Binary Ni–Nb bulk metallic glasses

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We studied the glass forming ability of Ni–Nb binary alloys and found that some of the alloys can be prepared into bulk metallic glasses by a conventional Cu-mold casting. The best glass former within the compositional range studied is off-eutectic $Ni_{62}Nb_{38}$ alloy, which is markedly different from those predicted by the multicomponent and deep eutectic rules. The glass formation mechanism for binary Ni–Nb alloys was studied from the thermodynamic point of view and a parameter γ^* was proposed to approach the ability of glass formation against crystallization. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2158130]

Bulk metallic glasses (BMGs) as a prominent class of functional and structural materials with unique properties have attracted intensive interests due to their considerable significance in science and technology.[1–11] In order to make the best use of these noncrystalline materials, the key problem is to develop BMGs with improved properties and excellent glass forming ability (GFA). It is commonly regarded that the formation of metallic glasses is controlled by two factors, i.e., the cooling rate and the composition of the alloys. The critical cooling rate, which is the most effective gauge for GFA of the alloys, is hard to be measured experimentally. Hence, a great deal of efforts have devoted to the investigation on the composition of glass forming alloys. Inoue *et al.*[11] and Johnson[1] framed the empirical rules to predict the element selection and compositional range of glass forming alloys. These rules have played an important role as a guideline for synthesis of BMGs for the last decade.

Binary alloys are usually considered to have a lower GFA due to their lack of complicated structure with atomic configuration according to the "confuse principal."[2,3] However, recent experimental results have shown that binary Zr–Cu alloys can also be vitrified into BMGs.[12–14] In contrast with the deep eutectic rule, the better glass formers in Zr–Cu binary alloy system such as $Zr_{35.5}Cu_{64.5}$ and $Zr_{50}Cu_{50}$ are off eutectic. Therefore, the empirical rules for glass formation, that is, multicomponent alloys with composition near deep eutectic, could be no longer the major concern for designing BMGs.

In this work, we reported that some of the Ni–Nb binary alloys can be prepared into fully glassy rods up to 2 mm in diameter by a conventional Cu-mold casting method. The best glass former within the compositional range studied is off-eutectic $Ni_{62}Nb_{38}$ alloy, which is different from those predicted by the multicomponent and deep eutectic rules. The glass formation mechanism of the binary alloys was studied from the thermodynamic point of view based on Miedema's calculation model.

Ingots of Ni–Nb binary alloys with different compositions were prepared separately by arc-melting of 99.9% (at. %) pure Ni and Nb in titanium-gettered argon atmosphere. The rods of 2 mm in diameter were prepared by suction casting under argon atmosphere. The structure of the samples was characterized by x-ray diffraction (XRD) on a Philips diffractometer using Cu K_α radiation. The microstructure of the as-cast rod was observed on a JEOL JEM-2010 F high-resolution electron microscope (HREM). The specimen for HREM observation was prepared under pure argon atmosphere on a GATAN 691 precision ion polishing system. High-temperature differential scanning calorimetry (HTDSC) curve was carried out under a purified argon atmosphere in a TA INSTRUMENT SDT-Q600 DSC at a heating rate of 20 K/min.

Figure 1 shows the XRD patterns of as-cast Ni_xNb_{100-x} (x=59.5, 60.5, 61, 61.5, 62, and 62.5) rods. It is noted that the crystalline Bragg peaks existed in the patterns for the rods of eutectic $Ni_{59.5}Nb_{40.5}$ and near-eutectic $Ni_{60.5}Nb_{39.5}$ and $Ni_{61}Nb_{39}$, implying the lower glass forming ability of the alloys. In contrast, the broadened XRD patterns of off-eutectic $Ni_{61.5}Nb_{38.5}$, $Ni_{62}Nb_{38}$, and $Ni_{62.5}Nb_{37.5}$ samples could suggest their amorphous nature. But by a careful examination, there still exist some small crystalline peaks in the XRD patterns of $Ni_{61.5}Nb_{38.5}$ and $Ni_{62.5}Nb_{37.5}$ samples. Only the $Ni_{62}Nb_{38}$ as-cast rod exhibits typical broad diffrac-

