Role of Atomic Size on Glass Formability and Thermal Stability of Al-Based Amorphous Alloys

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The glass forming ability and thermal stability of the quenched amorphous phase are evaluated in $\text{Al}_{87}\text{Ni}_7\text{Gd}_{6-x}(\text{Ca}, \text{Sr}, \text{Ba})_x$ alloys in terms of large atomic size effects of Alkali metals. Thermal analysis indicates that the thermal stability of the quenched amorphous phase decreases with the addition of Ca and increases with the addition of up to 2 at% Sr and Ba, as seen in the change of primary crystallization peak temperature and activation energy for primary crystallization. However, the enhanced thermal stability of the quenched amorphous phase with the addition of Sr and Ba does not lead to easier glass formation. The critical thickness of the quenched ribbons with completely amorphous phase is found to decrease from 300 to 70 μm as the content of Alkali elements is increased at the expense of Gd. These results reveal the different effects of atomic size on the glass forming ability and the thermal stability of the quenched amorphous phase against crystallization.

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1. Introduction

Al-based amorphous alloys, especially Al-TM-RE (TM: transition metals; RE: rare earth metals), have attracted much attention due to their combination of high specific strength, good ductility and good corrosion resistance.¹⁻³⁾ Compared to the bulk glass formers, Al-TM-RE alloy system is unique in that it can be quenched into the amorphous phase only in the solute-rich composition range.^{3,4)} This uniqueness is also exhibited in that the addition of more components does not improve the glass forming ability (GFA) of the Al-TM-RE ternary alloy.^{5,6)} There is no detectable difference in GFA for $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ and $\text{Al}_{85}\text{Si}_2\text{Ni}_5\text{Fe}_1\text{Co}_1\text{Gd}_5\text{Y}_1$ alloys.⁵⁾ This indicates the failure of "confusion principle" concept for glass formation⁷⁾ as a method to improve GFA in Al-based alloy system.

With the aim of improving the GFA of Al-based alloys, other factors must be considered which may influence GFA. The present paper focuses on the atomic size effect. It is known in the bulk glass formation systems that components with well distributed atomic sizes are favorable for glass formation.^{8,9)} Previous studies of atomic size effects on GFA have been carried out in Al-RE-Ni alloys by using different RE metals to obtain different average RE atomic sizes.⁶⁾ However, the small atomic size difference between various RE metals is also accompanied by the small difference in chemical interaction of RE metals with Al, which might influence the evaluation of the atomic size effect on GFA. In this work, starting from $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$, a fourth component is introduced with a markedly larger atomic size. Here Alkali metals (Ca, $r_{\text{Ca}} = 0.197 \text{ nm}$, Sr, $r_{\text{Sr}} = 0.215 \text{ nm}$, and Ba, $r_{\text{Ba}} = 0.222 \text{ nm}$) were selected because they have much larger atomic sizes than the present components ($r_{\text{Ni}} = 0.124 \text{ nm}$, $r_{\text{Al}} = 0.143 \text{ nm}$ and $r_{\text{Gd}} = 0.179 \text{ nm}$) and because the chemical interaction of these three Alkali metals with Al are quite comparable. The interaction parameter,¹⁰⁾ λ_{AB} , defined as the change of enthalpy when adding one mole solute B to an in-

finite solvent A, is used to characterize the chemical interaction between element A and B. According to Miedema's calculation,¹⁰⁾ $\lambda_{\text{AlCa}} = -97 \text{ kJ/mol}$, $\lambda_{\text{AlSr}} = -90 \text{ kJ/mol}$ and $\lambda_{\text{AlBa}} = -94 \text{ kJ/mol}$. Therefore, the changes in GFA and/or other properties can be attributed to the different atomic sizes of the Alkali metals.

