Formation of Metastable Phases and Their Effect on the Glass-Forming Ability of Cu-Hf Binary Alloys

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In this work, the glass-forming ability (GFA) of Cu-Hf binary alloys was systematically studied and some metastable phases were observed in the rapidly quenched samples. The microstructure of a Cu₅₀Hf₅₀ as-cast rod between the surface and the central region was carefully examined, and the composition of the unknown metastable phase was identified to be about Cu₅₀Hf₅₀. The formation mechanism of metastable phases and their effect on the GFA of Cu-Hf binary alloys was also investigated. Taking the metastable phases into account, the parameter γ* was revised, and its prediction of the GFA of Cu-Hf binary alloys was found to be roughly in accordance with the experimental results.

Keywords: bulk metallic glass, metastable phase, thermodynamic modeling

1. Introduction

In recent years, bulk metallic glasses (BMGs) with excellent glass-forming ability (GFA) have been developed in many multi-component alloy systems. These materials exhibit distinct properties, such as a high strength and excellent corrosion resistance.⁸⁻¹⁰ To make the best use of these non-crystalline materials, it is important to develop BMGs with an excellent GFA, and thus a great deal of effort has been made to investigate the GFA of the alloys.⁶⁻⁹

It is commonly held that the formation of metallic glasses is controlled by two factors, the cooling rate and the composition of the alloys. Although it is the most effective gauge of the GFA of alloys, the critical cooling rate has seldom been measured experimentally. However, many empirical rules have been proposed to predict the element selection and compositional range of glass-forming alloys. Of these, the empirical rules framed by Johnson² and Inoue et al.³ have played an important role in guiding the synthesis of multi-component BMGs in the past decade, but they appear not to be valid for designing binary BMGs.¹⁰⁻¹⁵

Recently, we intensively studied the GFA of several binary alloy systems, and proposed a new parameter γ* (γ* = ΔH₂max-ΔH₂amor, where ΔH₂amor is the forming enthalpy of the metallic glasses, ΔH₂inter is the forming enthalpy of their intermetallic counterparts) for the evaluation of the relationship between the alloy composition and the GFA of binary alloys.¹³⁻¹⁵ The parameter has proved useful in predicting the better glass former of several binary alloy systems.¹³⁻¹⁶

However, the formation of intermediate metastable phases may dramatically influence the value of parameter γ* and the apparent GFA of alloys.¹³⁻¹⁵ Previous experimental results have shown that the intermediate metastable phases are easily precipitated from the supercooled liquid of glass-forming alloys upon rapid quenching, especially when the cooling rate is slightly lower than the critical cooling rate.¹⁷⁻²⁰ In this work, the formation mechanism of metastable phases and their effect on the glass-forming ability of Cu-Hf binary alloys is investigated. Taking the metastable phases into account, the parameter γ* is then revised to better predict the glass-forming ability of the alloys.

2. Experiments

Ingots of Cu-Hf binary alloys with different compositions were prepared separately by the arc melting of 99.9% (at%) pure Cu and Hf in an titanium-gettered argon atmosphere. Rods of 2 mm in diameter were prepared by suction casting under an argon atmosphere. The structure of the samples was characterized by XRD on a Rigaku D/ max-2550 diffractometer using Cu Kα radiation. The microstructure of a Cu₅₀Hf₅₀ as-cast rod was investigated carefully with a JEOL JSM-6700 F scanning electron microscope (SEM). The composition of the crystalline phases was detected with an Oxford INCA energy dispersive spectrometer (EDS). The formation enthalpy of the metallic glasses and their intermetallic counterparts including the intermediate metastable phases was calculated using Miedema’s model²¹⁻²³ as follows:

\[
\Delta H^{\text{amor}} = \Delta H^{\text{chem}}(\text{amor.}) + \Delta H^{\text{topo.}},
\]

\[
\Delta H^{\text{inter}} = \Delta H^{\text{chem}}(\text{inter.})
\]

where \(\Delta H^{\text{chem}}(\text{amor.})\) is the chemical mixing enthalpy of the amorphous state (glass), \(\Delta H^{\text{topo.}}\) the topology enthalpy of a glass, and \(\Delta H^{\text{chem}}(\text{inter.})\) the chemical mixing enthalpy of an intermetallic compound. The formation enthalpy, \(\Delta H^{\text{inter.}}\), of a composition between two adjacent intermetallic compounds can be calculated using the level principle.

