PRESSURE EFFECT ON CRYSTALLIZATION KINETICS OF AN Al–La–Ni AMORPHOUS ALLOY

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Abstract—The pressure effect on the crystallization kinetics of an amorphous Al89La6Ni5 alloy has been investigated by means of piston-cylinder measurements within a pressure range of 0–1.0 GPa. It was found that an applied pressure enhances the first primary crystallization, i.e. the precipitation of f.c.c.-Al from the amorphous phase. The crystallization temperature decreases from 495 to 440 K when the applied pressure increases from ambient to 0.9 GPa. Meanwhile, the thermal stability of the residual amorphous phase with the Al dispersion is elevated at higher pressures. The crystallization temperature of the residual amorphous phase increases by 35 K/GPa when the pressure increases. The observed pressure effect on the crystallization kinetics in the amorphous alloy, which cannot be interpreted by means of the pressure effect on atomic diffusion, may be well understood in terms of the volume change effect at the early stage of crystallization.

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1. INTRODUCTION

In recent years, Al-based amorphous alloys including Al–RE(La,Y,Ce)–TM(Fe,Co,Ni) systems with an Al concentration of about 90 at.% have attracted increasing attention owing to their high specific strength combined with good ductility [1–3]. By partially crystallizing the as-quenched Al-based amorphous alloys so that nanometer-sized f.c.c.-Al precipitates homogeneously in the amorphous matrix, one can achieve enhanced mechanical properties [4–8]. The extraordinary mechanical properties make this class of amorphous alloys (or amorphous/nanocrystalline composite materials) a promising candidate as advanced engineering materials. However, due to the high cooling rate required for producing the Al-based amorphous alloys by means of melt-quenching techniques, the as-produced amorphous alloys are generally powders or ribbons which are not suitable for engineering applications. In order to overcome this shortcoming, attempts have been made to fabricate the bulk sample of amorphous alloys by means of proper consolidation of the melt-quenched thin ribbons or powders [3, 9, 10]. In the consolidation process, one of the fundamental issues is the pressure effect on thermal stability of the amorphous phase that is critical for optimizing the consolidation parameters (temperature, pressure and time) in order to get a dense compact without devitrification of the amorphous alloy. On the other hand, the pressure effect on crystallization of the amorphous alloy is also crucial for the engineering application of these metastable materials as well. However, to the authors’ knowledge, the pressure dependence of the thermal stability of the Al-based amorphous alloys has not been studied yet.

Previous studies have shown that the external pressure retards the crystallization by raising the crystallization temperatures for most amorphous alloys [11–16]. This phenomenon is normally attributed to the pressure effect on the atomic diffusion during the crystallization process. Although an applied pressure will eventually create an obstacle for atomic diffusion during crystallization, some experimental observations cannot be interpreted merely by considering the atomic diffusion mechanism. For example, in the polymorphous crystallization of amorphous Se, in which atomic diffusion does not play a dominant role, it was found that an applied pressure elevates significantly the crystallization temperature [17]. Upon annealing Al-based amorphous alloys, normally a primary crystallization process occurs in which atomic diffusion plays a dominant role, one may reasonably anticipate that an applied pressure will decrease the atomic diffusivity and hence increase the primary crystallization temperature. This prediction needs to be verified by experimental measurements.

In the present paper, we report on an experimental investigation on pressure effects on the crystallization temperature for an Al89La6Ni5 amorphous alloy within a pressure range of 0–1.0 GPa. The applied pressure was found to decrease the primary...
crystallization temperature for the precipitation of f.c.c.-Al from the amorphous phase, while it increases the crystallization temperature of the residual amorphous phase. This phenomenon, which cannot be interpreted in terms of the atomic diffusion mechanism, will be analyzed by considering the volume change effect at the early stage of crystallization.

2. EXPERIMENTAL

An Al_{89}La_{6}Ni_{5} master alloy was prepared by arc melting a mixture of pure Al (99.99 wt%), La (99.99 wt%) and Ni (99.99 wt%) rods under purified argon atmosphere on a water-cooled copper hearth. The amorphous alloy ribbon about 4.5 mm wide and 40–60 μm thick was fabricated by using a single roller melt-spinning apparatus. The amorphism of the alloy ribbon was proven by X-ray diffraction (XRD) and thermal analysis experiments. XRD experiments were carried out on a Rigaku X-ray diffractometer with Cu-Kα radiation (12 kW). Thermal analyses were made by using a differential scanning calorimeter (DSC-7, Perkin-Elmer) under a flowing high-purity Ar atmosphere. The densities of the amorphous and as-crystallized Al_{89}La_{6}Ni_{5} samples were measured by means of hydrostatic weighing using CCl₄ as working fluid.

