CRYSTALLIZATION OF AL-GD-LA-NI METALLIC GLASSES

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ABSTRACT

The crystallization kinetics of Al-Gd-La-Ni metallic glasses to nanostructured phases are analyzed using differential scanning calorimetry and transmission electron microscopy. In a narrow alloy composition range near $Al_{88}Gd_6La_2Ni_4$, TEM reveals an amorphous phase separation that occurs upon annealing at low temperatures prior to crystallization. Al-enriched regions, typically 40 nm in diameter, bounded by rare-earth rich regions, are visible. Upon crystallization, α-Al forms preferentially at the interface between these phase separated regions. The relevance of this crystallization sequence to previous work in Al-RE-TM glasses and to the evolution of nanoscale microstructures common in the crystallization of other metallic glasses are discussed.

INTRODUCTION

Nanocrystalline alloys are interesting due to their improved mechanical properties, including hardness, strength, and corrosion resistance [1-2]. Further, devitrification of the glass is a superior method for nanostructure formation since it is not hindered by the impurity problems inherent in compaction processes. An improved understanding of the nucleation and growth processes involved will lead to an increased ability to control the microstructural evolution through annealing.

Although the crystallization behavior of Al-based and Zr-based metallic glasses has been studied extensively, the mechanisms that lead to primary crystallization on a nanometer scale are unclear. In some Zr-based alloys this has been attributed to spinodal decomposition in the liquid and glass [3-4]. Current explanations in Al-based alloys rely on either extremely high heterogeneous nucleation rates [5] or the formation of aluminum-rich regions in the glass adjacent to sub-critical-sized clusters, due to a coupling between long-range diffusion and interfacial attachment [6].

In this work, we report evidence for phase separation prior to crystallization within a narrow compositional range for an Al-[Gd-La]-Ni alloy. Subsequent crystallization appears to proceed first by preferential nucleation at the interface between the phase separated regions, followed by homogeneous nucleation inside the Al-rich regions when the interface regions are saturated. To our knowledge, this is the first evidence for phase separation in Al-rich Al-RE-TM metallic glasses. The degree to which this is important for the crystallization of other Al-based metallic glasses is yet unclear.

EXPERIMENT

Alloys were prepared by arc-melting mixtures of the constituent elements in the desired proportions on a water-cooled copper hearth in a gettered argon atmosphere. The ingots were subsequently remelted in a boron nitride crucible to avoid sample contamination, and quenched onto a rotating copper wheel (60m/s). The temperature of the melt during quenching was monitored with a one-color optical pyrometer to ensure adequate superheating above the alloy liquidus. For the electron microscopy crystallization studies, part of the uniform ribbons obtained were wrapped in Al foil and annealed in a lead-tin solder bath. This ensured short equilibration times relative to the total annealing times.

The as-quenched and annealed samples were characterized with a Rigaku x-ray diffractometer (XRD) using CuK$_\alpha$ radiation, a Perkin-Elmer Differential Scanning Calorimeter 7 (DSC) and a JEOL 2000FX transmission electron microscope (TEM) equipped with a Noran energy dispersive spectrometer. The ribbons were thinned for TEM studies using a Gatan ion mill; during milling, samples were cooled by a liquid nitrogen bath to minimize milling-induced transformations. Since ion irradiation can damage nanocrystalline and amorphous alloys, electrolytic jet-thinning, with a nitric acid and methanol mixture at -20°C, was also used to confirm that the microstructural features observed were not artifacts of the thinning procedures.