3. Results and Discussion

By calculating the formation enthalpies of metallic glasses (\(\Delta H^{\text{amor.}}\)), solid solutions (\(\Delta H^{\text{SS.}}\)), and stable intermetallic compounds (\(\Delta H^{\text{inter.}}\)) within the whole compositional range according to the equilibrium Cu-Hf binary phase diagram,²⁴...
the \( \gamma^* \) values were obtained from \( \text{Hf}_{22}\text{Cu}_{78} \) to \( \text{Hf}_{62}\text{Cu}_{38} \) based on the criterion \( \Delta H_{\text{amor.}} < \Delta H_{8.5}^{25,26} \) as shown in Fig. 1. The figure predicts that \( \text{Cu}_{50}\text{Hf}_{50} \) is the best glass former. However, according to our recent preliminary experimental results the critical diameter of the \( \text{Cu}_{50}\text{Hf}_{50} \) binary alloy is less than 1 mm, and the best glass former from \( \text{Cu}_{10}\text{Hf}_{7} \) to \( \text{CuHf}_{2} \) is \( \text{Cu}_{55}\text{Hf}_{45} \), which has a critical diameter of about 1.5 mm.\(^{27}\) This illustrates that the parameter \( \gamma^* \) is not so accurate for evaluating the GFA of Cu-Hf binary alloys.

It is noted that, similar to the situation with Nd-Fe binary alloys,\(^{28}\) the compositional difference between the two stable crystalline phases of the \( \text{Cu}_{50}\text{Hf}_{50} \) binary alloy is sufficiently large for the formation of metastable phases upon rapid quenching. According to the findings on Nd-based glass forming alloys, the formation of metastable phases may dramatically influence the apparent GFA of alloys.\(^ {19,20}\) It is therefore essential to examine the metastable phases of Cu-Hf binary alloys and to revise the parameter \( \gamma^* \) by taking their metastable phases into account.

The microstructure of \( \text{Cu}_{100-x}\text{Hf}_{x} \) \( (x = 50, 37, 35 \text{ and } 34) \) as-cast rods with a diameter of 2 mm as determined by XRD is shown in Fig. 2. The \( \text{Cu}_{62}\text{Hf}_{38} \) as-cast rod exhibits typical broad diffraction maxima of an amorphous structure. The crystalline Bragg peaks in the patterns for the rods of \( \text{Cu}_{50}\text{Hf}_{50}, \text{Cu}_{63}\text{Hf}_{37}, \text{and} \text{Cu}_{66}\text{Hf}_{34}, \) as marked in Fig. 1, illustrate the inferior GFA of these alloys. By careful examination, three kinds of phases in the \( \text{Cu}_{50}\text{Hf}_{50} \) as-cast rod can be found in the XRD patterns shown in Fig. 2. The phase marked \( \nabla \) in the XRD pattern of the \( \text{Cu}_{50}\text{Hf}_{55} \) as-cast rod also appears in the XRD patterns of \( \text{Cu}_{61.4}\text{Hf}_{38.6}, \text{Cu}_{60}\text{Hf}_{40}, \text{Cu}_{62}\text{Hf}_{38}, \text{and} \text{Cu}_{63}\text{Hf}_{37}, \) and is likely to be an \( \text{Cu}_{10}\text{Hf}_{7} \) intermetallic compound.\(^ {15}\) The Bragg peaks in the \( \text{CuHf}_{2} \) phase are marked \( \triangledown \) in Fig. 2. The remaining Bragg peaks, marked \( \blacklozenge \), suggest that there may be some unknown metastable phases in the \( \text{Cu}_{50}\text{Hf}_{50} \) as-cast rod.