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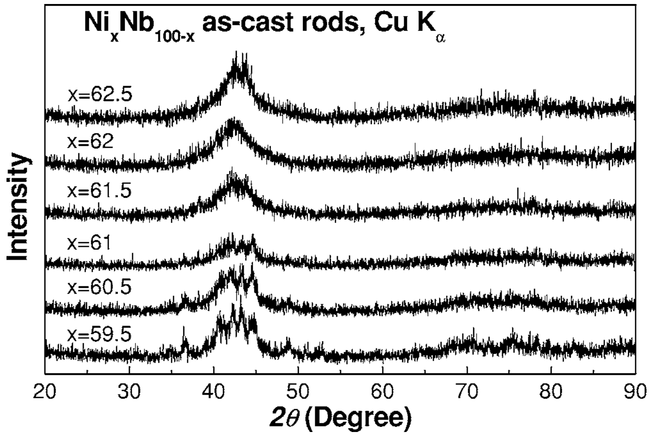

FIG. 1. XRD patterns of as-cast Ni_xNb_{100-x} (x=59.5, 60.5, 61, 61.5, 62, and 62.5) rods with a diameter of 2 mm.

tion maxima of amorphous structure and no obvious crystalline peaks can be found within the XRD resolution limits. We have studied the GFA of Ni–Nb binary alloys within the whole compositional range and found that $Ni_{62}Nb_{38}$ alloy should be the best glass former. Figure 2 shows the typical microstructure of $Ni_{62}Nb_{38}$ as-cast rod. In accordance with the XRD results, no obvious crystalline phases were found in the HREM images and thus the as-cast rod is fully amorphous.

Figure 3 shows the HTDSC traces of $Ni_{62}Nb_{38}$ sample at a heating rate of 20 K/min. A marked endothermic behavior before crystallization demonstrates a distinct glass transition with the onset temperature (T_g^{onset}) at about 892 K. Two sharp exothermic reactions occur after the glass transition associated with the transformations from supercooled liquid state to the equilibrium crystalline intermetallic phases. The onset temperatures for crystallizations (T_{x1}^{onset} and T_{x2}^{onset}) are about 932 and 981 K, respectively. The melting process of $Ni_{62}Nb_{38}$ alloy is shown in the inset of Fig. 3. The liquid temperature (T_l) for the alloy is about 1483 K. Therefore, the reduced glass transition temperature $T_{rg}(=T_g/T_l)$, the supercooled liquid region $\Delta T_x(=T_{x1}-T_g)$, and parameter $\gamma[=T_{x1}/(T_g+T_l)]$, which are usually employed to reflect the GFA of

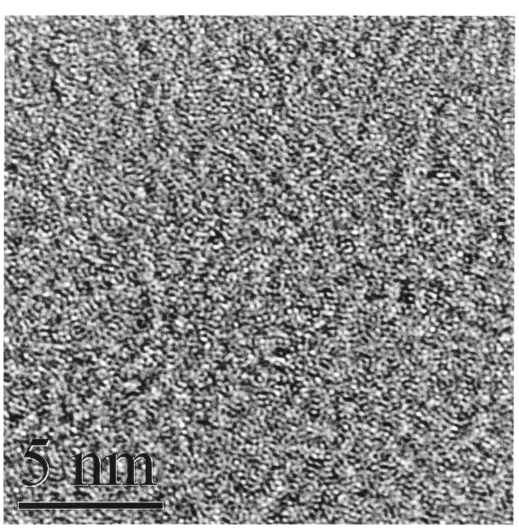

FIG. 2. HREM image of $Ni_{62}Nb_{38}$ as-cast rod.