A piston–cylinder pressure vessel with an internal diameter of 8 mm was used at pressures up to 1.0 GPa in a vacuum chamber (3 × 10⁻³ Pa). The experimental setup and measurement procedures were described in detail previously [17]. The amorphous ribbons with a total weight of about 0.5 g were placed into the vessel randomly after cleaning in acid (HCl). A thermal couple was placed under the vessel to monitor the sample temperature. The difference between the actual temperature of the specimen in the vessel and the temperature measured by the thermal couple was less than 3 K, and all the measured temperatures have been amended. The applied pressure accuracy is about ±1%. Prior to heating the sample under pressure, the specimen was compressed at 1.0 GPa for 30 min at ambient temperature in order to densify the ribbons.

3. RESULTS AND DISCUSSIONS

Figure 1(a) shows a typical measurement result of the pressure applied to the sample as a function of temperature with a preset pressure of 50 MPa. It is seen that upon heating, the pressure rises continuously due to the thermal expansion of the amorphous ribbon sample and the piston. When the sample temperature reaches about 470 K, a plateau appears in the P–T curve, which corresponds to a peak in the differential curve (dP/dT–T) as shown in Fig. 1(a). This implies that a densification process occurs due to a phase transformation with a negative volume change or alternatively due to an annihilation process of voids inside the compacted sample. The XRD results proved that the first peak originated from precipitation of f.c.c.-Al from the amorphous matrix. That is consistent with the DSC measurements [see Fig. 1(b)], i.e. a primary crystallization process occurs in the amorphous alloy, which is similar to the crystallization process in other Al-based alloys [1–3]. The second transition detected in the P–T (or dP/dT–T) curve appears at about 590 K, which corresponds to a further crystallization of the residual amorphous phase into intermetallic compounds including La₃Al₁₁, Al₃Ni, AlNi₃, and Ni₃La, as indicated by the XRD measurements. The peak temperatures determined in the dP/dT–T curve at a preset pressure of 50 MPa are very close to those from the DSC.
measurement at ambient pressure because the preset pressure is relatively low.

It is also noted from Fig. 1 that the first peak in the $dP/dT$ curve onsets at a lower temperature than that in the DSC curve. This may indicate an annihilation of voids (between amorphous ribbons) occurs due to the viscous flow effect of the amorphous ribbons under pressure during heating. It is known that upon heating, the amorphous solids normally undergo a glass transition prior to the onset of its first crystallization process. During the glass transition, the viscosity of the amorphous phase drops substantially by a few orders of magnitude. Therefore, the amorphous ribbon might yield under pressure prior to the primary crystallization, resulting in a densification of the compacted sample due to a substantial flow of the ribbons to fill up the voids between them.

Figure 2 gives the pressure vs temperature curves and the corresponding differential curves for the first transition under different pressures. One can find that, at higher pressures (c–g), the peak becomes deep and wide, and the peak temperature decreases significantly in comparison with those at low pressures. Apparently, a large peak is formed at higher pressures, which covers up the crystallization peak.

In order to identify the origin of the large peak at high pressures, XRD analyses were carried out in several samples that were heated to different temperatures under different pressures and quenched to room temperature, as indicated in Fig. 2. Figure 3 shows the XRD patterns of these samples. It is seen that sample H1 is still an amorphous phase, indicating the large peak at higher pressures does not result from the crystallization process of the amorphous phase. As discussed above, this peak can be reasonably attributed to the densification process due to yielding and flowing of the amorphous ribbons. When the applied pressure is low, the densification process is not evident, as shown in Figs 2(a) and (b), because the yielding strength of the ribbon might not be reached. When the pressure is increased, the amorphous ribbons may be yielded prior to crystallization and the onset temperature decreases with increasing pressure. When the pressure reaches 820 MPa, the yielding temperature drops to about 360 K. By extrapolating this variation tendency to room temperature, the pressure needed to yield the amorphous ribbon is estimated to be about 1200 MPa, which is close to the yielding strength of the Al-based amorphous alloy [3].

