Reductilization of an Embrittled Amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ Alloy by Water Quenching from Supercooled Liquid

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A water quenching treatment from supercooled liquid region was found to induce the ductilization of an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy which was embrittled by annealing in a wide temperature range up to the glass transition temperature (T_g). The tensile fracture surface appearance also changed from a shell-like pattern typical for the brittle amorphous alloy to a pattern consisting of smooth and vein regions typical for the ductile amorphous alloy. There is no appreciable difference in the fracture surface appearance between the melt-spun and the ductilized alloys. The embrittled samples exhibit a reversible endothermic reaction resulting from the annihilation of the short-range ordering developed during annealing, accompanied by a significant decrease of an exothermic reaction. On the other hand, the water-quenched sample with good ductility does not have the endothermic reaction and exhibits only the exothermic reaction in the entire temperature range up to T_g . Accordingly, the reductilization caused by water quenching is presumed to destroy the structure stabilized by the annealing-induced structural relaxation so as to rather close to the quenching-induced disordered atomic configuration. This has been supported by the results of X-ray diffraction.

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I. Introduction

It is generally known⁽¹⁾⁽²⁾ that a number of amorphous alloys belonging to Fe- and Co-based alloy systems exhibit a catastrophic loss of ductility upon annealing at temperatures well below the onset temperature of crystallization (T_x), though their amorphous alloys in as-quenched state possess good bending ductility. The catastrophic loss of ductility causes a severe limitation in practical uses of amorphous alloys at elevated temperatures. Accordingly, a number of studies on the annealing-induced embrittlement phenomenon in an amorphous single state without any appreciable crystalline phases have been carried out with the aim of clarifying the mechanism for the embrittlement phenomenon⁽¹⁾⁽²⁾ as well as of finding a technique to restore from the brittle state to the ductile state⁽³⁾. However, little has been obtained about a definite knowledge of the mechanism and technique. It has recently been reported that Fe-Ni-P and Cu-Ti amorphous alloys subjected to the first-stage embrittlement upon annealing at temperatures (T_a) well below T_x can be reductilized by heating for a short time at temperatures above T_a , followed by water quenching⁽⁴⁾, in addition to the reductilization by neutron irradiation⁽⁵⁾⁽⁶⁾. Furthermore, it has been pointed out⁽⁴⁾⁻⁽⁶⁾ from the measurement of relative density that the reductilization obtained by the two techniques is presumably due to

the introduction of excess free volume into the embrittled sample in which the excess free volume was lost by annealing. Thus, the reductilization treatments are valid only for the samples which were embrittled in a low T_a range by the loss of quenching-induced excess free volume. There is no report on the reductilization of the sample which was subjected to the second-stage embrittlement in a high T_a range where cooperative atomic rearrangement as well as the loss of free volume takes place. More recently, the present authors have found that a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous alloy exhibiting a distinct supercooled liquid region before crystallization can be reductilized from an annealing-induced embrittled state by water quenching of the sample from the temperature region in a supercooled liquid state, though the heat treatment in the amorphous solid proposed for the Fe-Ni-P and Cu-Ti systems⁽⁴⁾ does not induce a reductilization of the La-Al-Ni amorphous alloy embrittled at T_a as high as $0.95T_g$. This paper is intended to present the embrittlement-reductilization behavior for a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous alloy and to investigate the reason for the reductilization on the basis of the data of structural relaxation and X-ray diffraction for the samples subjected to the same annealing and water quenching treatments.