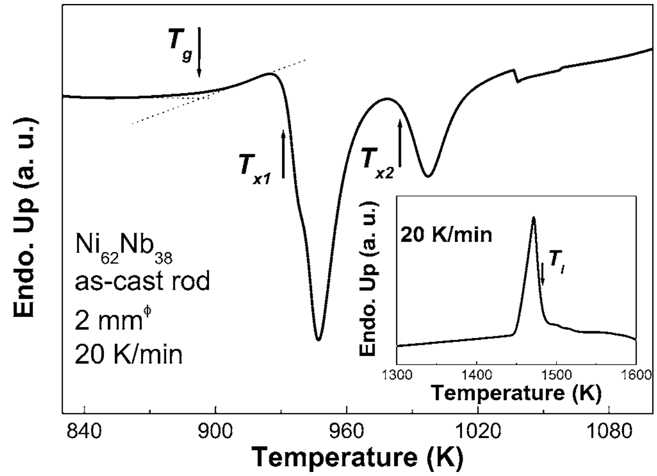

FIG. 3. HTDSC traces of $Ni_{62}Nb_{38}$ as-cast rod at a heating rate of 20 K/min. The inset is the melting process of $Ni_{62}Nb_{38}$ alloy.

the alloys,[8–11] are about 0.60, 40 K, and 0.392. The critical cooling rate R_c $\{=C_1 \exp[(-\ln C_1/\gamma_0)\gamma]$, where C_1 and γ_0 are constants$\}$ and critical section thickness $Z_c[=2.80\times 10^{-7}\exp(41.70\gamma)]$ were predicted accordingly[8,9] to be 57 K s^{-1} and 3.5 mm, respectively, which indicate the higher GFA of $Ni_{62}Nb_{38}$ alloy.

The better GFA of off-eutectic alloys, such as $Zr_{36}Cu_{64}$, $Zr_{36.5}Cu_{63.5}$, and $Zr_{50}Cu_{50}$ in Cu–Zr binary alloys[13,14] and $Ni_{62}Nb_{38}$ in the present work, has evoked tremendous interests recently. A phase selection diagram is proposed to explain the phenomena and it is suggested that the better glass former could be on the side with a steeper liquidus slope.[13] Nevertheless, their analysis can only provide a direction for good glass formers, rather than a specific alloy composition. According to our recent experimental results, the better glass former of Cu–Hf binary alloys ($Cu_{65}Hf_{35}$ amorphous rod, 2 mm in diameter) is on the side with a smoother liquidus slope.[15]

Thermodynamic analysis could be useful in evaluating the composition of a good glass former in more detail. Inoue and co-workers proposed a thermodynamic model to determine glass-forming compositions from empirical rules. They calculated the mixing enthalpy (ΔH) and mismatch entropy (S_σ) of glass forming alloys, and thus obtained the critical value of ΔH and S_σ for the high GFA of multicomponent metallic glasses.[16,17] However, because glass formation is always a competing process between supercooled liquid and the resulting crystalline phase, the 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.[8,9] Therefore, consideration of the formation enthalpy for crystalline phases, as well as that for the glass phase, could be very important for evaluating the glass formation and the GFA of metallic glasses.

From a thermodynamic point of view, binary alloys with well-defined phase diagrams and low eutectic temperatures provide ideal model systems for the study of the GFA of