RESULTS AND DISCUSSION

Previous studies of glass formation in $Al_{88}Gd_xLa_{8-x}Ni_4$ ($0 \le x \le 8$) alloys showed that $Al_{88}Gd_6La_2Ni_4$ is the optimum composition for glass formation and crystallization studies[7]. Those alloys show a clear glass transition T_g at 230°C in nonisothermal DSC studies (Fig. 1) and precipitate nanometer-sized α-Al grains in the amorphous matrix upon crystallization at the onset temperature (T_x) of 242°C . The XRD peaks from this alloy are broad, consistent with an amorphous structure. TEM examinations of the as-quenched alloys reveal broad rings in the diffraction patterns, characteristic of amorphous materials, and no regular contrast patterns in bright field images (Fig 2a). The existence of a crystallization peak in isothermal DSC, consistent with nucleation and growth and not grain growth, provides further evidence that the as-quenched samples are amorphous. In the temperature range where this peak was detectable, it occurred within the first minute of the transformation. The peak could only be distinguished from the DSC transient when a second isothermal scan was performed and used as a baseline. This technique is valid since the specific heats and heat transfer characteristics of the samples do not appear to change markedly upon formation of the α-Al/amorphous composite. The sum of the enthalpies measured for the isothermal DSC scans with those measured in subsequent nonisothermal scans are comparable to the values measured for nonisothermal scans of the as-quenched ribbons. This confirms that the DSC instrumental transients were correctly taken into account for the measurements of the isothermal peaks reported here.

Phase Separation

Isothermal anneals for various times were made at different temperatures (190°C, 220°C, and 250°C), which are at and below the crystallization onset in a nonisothermal DSC scan (20 C/min), T_x = 242°C. Samples annealed at 220°C, 22°C below T_x, showed possible evidence for phase separation developing at short annealing times (within several minutes). XRD scans of these samples showed no evidence for crystal phases. However, a comparison between the TEM microstructures observed in bright-field studies for the as-quenched alloy and a sample annealed for 1 minute (Fig.2) shows the development of contrast upon annealing. Approximately spherical weakly scattering regions, with a typical diameter of 40 nm, are surrounded by more strongly scattering boundaries. The selected area diffraction patterns still show wide amorphous halos, with no evidence for rings from α-Al. Microdiffraction on both the spherical regions and the boundaries also showed no evidence of crystallinity. Similar results were obtained in the samples prepared by ion-milling and electrochemical jet-thinning, suggesting that they do not arise from thinning damage alone.

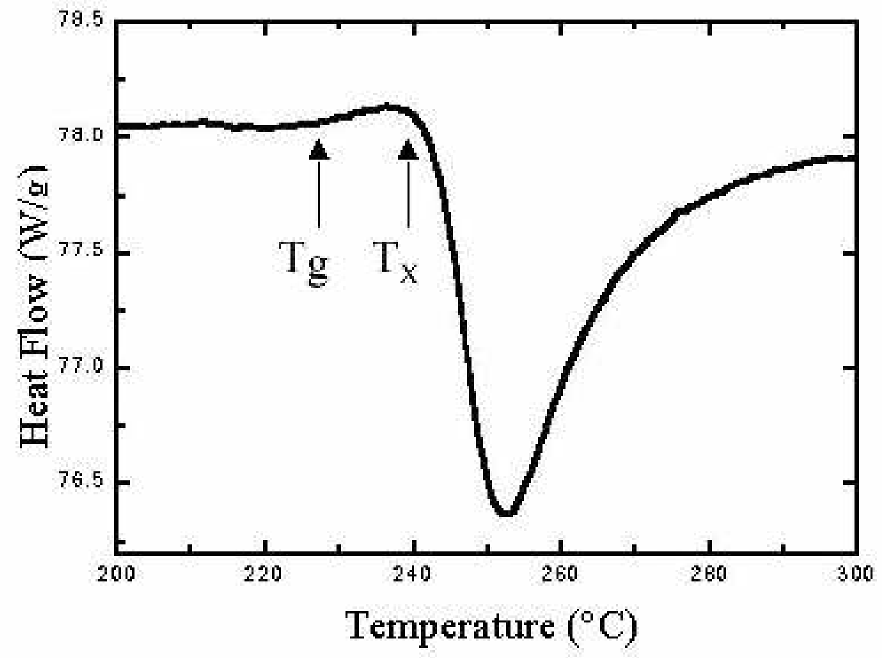

Fig.1. DSC scan of $Al_{88}Gd_6La_2Ni_4$ at 20°C/min.

