass former among Cu–Hf, Cu–Zr and Ni–Nb or even other binary alloys.

Acknowledgments

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