2. Experimental

Alloy ingots were prepared by melting nominal amounts of high purity elements in an arc-furnace under an inert argon atmosphere. Alloy melting was repeated four times to ensure homogeneity of composition. Amorphous ribbons were made by the single roller melt spinning technique under a partial helium atmosphere. A series of discrete wheel speeds from 300, 600 and 1200 revolution per minute (min^{-1}) was employed to evaluate the GFA of different compositions. A wheel speed of 3000 min^{-1} , corresponding to a tangential speed of about 30 m/s, was used to prepare samples for thermal stability analysis. The amorphous nature of the quenched ribbons was verified by X-ray diffraction (XRD), using $\text{CuK}\alpha$ radiation. Assessment of the thermal stability of the amorphous ribbons against crystallization was carried out on a differential scanning calorimeter (DSC) under a flowing pure argon atmosphere. The regular heating rate was 20 K/min. The temperature was calibrated using standard In and Zn samples for different temperature ranges. Examination of the melting behavior for samples with different compositions was done using a differential thermal analysis (DTA) system. The temperature was calibrated using standard Al and Au samples for different temperature ranges. Samples were heated from room temperature to 1373 K at a heating rate of 10 K/min.

3. Results and Discussion

A series of wheel speeds of 300, 600 and 1200 min^{-1} was used to make ribbons of $\text{Al}_{87}\text{Ni}_7\text{Gd}_{6-x}(\text{Ca}, \text{Sr}, \text{Ba})_x$ ($x = 1-3 \text{ at\%}$) alloys. Examination of the structure of the quenched

ribbons by X-ray diffraction revealed that at 300 min^{-1} , only alloys of $x = 1$ can be quenched into fully amorphous phase with a ribbon thickness of $250\text{--}300 \mu\text{m}$. At 600 min^{-1} , fully amorphous phase is obtainable for alloys of $x = 2$, the resulting ribbon thickness is $130 \pm 20 \mu\text{m}$. As-quenched ribbons for alloys of $x = 3$ are fully amorphous at 1200 min^{-1} with a ribbon thickness of $70 \pm 20 \mu\text{m}$. For the three alloy series, the thickness of the quenched ribbons with a fully amorphous phase decreases with increasing Ca, Sr and Ba content and does not show an obvious atomic size dependence.

Figure 1 presents the DSC curves for quenched ribbon samples of the three alloy series, where (a), (b) and (c) correspond to the addition of Ca, Sr and Ba, respectively. The addition of Ca leads to a monotonic decrease in the primary crystallization peak temperature (T_p) of the quenched amorphous alloys, from 487 K for $x = 1$ to 465 K for $x = 3$, indicating a decrease in thermal stability of the quenched amorphous phase against crystallization. While the addition of Sr and Ba from 1 to 2 at% increases T_p , a further addition of Sr and Ba makes T_p decrease, showing a maximum T_p at $x = 2$ at%. The variation of T_p as a function of composition for the three alloy series is summarized in Fig. 2. Although the addition of Sr and Ba results in a similar tendency in T_p , the alloys containing Ba exhibit higher T_p than those containing the same content of Sr, for example, T_p is 519 K for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Ba}_2$ while it is 506 K for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Sr}_2$. This indicates that the addition of an element with a larger atomic size is more effective in enhancing the thermal stability of the quenched amorphous phase.

The thermal stability of an amorphous phase can also be characterized by the apparent activation energy for crystallization. Using the Kissinger formulation,¹¹⁾ $\ln(T_p^2/B) = -E_c/RT_p + C$, where T_p is the primary crystallization peak temperature at a heating rate of B , R is the gas constant and C is a constant, the apparent activation energy E_c for crystallization can be obtained by plotting $\ln(T_p^2/B)$ against $1/T_p$, which should be a straight line with a slope of $-E_c/R$. The determined activation energy for primary crystallization is 149 kJ/mol for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Ca}_2$, 183 kJ/mol for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Sr}_2$ and 190 kJ/mol for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Ba}_2$. Compared to 165 kJ/mol for $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$, it is observed that the thermal stability of the resulting amorphous phase is decreased by the addition of Ca but increased by the addition of Sr and Ba.