Figure 3 shows the morphology of the cross-section of the \( \text{Cu}_{50}\text{Hf}_{50} \) as-cast rod and the back-scattered electron images of the surface area (b), Area I (c), Area II (d), and Area III (e).
average composition of the bright phase in Area II, which is about Cu_{42}Hf_{58}, is different from that of any of the equilibrium phases in the Cu-Hf binary alloy system. This indicates that metastable phases do exist in rapidly quenched Cu_{50}Hf_{50} alloys.

To understand the formation mechanism of the metastable phases, the nucleation and growth theory according to the Cu-Hf equilibrium phase diagram is applied in the analysis. The stable intermetallic phases, CuHf and CuHf_{2}, crystallize from the Cu_{50}Hf_{50} melt under an equilibrium state. However, as the equilibrium crystallization of the melt requires chemical redistribution and diffusion over a longer distance between the two stable intermetallic phases, the formation of equilibrium phases of the Cu_{50}Hf_{50} alloy will be suppressed at high cooling rates due to the large compositional difference of the two equilibrium intermetallic phases, which can be as high as 25 at%. Furthermore, the metastable phases will be formed within the composition ranging from the Cu_{50}Hf_{50} melt to the CuHf_{2} intermetallic compounds, not only because CuHf_{2} is the primary crystallization phase according to the equilibrium phase diagram, but also because of the much larger compositional difference between the melt and CuHf_{2} than the difference between the melt and Cu_{10}Hf_{2}. As a result, a metastable phase with a composition around Cu_{42}Hf_{58} was observed in the rapidly quenched Cu_{50}Hf_{50} binary alloy.

Taking the metastable Cu_{42}Hf_{58} phase into account, the formation enthalpies of the intermetallic compounds ($\Delta H_{\text{inter}}$) of the Cu-Hf binary alloys were re-calculated to investigate the influence of the metastable phases on the GFA of the alloys. Figure 4 shows the glass forming enthalpies ($\Delta H_{\text{amor}}$), revised $\Delta H_{\text{amor}}$, and $\gamma^*$ of the Cu-Hf binary alloy system. The formation enthalpies of the stable intermetallics in the Cu-Hf binary alloys were also studied experimentally by Kleppa and Watanabe. Their results show some slight differences from those calculated by the Miedema’s method. It is considered that the differences are due to the non-uniform composition, the presence of few metal oxides at high temperatures, or the existence of the short range orders in the alloys. As a semi-empirical theory, the Miedema’s method is, however, still very useful in most cases. Figure 4 illustrates that the best glass former in the whole compositional range of the Cu-Hf binary alloys is about Cu_{65}Hf_{35}, although Cu_{55}Hf_{40} is also a good candidate. This result is roughly in accordance with the critical diameters of Cu_{65}Hf_{35} (about 2 mm) and Cu_{55}Hf_{40} (about 1.5 mm). It is concluded that if the effect of metastable phases is taken into consideration, then parameter $\gamma^*$ is still a useful guideline to identify the best glass former of binary alloys.

4. Conclusion

The formation of metastable phases and their effect on the GFA of the Cu-Hf binary alloy system were studied. Some unknown metastable phases were observed in the rapidly quenched Cu_{50}Hf_{50} sample, and the rough composition of the metastable phase was detected to be about Cu_{42}Hf_{58}. The formation of the metastable phase is held to be due to the large compositional difference between the two equilibrium crystalline phases and the suppression of atomic activation energy at high cooling rates. By calculating the formation enthalpy of the metastable phases, the parameter $\gamma^*$ of the Cu-Hf binary alloys has been revised. The results obtained with the revised parameter are roughly in accordance with the experimental results.

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