RAPID PUBLICATION

Mg-Ni-La Amorphous Alloys with a Wide Supercooled Liquid Region

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New Mg-Ni-La amorphous alloys exhibiting the glass transition phenomenon were found to form in a wide compositional range of 10 to 40 at% Ni and 5 to 30 at% La by the melt-spinning technique. The glass transition temperature (T_g) increases from 427 to 453 K with increasing La content while no distinct change of T_g with Ni content is seen. The temperature span $\Delta T_x (= T_x - T_g)$ between T_g and onset temperature of crystallization (T_x) increases first with increasing Ni and La content, shows the largest value of 58 K for $Mg_{50}Ni_{30}La_{20}$, and then decreases. This ΔT_x value is larger than that for Pd-based amorphous alloys, being comparable to that for a $Pt_{60}Ni_{15}P_{25}$ amorphous alloy which exhibits the widest T_x among amorphous metallic materials. Specific heats of the amorphous solid and supercooled liquid were also determined for the $Mg_{50}Ni_{30}La_{20}$ amorphous alloy.

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I. Introduction

It has recently been reported that an amorphous phase forms in wide compositional range in rapidly solidified Al-M-Ln⁽¹⁾⁽²⁾ and Mg-M-Ln⁽³⁾ (M=transition metal, Ln=lanthanide metal) alloys and their amorphous alloys exhibit high mechanical strengths and good ductility. Furthermore, the amorphous alloys in Al-Ni-Ln⁽⁴⁾, Al-Co-Ln⁽⁵⁾ and Mg-Ni-Ce⁽⁵⁾ systems were found to exhibit a clear glass transition phenomenon at temperatures just below onset temperature of crystallization (T_x). The temperature span $\Delta T_x (= T_x - T_g)$ between glass transition temperature (T_g) and T_x is in the range of 15 to 35 K for the Al- and Mg-based amorphous alloys. The largest ΔT_x value is comparable to that (35–40 K) for Pd-Cu-Si⁽⁶⁾ and Pd-Ni-Si⁽⁷⁾ amorphous alloys and about two times as large as that (18 K)⁽⁸⁾ for a $Ni_{81}P_{10}B_6Al_3$ amorphous alloy which exhibits

the most clear glass transition in Fe-, Co- and Ni-based amorphous alloys. However, the ΔT_x values for the Al- and Mg-based amorphous alloys are smaller than those (50 to 60 K) for Pd-Ni-P⁽⁹⁾ and Pt-Ni-P⁽⁶⁾ amorphous alloys exhibiting the widest supercooled liquid region in metallic amorphous materials. Finding of Al- and Mg-based amorphous alloys with a wide supercooled liquid region is important because the consolidation from atomized amorphous powders to an amorphous bulk is expected to be easily made in the supercooled liquid region. Most recently, the authors have found that Mg-Ni-La amorphous alloys prepared by liquid quenching possess a wide supercooled liquid region reaching about 60 K. This paper presents alloy compositions of Mg-Ni-La amorphous alloys at which the wide supercooled liquid region is observed, specific heats of the amorphous solid and supercooled liquid and the difference in specific heat between the two states.

II. Experimental Details

Mg-Ni-La alloys with compositions above

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50 at% Mg were used in the present study. The Mg-Ni-La ingots were prepared by induction-melting a mixture of pure Mg (99.99 mass%) metal and Ni-La alloy in a purified argon atmosphere. The compositions are nominally expressed in atomic per cent. From the master alloy ingots, ribbons with a rectangular cross section of about $0.02 \text{ mm} \times 1 \text{ mm}$ were prepared by a single roller melt-spinning technique in an argon atmosphere. The amorphous nature of the melt-spun ribbons was examined by X-ray diffractometry and transmission electron microscopy (TEM) techniques. The specific heat (C_p) associated with structural relaxation, glass transition and crystallization was measured with a differential scanning calorimeter (DSC). Care was taken to reduce the thermal drift by prewarming the calorimeter for at least 5 h in the temperature range of interest. The accuracy of the data was about $\pm 0.4 \text{ J/mol-K}$ for absolute C_p values and better than $\pm 0.1 \text{ J/mol-K}$ for the relative C_p or ΔC_p measurements. The samples were first scanned at 0.67 K/s (40 K/min) to the temperature of the supercooled liquid to obtain data in the as-quenched state, and then cooled to room temperature. The $C_p(T)$ measurement was immediately repeated *in situ* to obtain data of the control sample. This test procedure is essential in order to eliminate any possible error that might result from the drift in the calorimeter between the measurements. The change in the calorimetric behavior upon reheating was used to monitor the structural relaxation process.

III. Results and Discussion

Figure 1 shows the compositional range in which an amorphous Mg-Ni-La phase forms by melt spinning, along with the data of T_g and T_x . The glass formation range is 10 to 40 at% Ni and 0 to 30%La and the minimum solute content for the amorphization is 10%. Furthermore, it is notable that an amorphous phase is formed even in Mg-Ni binary system. Here, it appears important to point out that the glass formation range in the Mg-Ni-La system is much wider than that (3 to 35%Ni and 3 to 25%Ce)⁽³⁾ in the Mg-Ni-Ce system. Figure 1

Fig. 1 Compositional range for formation of amorphous phase and the changes of glass transition temperature (T_g) and crystallization temperature (T_x) in rapidly solidified Mg-Ni-La alloys: (○ and ◐) amorphous; (◑) amorphous plus crystalline; (●) crystalline. The mark of ■ represents that reactivity between molten alloy and quartz nozzle is too high to eject the molten alloy through an orifice of the nozzle probably because the high Ni content causes an increase of melting temperature.