Isothermal DSC measurement of the resulting amorphous alloys also reveals the effects from adding large atomic size components. Figure 3 shows the isothermal DSC curves for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4(\text{Ca}, \text{Sr}, \text{Ba})_2$ amorphous alloys; included in Fig. 3 is the curve for $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ amorphous alloy for comparison. For $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ and $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Ca}_2$, a series of holding temperatures was selected and in all cases the crystallization process does not show a peak shift at different holding temperatures which ranged from 440 to 455 K . Detailed studies of the crystallization of amorphous $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ will be reported elsewhere.¹²⁾ For $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Sr}_2$, a trace of a crystallization peak, as marked in the figure, can be detected which shifts to longer times as the holding temperature is decreased. While for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Ba}_2$, a clear crystallization peak is visible and crystallization becomes sluggish at a lower holding temper-

Fig. 1 DSC curves for quenched amorphous ribbon samples at a heating rate of 20 K/min , (a) $\text{Al}_{87}\text{Ni}_7\text{Gd}_{6-x}\text{Ca}_x$, (b) $\text{Al}_{87}\text{Ni}_7\text{Gd}_{6-x}\text{Sr}_x$ and (c) $\text{Al}_{87}\text{Ni}_7\text{Gd}_{6-x}\text{Ba}_x$.

ature. A sluggish crystallization process at a lower holding temperature means that a longer incubation time for nucleation is needed and that the nucleation process is related to thermal atomic motion.

Non-isothermal and isothermal DSC measurements indicate enhanced thermal stability of the quenched amorphous alloys upon adding up to 2 at% Sr and Ba. However, the enhanced thermal stability does not lead to an improved GFA. As described above, the ribbon thickness for a wholly amorphous phase is markedly decreased by adding Sr and Ba when

Fig. 2 Variation of the primary crystallization temperature as a function of the content of Ca, Sr and Ba.

Fig. 3 Isothermal DSC curves for $\text{Al}_{87}\text{Ni}_7\text{Gd}_4(\text{Ca}, \text{Sr}, \text{Ba})_2$ quenched amorphous samples, also shown is the curve for $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ quenched amorphous sample for comparison.

compared to the ternary $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ alloy, revealing the different effects of large atomic size components on the thermal stability against crystallization and GFA.

Both the thermal stability of amorphous alloys and GFA are related to the atomic mobility of the alloy components. The thermal stability of amorphous alloys against crystallization involves solid state atomic diffusion which proceeds through atom jumping and is best described with an Arrhenius diffusivity; while GFA is more concerned with the liquid state atomic diffusion. In the liquid state, due to the larger average free volume per atom of the component atoms, atomic diffusion is more dependent on the viscosity of the alloy melt. Experimentally the atomic diffusivity in the liquid state is inversely proportional to the melt viscosity. Hence the solid and liquid state atomic diffusivities exhibit different atomic size dependencies. Studies of Ni and Al diffusion as radio-tracers in a Zr-based supercooled alloy indicate that at low temperatures the diffusivity of Al is 3 orders of magnitude lower than for Ni due to the larger atomic size of Al, while their diffusivities show a tendency to merge at higher temperatures.¹³⁾ Quasielastic neutron scattering experiments on $\text{Zr}_{46.75}\text{Ti}_{18.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{22.5}$ (V1) alloy revealed that above the

Fig. 4 DTA curves for $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ and $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Sr}_2$ alloys at a heating rate of 10 K/min to show the melting behavior.