From Fig. 3 one can see that at high pressures, the primary crystallization of f.c.c.-Al in the amorphous matrix occurs after the large peak of the $dP/dT$ curve in Fig. 2. At a heating rate of 8 K/min, the amorphous ribbon crystallizes at about 448 K under 900 MPa, while no phase transition occurs until 470 K under 40 MPa. Similar XRD experiments were carried out for the samples under other pressures [Figs 2(b)–(f)]. According to the XRD results for the samples under different pressures, the crystallization temperature can be determined, as indicated by the dotted line. It is obvious that the crystallization temperature decreases evidently as the applied pressure rises, indicating that the applied pressure significantly enhances the precipitation of f.c.c.-Al from the amorphous phase.

Figure 4 illustrates the $P$–$T$ and $dP/dT$–$T$ curves for the second transition, i.e. the crystallization of the residual amorphous phase into intermetallic compounds. The crystallization temperature was found to increase evidently with pressure from 600 K at 30 MPa to 633 K at 1.0 GPa. XRD experiments verified these results. It implies that the applied pressure enhances the thermal stability of the residual amorphous phase with the f.c.c.-Al dispersion.

Figure 5 summarizes the pressure dependence of the crystallization temperatures for the two crystallization processes in the Al–La–Ni amorphous alloy. The data for ambient pressure were obtained in DSC experiments, which showed a good agreement with the data obtained in the piston–cylinder
measurements. With an increase of the applied pressure, the primary crystallization is shifted to lower temperatures while the second crystallization process of the residual amorphous phase is shifted to higher temperatures. It means the temperature gap between the primary crystallization of f.c.c.-Al and the subsequent crystallization of intermetallics is widened by application of pressure from about 100 K at ambient pressure to about 190 K at 1.0 GPa. By extrapolating this tendency, one may anticipate that when a pressure of about 2.5 GPa is applied, f.c.c.-Al precipitation may occur even at room temperature. This speculation might be correlated with a previous observation of f.c.c.-Al precipitation within the shear bands induced by bending of an Al$_{87}$Y$_4.3$Ni$_{8.7}$ amorphous alloy at room temperature [18], although the crystallization was attributed to the large permanent strain within the shear bands. During bending of an amorphous ribbon, the local pressure at the compression side might be as high as a few GPa, under which it is possible to initiate the primary crystallization of Al precipitation even at room temperature. In the sample which has undergone a large permanent deformation, e.g. sample H1 in Fig. 2, there is no evidence of crystallization from the XRD pattern (Fig. 3). Therefore, it can be speculated that the precipitation of Al during bending the amorphous alloy is probably due to the high pressure effect on the primary crystallization kinetics in the amorphous Al-based alloy.

It is normally anticipated that for a primary crystallization process, in which atomic diffusion is dominating, an applied pressure will depress the atomic diffusivity and hence elevate the crystallization temperature. However, our observation in the present study is that an applied pressure significantly decreases the primary crystallization temperature. This is obviously contradictory with the prediction based on the atomic diffusion mechanism. Our isothermal DSC analysis indicated that the primary crystallization process is a nucleation (with a decreasing nucleation rate) and three-dimensional diffusion-controlled growth progress, with a typical Avrami exponent of 2.5 [19], which agrees with the observations in other Al-based amorphous alloys [20, 21]. It is obvious that the pressure effect on atomic diffusion is not the major factor governing the primary crystallization process in the Al-based amorphous alloys under pressure.

From a thermodynamic point of view, the free energy change for forming a sphere crystal nucleus in an amorphous phase under a pressure $P$ can be expressed as

$$\Delta G^*(T,P) = \frac{1}{6} \pi d^3 (\Delta G_v + E) + \pi d^2 \gamma + P \Delta V$$

(1)

where $d$ is the diameter of the crystalline nucleus, $\Delta G_v$ the free energy change for forming the unit volume crystalline phase, $E$ the elastic energy induced by the volume change during the transformation in the solid state, $\gamma$ the interfacial energy of the crystalline/amorphous (c/a) interface, and $\Delta V$ the volume change for forming this nucleus. One can see the volume change during the transformation becomes one of the controlling factors when pressure is applied.