II. Experimental Details

An amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy with a significant supercooled liquid region before crystallization was used in the present study. The alloy was produced by melt spinning in an argon atmosphere and had a ribbon form with a thickness of 0.05 mm and a width of 1.5 mm. The glass transition temperature (T_g) and T_x of the amorphous

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alloy have been reported to be 476 and 545 K⁽⁷⁾, respectively, at a heating rate of 0.67 K/s. The as-quenched ribbon sample was sealed in an evacuated quartz capsule and annealed for 1.8 ks in the temperature range of 360 to 490 K. The reductilization for the samples embrittled by the annealing treatment was tried by heat treatment consisting of quick heating for 30 s at different temperatures between 460 and 540 K in a silicon oil bath, followed by water quenching. The embrittlement and reductilization behaviors for the annealed and water-quenched samples were examined at room temperature by measuring the radius of curvature at which the fracture takes place in a simple bending test⁽⁸⁾. The bending strain (ε_f) at the fracture was evaluated by $\varepsilon_f = t/(L - t)$. Here, L is the distance between parallel plates at fracture and t is the thickness of the ribbon specimen. When a specimen can be bent by 180 degrees without failure, $\varepsilon_f = 1$ and the ribbon is fully ductile. If the ribbon fractures upon bending below 180 degrees, ε_f is less than unity, indicating that the ribbon is brittle.

The structural relaxation behavior for the as-quenched, embrittled and reductilized samples was examined by measuring the temperature dependence of apparent specific heat, $C_p(T)$ at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). The accuracy of the data was about ± 0.4 J/mol·K for absolute C_p values and better than ± 0.1 J/mol·K for the relative C_p or ΔC_p measurements. The samples were first scanned at 0.67 K/s to the temperature of the supercooled liquid to obtain data in the annealed or water quenched state, and then cooled to room temperature. The $C_p(T)$ measurement was immediately repeated *in situ* to obtain data on 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.

In addition, the atomic structures of the as-quenched, embrittled and reductilized samples were investigated by X-ray diffraction. The as-quenched ribbons were annealed for 1.8 ks at 470 K in order to prepare the embrittled samples. These embrittled ribbons were reductilized by further annealing for 30 s at 510 K, followed by water quenching. These ribbons were prepared for X-ray measurements by closely arranging them on aluminum frames of about 20 mm width and 15 mm height. The scattering intensity was measured with a molybdenum X-ray target and a singly bent graphite monochromator in diffracted beams. After the corrections for absorption and polarization, the intensity was converted to the coherent scattering intensity in electron units per atom with the generalized Krogh-Moe-Norman method⁽⁹⁾, using the X-ray atomic scattering factors⁽¹⁰⁾ including the anomalous dispersion terms⁽¹¹⁾ and the Compton scattering intensities⁽¹²⁾.

The so-called reduced interference function $Qi(Q)$ was obtained using the coherent scattering intensity I_{cu}^{coh} , by

$$Qi(Q) = (I_{cu}^{coh}(Q) - \langle f^2 \rangle) / \langle f \rangle^2, \quad (1)$$

where $Q = 4\pi \sin \theta / \lambda$ (θ is a half of the scattering angle

and λ is the X-ray wavelength). The term of $\langle f \rangle$ is the average of the atomic scattering factors and $\langle f^2 \rangle$ is the average of the squared atomic scattering factors. The Fourier transform of the interference function gives the reduced radial distribution function (RDF), that is,

$$G(r) = 2/\pi \cdot \int_0^\infty Qi(Q) \sin(Qr) dQ \quad (2)$$

In order to clarify the relation between the reductilization behavior and the tensile fracture appearance, the tensile fracture surface appearance in the melt-spun, annealed and water-quenched states was also examined by scanning electron microscopy (SEM). The tensile fracture was made at a strain rate of $1.7 \times 10^{-4} \text{ s}^{-1}$ and room temperature by using an Instron-type tensile testing machine.

III. Results and Discussion

Figure 1 shows the change of the fracture strain (ε_f) as a function of annealing temperature (T_a) for an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ ribbon. Although the ε_f remains unchanged in the T_a range below 416 K, it decreases drastically from 1.0 to 0.04 in the narrow temperature range between 416 and 434 K and shows a nearly constant value of about 0.03 in the temperature range above 434 K. The change of ε_f with T_a indicates clearly that the La-Al-Ni amorphous ribbon becomes brittle at 416 K in the case of annealing time of 1.8 ks. The ratios of the onset temperature of the annealing-induced embrittlement to T_g and T_x are 0.87 and 0.76, respectively.