liquidus temperature the differences in the diffusion coefficients of the various components in the liquid alloy are less than 1 order of magnitude.¹⁴⁾ Therefore, liquid state atomic diffusion seems to be less dependent on atomic size than solid state atomic diffusion. However, for bulk metallic glass systems, the alloy melt is thermodynamically unstable when it is cooled below the liquidus temperature due to their eutectic composition. The viscosity of the supercooled alloy melt has a strong temperature dependence and increases rapidly with lower temperatures, resulting in atomic diffusion changing from liquid-like to solid-like at relatively high temperatures. Studies of the V1 supercooled melt indicated that atomic diffusion can't be described by liquid-state atomic diffusion formula when the alloy melt is only cooled to 850 K, from its liquidus point of 1026 K, while Arrhenius diffusivity describes the atomic diffusion process.¹⁵⁾ On the other hand, in Al-based amorphous alloys, or generally in the non-eutectic glass formation alloys, the metastable liquid phase is retained upon rapid cooling over a rather wide temperature range below the liquidus temperature. The liquidus-solidus temperature range is 250 K (from 1167 to 915 K) for $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ ⁵⁾ and it remains practically unchanged when Ca, Sr and Ba are added to replace Gd. As shown in Fig. 4, $\text{Al}_{87}\text{Ni}_7\text{Gd}_4\text{Sr}_2$ and $\text{Al}_{87}\text{Ni}_7\text{Gd}_6$ alloys exhibit a quite comparable melting behavior. Although no experimental data of viscosity are available, one can reasonably assume that the viscosity increase of the supercooled Al alloy melt from the liquidus to the solidus temperature is not as rapid as in the case of bulk metallic glasses. Hence liquid-state atomic diffusion is dominant over a larger temperature range in Al-based alloys. Therefore, compared to the eutectic bulk metallic glasses,^{15–18)} atomic diffusion in the liquid state plays a more important role in GFA for Al-based alloys. In this case, the atomic size effect on liquid diffusivity, and then on GFA, was weakened further by the wide liquidus-solidus temperature range.

Although GFA is weakly dependent on the atomic size of components in the Al-based alloy system, the decrease in GFA by adding Ca, Sr and Ba to replace Gd can't be explained in terms of large atomic size. This reveals the importance of chemical interaction of these solute atoms with the main component Al. As mentioned before, the interaction param-

ter of Alkali metals with Al is around -90 kJ/mol, however, the interaction parameter between Al and Gd is -181 kJ/mol, meaning that the chemical interaction between Al and Gd is much stronger than those between Alkali metals and Al. Considering the weak dependence of GFA on atomic size, the decrease in GFA by adding Ca, Sr and Ba to replace Gd can be attributed to the decreased chemical interaction between (Ca, Sr, Ba) and Al than that between Gd and Al. Similarly, the comparable chemical interaction of Ca, Sr, Ba with Al is believed to be the reason why the GFA by adding a same content of Ca, Sr and Ba to replace Gd does not show an atomic size dependence. On the other hand, the atomic size effect is more obvious in solid-state atom diffusion. By adding Sr and Ba to replace Gd, the enhancement of the thermal stability of the quenched amorphous phase due to large atomic size effects can compete against the decrease of thermal stability due to the weakened chemical interaction. While Ca has a relatively smaller atomic size, the enhancement of the thermal stability due to its addition might not be able to compensate the decrease in the thermal stability due to the weakened chemical interaction. As a result of the competition of these two factors, the quenched amorphous alloys containing Sr and Ba exhibit an enhanced thermal stability while the addition of Ca leads to a decrease in the thermal stability.

4. Summary

The glass forming ability and thermal stability of the quenched amorphous phase have been evaluated in $\text{Al}_{87}\text{Ni}_7\text{Gd}_{6-x}(\text{Ca}, \text{Sr}, \text{Ba})_x$ alloys in terms of large atomic size effects of Alkali metals. It is found that the maximum thickness of the quenched ribbon with completely amorphous phase decreases with increasing content of Alkali elements at the expense of Gd. Thermal analysis indicates that the addition of Ca decreases the primary crystallization temperature monotonically with increasing Ca content while the addition of up to 2 at% Sr and Ba increases the primary crystallization temperature, and that further increasing Sr and Ba content leads to a decrease of the primary crystallization temperature, showing a maximum at 2 at%. Isothermal measurements show that the addition of Sr and Ba stabilizes the nucle-

ation process and leads to a well defined nucleation and crystal growth peak in isothermal curves. The addition of larger atomic size components enhances the thermal stability of the quenched amorphous phase but does not result in a practically improved GFA, revealing the different effects of atomic size on the glass forming ability and the thermal stability of the quenched amorphous phase.

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