Crystallization of an amorphous solid is normally regarded as a process taking place by crystal nucleation and subsequent growth. During the nucleation process, a crystalline embryo is formed in the amorphous matrix, and meanwhile a c/a interface is constructed simultaneously. The c/a interface is lower coordinated compared with the crystalline phase and the amorphous phase. The interface between the amorphous and crystalline phase should be considered in the calculation of the volume change $\Delta V$, especially when the crystallite size is small. For an extremely small crystalline embryo the volume ratio of interface/crystallite is high, and the contribution of interface to the total volume change is significant during the nucleation process.

We have investigated the crystallization behavior of amorphous Se under pressure [17]. According to our calculation the overall volume change is positive at the start of nucleation. Hence, the formation of Se nucleus needs more energy to overcome the enhanced energy barrier due to the volume expansion, which results in the increase of crystallization temperature.

In the present study, the precipitation of f.c.c.-Al from amorphous matrix can be expressed as

$$\text{am} \rightarrow \text{Al (f.c.c.)} + \text{am'} + \text{c/a interface}.$$  

Hence, the volume change when forming a spherical Al nucleus with a diameter of $d$ can be simplified as

$$\Delta V = aV^{\text{f.c.c.}} + bV^{\text{am'}} + cV^{\text{in}} - (a + b + c)V^{\text{am}}$$  

(2)

where $V^x$ is the molar volume of the $x$ phase, and
Fig. 6. The calculated volume change for forming a f.c.c.-Al nucleus in the amorphous phase as a function of the nucleus diameter at different pressures and with different c/a interface thickness (δ).

The residual amorphous phase (amorphous alloy are not available. In this paper, the residual amorphous phase in Al–La–Ni amorphous alloy increased after Al precipitation [22]. However, the modulus data of the residual amorphous phase (am) as 85 GPa, which is calculated from its bulk modulus of Al is 75 GPa. Experimental evidence shows that the strength of the Al-based amorphous alloy increased after Al precipitation [22]. However, the modulus data of the residual amorphous phase in Al–La–Ni amorphous alloy are not available. In this paper, the residual amorphous phase (am) is assumed to possess the same bulk modulus as the initial amorphous phase (am) as 85 GPa, which is calculated from its Young’s modulus of 75 GPa [23].

The excess volume of the interface is related to the interfacial energy by [24, 25]

$$\frac{\Delta H^{am} + (\gamma/\delta)V^in}{\Delta H^{am}} = \frac{\Delta V^{in}}{\Delta V^{am}}$$

(3)

Here, the excess entropy of the interface is neglected. Turnbull [26] has found that the ratio of γ to the melting enthalpy is approximately 0.45 for most metals. Assuming this ratio is the same for the amorphous phase since the amorphous solid can be considered as a supercooled liquid, ΔV^{am}/ΔV^{am} is 1.45 according to equation (3).

Figure 6 shows the volume change of the primary crystallization process as a function of the nucleus size at different pressures in the Al-based amorphous alloy. One can see that the volume changes are negative, and slightly increases at higher pressures. The results for different c/a interface thicknesses are nearly the same. According to equation (1), one may expect that the free energy change ΔG^{am} will be decreased by PΔV at higher pressure if the interface energy is constant within the pressure range of 0–1 GPa. Because the nucleation work ΔG^{*} is the maximum value of ΔG^{am}, which can be obtained when dΔG^{am}/dδ = 0, ΔG^{*} is also decreased when the applied pressure increases. Consequently, the primary crystallization temperature of the Al–La–Ni amorphous alloy will decrease with an increasing pressure.

For the second crystallization process of the residual amorphous phase into intermetallic compounds, which can be considered as a eutectic crystallization, an applied pressure suppresses the crystallization by increasing the crystallization temperature. This phenomenon may be analogous with the observations in eutectic crystallization of other amorphous alloys, e.g. Ni80P20 amorphous alloy [11]. The pressure effect on the eutectic crystallization kinetics should also be further investigated in terms of the volume change effect at the early stage of crystallization, which is in progress.

4. CONCLUSIONS

The applied pressure enhances the precipitation of the f.c.c.-Al from the amorphous phase. The primary crystallization temperature decreases from 495 to 440 K when the pressure increases from ambient to 0.9 GPa. On the other hand, the crystallization temperature for the residual amorphous phase increases from 598 to 633 K due to the pressure increase from 0 to 1.0 GPa. We believe that the pressure effect on the crystallization kinetics of amorphous solids depends on the volume change during the transformation, especially at the initial stage of nucleation in which the significant effect of the crystalline/amorphous interface formation should be taken into account.

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