Figure 2 shows the thermograms of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous samples annealed for 1.8 ks at different temperatures ranging from 390 to 450 K including the ductile-brittle transition temperature. Here, the $C_{p,q}$ and $C_{p,a}$

Fig. 1 Change in the bending fracture strain (ε_f) as a function of annealing temperature (T_a) for a melt-spun $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous alloy annealed for 1.8 ks.

Fig. 2 The temperature dependence of apparent specific heat ($C_{p,a}$) of a melt-spun $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous alloy annealed for 1.8 ks at different temperatures between 390 and 450 K. The data of the as-quenched ($C_{p,q}$) sample and the sample heated for 60 s at 520 K ($C_{p,s}$) are also shown for comparison.

denote the specific heat curves of the as-quenched and annealed samples, respectively, and the $C_{p,s}$ represents the specific heat curve during reheating of the sample which was heated once to 510 K in the supercooled liquid region. The C_p value of the melt-spun sample is about 22.5 J/mol·K near room temperature. On subsequent heating, C_p begins to decrease at about 350 K, indicative of a structural relaxation, and shows a minimum value at about 434 K. With a further increase in temperature, C_p increases gradually up to about 460 K and then increases rapidly in the glass transition range from 470 to 500 K and reaches 37.0 J/mol·K for the supercooled liquid around 515 K. With further increasing temperature, the C_p value of the supercooled liquid decreases gradually and then rapidly due to crystallization at 545 K.

The heating curve of the sample embrittled by annealing at T_a above 416 K, $C_{p,a}$, shows a $C_p(T)$ behavior which closely follows the specific curve of the reference sample, $C_{p,s}$, up to each T_a , and then exhibits an excess endothermic peak relative to the reference sample before merging with that of the melt-spun sample at a temperature below $T_g = 476$ K. The $C_{p,a}$ of the sample without the loss of ductility subjected to annealing for 1.8 ks at 390 K begins to decrease at about 420 K due to the heating-induced irreversible structural relaxation. In other words, the internal energy of the sample decreases by an enthalpy (ΔH_{exo}) of 662 J/mol corresponding to the area marked with oblique line. The irreversible enthalpy ΔH_{exo}

Fig. 3 Change in the exothermic heat of structural relaxation (ΔH_{exo}) as a function of T_a for a melt-spun $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous alloy.

was defined by $\Delta H_{\text{exo}} = \int \Delta C_p dT$, $\Delta C_p (= C_{p,a} - C_{p,q}) \geq 0$.

Figure 3 shows the ΔH_{exo} value as a function of T_a for the La-Al-Ni amorphous samples. The ΔH_{exo} increases gradually with increasing T_a in the temperature range below 430 K and shows a constant value at temperatures above 440 K, indicating that the irreversible structural relaxation is completed upon annealing for 1.8 ks at temperatures above 430 K. As shown in Fig. 1, the annealing-induced embrittlement takes place for the sample in which the ΔH_{exo} is released by about 74%, indicating that there is a rather close correspondence between the embrittlement tendency and the release of ΔH_{exo} .

In addition to the ΔH_{exo} corresponding to the difference between $C_{p,a}$ and $C_{p,q}$, only for the samples embrittled upon annealing at T_a above 420 K shown in Fig. 2, one can notice the difference between $C_{p,a}$ and $C_{p,s}$ corresponding to an endothermic reaction which can be evaluated by equation, $\Delta H_{\text{endo}} = \int \Delta C_p (= C_{p,a} - C_{p,s}) dT$, $\Delta C_p (= C_{p,a} - C_{p,s}) \geq 0$. That is, the ΔH_{endo} reaction is recognized only for the embrittled samples. It has been reported⁽¹³⁾ that the endothermic reaction takes place reversibly by the reversion of an annealing-induced relaxed structure into an unrelaxed structure upon heating to a higher temperature above T_a . Accordingly, the development of the structural relaxation leading to the endothermic reaction appears to take place only in the embrittled samples, indicating the possibility that the embrittlement takes place through the development of structural relaxation leading to the endothermic reaction. In other words, the annealing treatment which does not cause the appearance of the endothermic reaction does not have a harmful influence on the good bending ductility which is inherent to an as-quenched amorphous alloy.