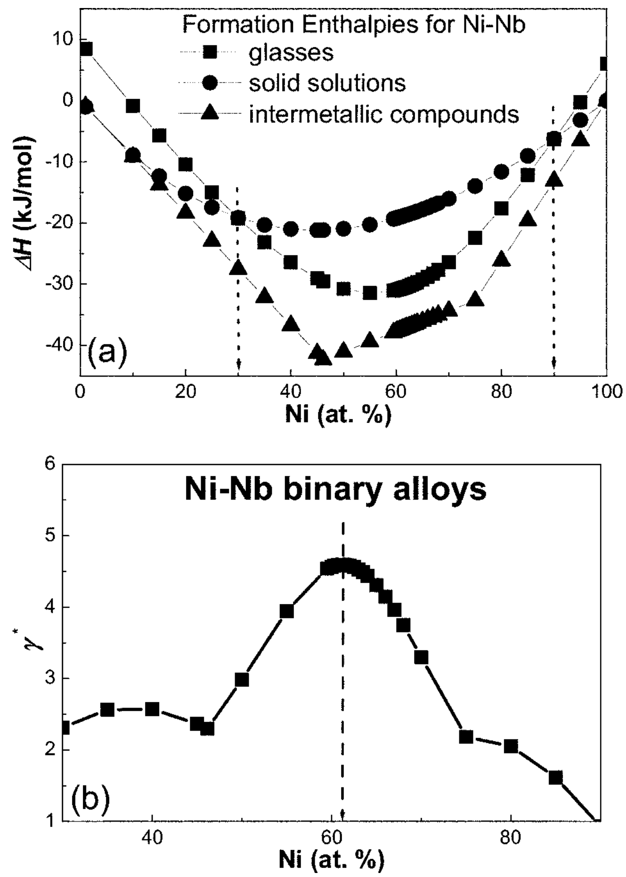

FIG. 4. Calculated formation enthalpies for solid solutions, metallic glasses, and intermetallic compounds of Ni–Nb binary alloys; (b) the dependence of parameter γ^* on Ni concentration in Ni–Nb binary alloys.

metallic glasses. Figure 4(a) shows the formation enthalpies of glasses (ΔH^{amor}), solid solutions (ΔH^{SS}), and intermetallic compounds ($\Delta H^{\mathrm{inter}}$) of Ni–Nb binary alloys calculated by the Miedema's model.[18,19] The compositions of a possible glass former studied in this work should be ranging from about $Ni_{30}Nb_{70}$ to $Ni_{90}Nb_{10}$ [as marked in Fig. 4(a), dash line][20–22] because it is commonly regarded[23] that the alloys could be vitrified into an amorphous state only when $\Delta H^{\mathrm{amor}} < \Delta H^{\mathrm{SS}}$. The formation enthalpy, $\Delta H^{\mathrm{inter}}$, of a composition between two adjacent intermetallic compounds is calculated using the level principle. Since the contribution from entropies is much smaller as compared with that from the formation enthalpy of solid compounds,[18] we can neglect the entropy contribution and express the new parameter for glass formation, γ^*, in terms of formation enthalpies alone.

It is known that crystallization processes must be fully suppressed in order to form a glass.[10] Thus, from a thermodynamic point of view, the formation of the metastable amorphous state should involve two aspects: (1) the driving force ($-\Delta H^{\mathrm{amor}}$) for glass formation and (2) the resistance ($\Delta H^{\mathrm{amor}} - \Delta H^{\mathrm{inter}}$) for glass formation against crystallization, which is the difference between the driving force for glass and intermetallic compound ($-\Delta H^{\mathrm{inter}}$). The parameter of GFA, γ^*, which represents the relationship between GFA and the two aspects mentioned above, can be expressed as follows:

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

Figure 4(b) illustrates the relationship between parameter γ^* and the composition of the alloys. As a thermodynamic factor concerning the effect of both driving force and resistance synthetically on the GFA of the alloys, parameter γ^* indicates that alloy with composition around $Ni_{61.5}Nb_{38.5}$ is the better glass former. The predicted result is roughly in accordance with the experimental data in the present work. The slight difference between the calculated and experimental results could be due to the neglecting of entropy contribution. Actually, we have predicted the better glass former in Cu–Zr and Cu–Hf binary alloys[15] 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 results. Therefore, parameter γ^* could be used as a useful guideline to identify the best glass former of Ni–Nb, Cu–Zr, Cu–Hf, or even other binary alloys.

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