Fig. 2 Changes in the glass transition temperature (T_g) and crystallization temperature (T_x) as a function of Ni or La concentration for Mg-Ni-La amorphous alloys.

also shows that the glass transition phenomenon was observed in the range of 10 to 40%Ni and 5 to 35%La corresponding to a great portion of the glass formation range.

On the basis of the data shown in Fig. 1, T_g and T_x of the Mg-Ni-La amorphous alloys are plotted as a function of Ni or La content in Fig. 2. One can notice a difference in the compositional dependences of T_g and T_x . That is,

T_g increases gradually from 427 to 453 K with an increase of La content from 5 to 25% and becomes constant in the higher La concentration range, while no significant change of T_g is seen in the wide concentration range of 10 to 40%Ni. On the other hand, T_x increases from 450 to 509 K with increasing Ni content in the entire Ni concentration range. Similarly, as the La content increases, T_x increases first, shows a maximum value of 509 K at 20%La and then decreases to about 477 K. Comparing the compositional dependence of T_x with the equilibrium phase diagrams⁽¹⁰⁾ of Mg–Ni and Mg–La alloys, one can notice a similar change between T_x and melting temperature (T_m). The T_m of Mg–Ni alloys tends to increase with increasing Ni content in the entire Ni range, while that of Mg–La alloys increases first, shows a maximum value at about 25%La and then decreases with further increasing La content. On the contrary, T_g is independent of T_m , in agreement with the previous data⁽⁹⁾ for (Pd–Ni)₈₀P₂₀ amorphous alloys. It is generally known⁽⁷⁾ that T_g tends to increase with increases of the magnitude and number of the attractive bondings among the constituent atoms. Although the reason for the increase of T_g with an increase of La content is probably due to the increase of the number of the Mg–La bonding with an attractive interaction, the same concept cannot be applied to the interpretation for the change of T_g with Ni content in which T_g shows a nearly constant value in the wide range of 10 to 40%Ni.

Figure 2 also shows that the temperature span (ΔT_x) between T_g and T_x reaches as large as 58 K for Mg₅₀Ni₃₀La₂₀, indicating the existence of a very wide supercooled liquid region. The T_x value is larger than that (35 to 50 K) for Pd–Cu–Si⁽⁶⁾, Pd–Ni–Si⁽⁷⁾ and Pd–Ni–P⁽⁸⁾ amorphous alloys as well as that (15 to 35 K) for Fe⁽⁸⁾, Ni⁽⁸⁾, Cu⁽⁶⁾ and Al⁽⁴⁾-based amorphous alloys, being comparable to that (55 to 60 K)⁽⁶⁾ for Pt–Ni–P amorphous alloys having the widest supercooled liquid region in amorphous metallic materials. The reason for the appearance of the wide supercooled liquid region for the Mg₅₀Ni₃₀La₂₀ amorphous alloy is under investigation.

Figure 3 shows the DSC curve of an amor-

Fig. 3 DSC curve of an amorphous Mg₅₀Ni₃₀La₂₀ alloy.

Fig. 4 The thermogram $C_{p,q}(T)$ of an amorphous Mg₅₀Ni₃₀La₂₀ alloy in the as-quenched state. The solid line represents the thermogram $C_{p,s}(T)$ of the sample heated to 485 K.

phous Mg₅₀Ni₃₀La₂₀. The wide supercooled liquid region below T_x was observed. Figure 4 shows the thermogram of an amorphous Mg₅₀Ni₃₀La₂₀ alloy with the widest supercooled liquid region. The C_p value of the as-quenched phase is 22.7 J/mol·K near room temperature. As the temperature rises, the C_p value increases gradually and begins to decrease, indicating an irreversible structural relaxation at about 326 K. With a further increase in temperature, the C_p value reaches its minimum at about 420 K,

then increases rapidly in the glass transition range from 440 to 475 K and reaches 41.6 J/mol-K for the supercooled liquid around 480 K. With further increased temperature, the supercooled liquid crystallizes at 509 K. It is also seen in Fig. 4 that the amorphous alloy has a large difference, $\Delta C_{p,s \rightarrow l}$, in specific heat between the amorphous solid and supercooled liquid reaching 17.4 J/mol-K. The difference in $C_p(T)$ between the as-quenched and the reheated states, $[\Delta C_p(T)]$, manifests the irreversible structural relaxation which is presumed to arise from the annihilation of various kinds of quenched-in "defects" and the enhancement of the topological and chemical short-range ordering through the atomic rearrangement. The details of the structural relaxation behavior will be described elsewhere.

The $C_{p,s}$ curve of the reheated (control) sample is unaffected by thermal changes and consists of configurational contributions as well as those arising from purely thermal vibrations. Therefore, the vibrational specific heat, $C_{p,v}$, for the amorphous alloy was extrapolated from C_p values in the low temperature region and is a linear function of temperature such that,

$$C_{p,v} = 22.6 + 1.92 \times 10^{-2}(T - 360) \text{ J/mol-K},$$

$$(360 < T < 440 \text{ K}). \quad (1)$$

Similarly, the equilibrium specific heat, $C_{p,e}$, of

the supercooled liquid, including the vibrational and configurational specific heat, can be expressed by eq. (2) based on the data shown in Fig. 4,

$$C_{p,e} = 39.5 + 6.35 \times 10^{-2}(497 - T) \text{ J/mol-K},$$

$$(485 < T < 509 \text{ K}). \quad (2)$$

In conclusion, the finding of the Mg-Ni-La amorphous alloys with the supercooled liquid over a wide temperature range and the clarification of the thermodynamic properties are very important for subsequent development of the consolidation into an amorphous bulk from the amorphous powder or ribbon.

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