The endothermic reaction for the sample annealed at T_a above 420 K is a reversible process⁽¹⁴⁾. Accordingly, when the endothermic reaction of the embrittled sample is eliminated by subsequent heat treatment, it is expected that the embrittled sample changes into a ductile state. It is generally known that the structural relaxation caused

by annealing can be eliminated by water quenching from the supercooled liquid state between T_g and T_x , accompanied by the introduction of disordered atomic configuration leading to an exothermic reaction. Accordingly, the change in the ϵ_f as a function of water quenching temperature was examined for the La–Al–Ni amorphous alloy embrittled by annealing for 1.8 ks at a high temperature of 450 K corresponding to $0.95 T_g$. As shown in Fig. 4, the samples which were quenched from the temperature region between T_g and T_x into water exhibit a fully restored ductility defined by $\epsilon_f = 1.0$. In order to confirm the reductilization phenomenon of the embrittled sample, the fracture surface appearance was observed by SEM. Figure 5 shows the tensile fracture surface appearance of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous samples in a melt-spun state, an annealed state for 1.8 ks at 450 K and a water-quenched state from 510 K after the annealing. It is seen that the fracture surface appearance of the three samples corresponds to the ductile, brittle and ductile states, respectively. That is, the ductile samples in the melt-spun and the water-quenched states exhibit the surface appearance consisting of a smooth region caused by shear sliding and a vein region by subsequent catastrophic failure. On the other hand, the embrittled sample shows a shell-like pattern. It should be noted that the shell-like pattern for the embrittled sample changes to the pattern consisting of smooth and vein regions characteristic to the ductile amorphous sample. It is believed that this is the first evidence of the fracture surface appearance revealing the recovery of the embrittled to reductilized states for amorphous metallic materials.

Figure 6 shows the thermograms of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous samples subjected to water quenching from the temperature range of 480 to 540 K after annealing for 1.8 ks at 450 K. The samples reductilized by water quenching from the temperature above T_g (≈ 470 K)

Fig. 4 Change in the bending fracture strain (ϵ_f) as a function of water quenching temperature (T_Q) for an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy embrittled upon annealing for 1.8 ks at 450 K.

show only the exothermic reaction due to structural relaxation and one cannot see an endothermic peak which was observed for the embrittled sample. On the other hand, the sample subjected to water quenching from the temperatures of 450 and 460 K below T_g remains brittle and shows a similar endothermic reaction as that for the an-

Fig. 5 Tensile fracture surface appearance of an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy. (a) melt-spun, (b) annealed for 1.8 ks at 450 K, (c) water-quenched from 510 K after annealing for 1.8 ks at 450 K.

Fig. 6 The temperature dependence of apparent specific heat ($C_{p,a}$) of an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy subjected to water quenching from different temperatures between 450 and 540 K after annealing for 1.8 ks at 450 K. The data of $C_{p,q}$ and $C_{p,s}$ are also shown for comparison.

nealed sample. These data allow us to derive the conclusion that the structural change in the amorphous phase leading to the disappearance of the endothermic reaction as well as the appearance of the exothermic reaction plays an important role in the achievement of the reductilized state. It has been reported⁽¹⁵⁾ that the endothermic reaction is due to the annihilation of the relaxed atomic configuration and the exothermic reaction due to the development of structural relaxation from the quenching-induced disordered state. Accordingly, the reductilization caused by water quenching from the temperature region between T_g and T_x is presumed to originate from the annihilation of the annealing-induced relaxed structure and the introduction of quenching-induced disordered structure.