In the absence of crystallization, the observed contrast must therefore arise from composition or thickness variations, due to differences in the milling rates of the two amorphous regions. EDS studies indicated a slightly elevated rare-earth concentration in the strongly scattering regions, as if rare earth elements had segregated to these boundaries. Quantification of the compositional difference with the JEOL 2000FX was difficult, however, due to sample drift and beam spreading outside of the small regions (≈10 nm in diameter) and the relatively low concentration of the rare earth. More detailed studies of the compositional difference on phase separation, using electron energy loss spectroscopy (EELS) image filtering, are in progress. Isothermal anneals made at a slightly lower temperature of 190°C (52°C below T_x) for 1 to 2 hours produced a clearer development of the phase-separated regions prior to crystallization. Weakly scattering regions with a similar length scale to those produced by annealing at 220°C were found. In some regions, however, the morphology changed from spherical to row-like.

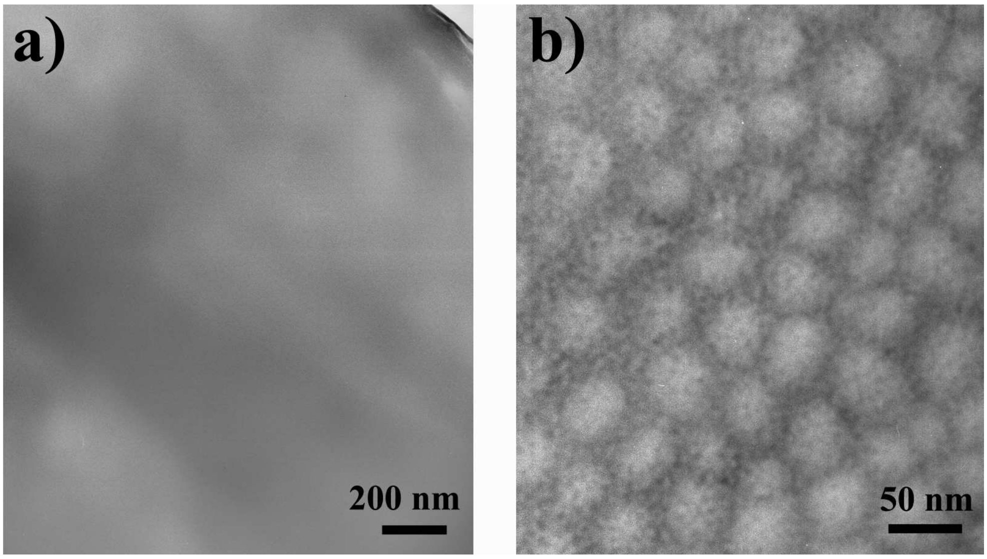

Fig. 2. a) as-quenched $Al_{88}Gd_6La_2Ni_4$ and b) $Al_{88}Gd_6La_2Ni_4$ annealed for one minute at 220°C.