The interference functions of the as-quenched, embrittled and reductilized samples are shown in Fig. 7. Some differences are observed in the interference functions of the as-quenched and embrittled samples. For example, a shift towards smaller Q values and increase in an amplitude of the oscillations. Similar structural variations related to the structural relaxation process due to annealing are commonly observed in other amorphous alloys⁽¹⁶⁾. On the other hand, the interference functions of the embrittled and reductilized samples are almost identical, which implies that the reductilization process is not accompanied with a distinct change in the total atomic structure. Nevertheless, the following observation may be suggested in terms of the near neighbor

Fig. 7 Interference functions $Q_i(Q)$ of (a) embrittled (full curve) and as-quenched (dotted curve) samples and their difference in the top, and (b) those of reductilized (dotted curve) and embrittled (full curve) and their difference in the bottom. Densities of the as-quenched, embrittled and reductilized samples are 5.83, 5.91 and 5.95 Mg/m^3 , respectively.

atomic distribution described in the reduced RDFs of Fig. 8. By comparing the reduced RDF of the as-quenched sample with the embrittled sample, the main peak shows a shift towards larger r , and the first peak maximum becomes more intense and sharper in the embrittled sample. Because of the ternary system, the reduced RDF is a sum of the 6 partial reduced RDFs of the 6 different atomic pairs. Thus, the separation of the reduced RDF into the partial RDFs is practically impossible in the present measurements alone. However, referring to the Goldschmidt radii of La (0.187 nm), Al (0.143 nm) and Ni (0.124 nm)⁽¹⁷⁾, it is likely that the environmental structure around La is mainly changed in the embrittlement process. On the other hand, the reductilization process produces a slight shift of the first peak maximum towards a smaller r , and the sharpness of the peak is decreased and smoothed out at some details as shown in the bottom of Fig. 8. The differences of the reduced RDFs between the embrittled and as-quenched samples, and between the reductilized and embrittled samples in the nearest-neighboring region from 0.2 nm to 0.45 nm are magnified and shown with the full and dotted curves in the middle of Fig. 8. The profiles of the difference show an inverse pattern of $G(r)$. Consequently, it appears that the reductilization process is reversed by the embrittlement process.

Srolovitz *et al.*⁽¹⁸⁾ explained the width and height of the peaks of the RDF by the atomic-level hydrostatic stress introduced into amorphous solids by rapid quenching and mentioned that the width of the hydrostatic stress

Fig. 8 Comparison of reduced radial distribution functions $G(r)$ of embrittled (full curve) and as-quenched (dotted curve) samples in the top and those of reductilized (dotted curve) and embrittled (full curve) in the bottom. The difference of the $G(r)$ between the embrittled and as-quenched samples, and between the reductilized and embrittled samples in the nearest neighboring region from 0.2 nm to 0.45 nm are shown in the middle.

distribution provides an indication regarding the degree of the structural relaxation of the amorphous solids. According to their discussion, the features of the RDF observed in the reductilization process are related with the wider stress distribution. Although the relaxed structure in the embrittled sample does not change much by annealing at a temperature above the T_g , the stress fluctuation is introduced by water quenching from the supercooled liquid region on the analogy of the sample rapidly quenched from the melt. It appears that this introduced stress fluctuation stabilizes the amorphous alloys with a disordered atomic configuration⁽¹⁹⁾ and recovers the ductility.

IV. Conclusion

The $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ amorphous alloy embrittled by annealing for 1.8 ks at high temperatures between $0.87T_g$ and $1.0T_g$ exhibits an excess endothermic peak on the

reheated DSC curve, accompanied by the disappearance of the endothermic peak. The subsequent water quenching from the temperature region between T_g and T_x causes a reductilization even for the sample embrittled at high temperatures near T_g , accompanied by an annihilation of the endothermic reaction and an appearance of the exothermic reaction. Since the endothermic peak which was observed for the embrittled samples originates from the development of the reversible relaxed structure, the annealing-induced embrittlement seems to result from the development of the reversible relaxed structure and the annihilation of the disordered atomic configuration. The X-ray diffractometry data also support that the water quenching of the embrittled samples from the supercooled liquid region causes the structural change of relaxed to unrelaxed atomic configurations. It is therefore concluded that the reductilization can be obtained for the sample which was subjected to the heat treatment so as to suppress the development of reversible relaxed structure and to introduce a disordered structural state.

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