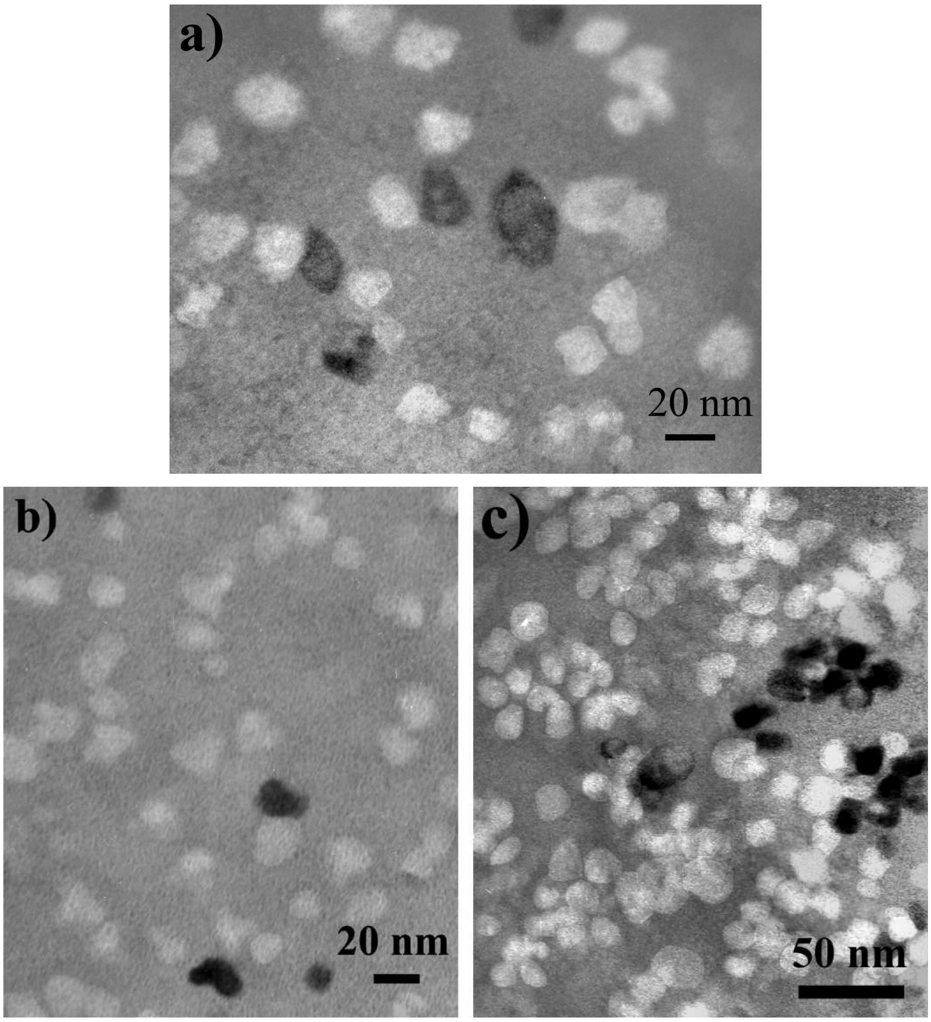

Fig. 3. $Al_{88}Gd_6La_2Ni_4$ annealed for a) 10 hours at 190°C, b) 1 hour at 220°C and c) 10 minutes at 250°C

Crystallization Behavior

Isothermal anneals at 190°C (52°C below T_x) show evidence for the preferential nucleation of the α-Al at the boundary between the two phase separated regions (Fig. 3a). Evidently, the α-Al wets this boundary, leading to a lowered interfacial free energy. The adjacent schematic clarifies the observed microstructure (Fig.3b).

Isothermal anneals made at 220°C for various times (3, 4, 5, 10 min) produced a spatially inhomogeneous grain distribution of α-Al, which is not surprising given that the nucleation and growth occurred in compositionally inhomogeneous phase-separated regions. The α-Al grains were often clustered together, leaving relatively large regions untransformed(Fig. 3b).

Isothermal anneals made at 250°C, slightly above the crystallization onset temperature, showed a larger nucleation rate, producing a more dense microstructure with a slightly smaller average grain diameter of around 10 nm (Fig. 3c). In this case, preferential nucleation at the phase boundaries likely occurred first, followed by homogeneous nucleation within the Al-rich regions.

As noted earlier in Al-based glasses, an abnormal growth rate was observed [8-9]. Growth slowed abruptly after the grains reached a maximum diameter of approximately 20 nm. After α-Al crystallization near these interfaces, the remainder of the Al-rich regions was subsequently transformed by further nucleation and growth in the interior of the region. The rare-earth rich regions remained amorphous.

Related Al-RE-TM systems

To assess the impact of this result on the crystallization behavior in related Al-RE-TM glasses, a preliminary study was made to determine if phase separation is a universal phenomenon in these alloys. Because mass/thickness contrast is masked in fully transformed nanocrystal samples, examinations were made of as-quenched ribbons of some other compositions after long annealing times at 60°C below the crystallization onset. No evidence was found in these anneals for phase separation prior to crystallization in the $Al_{88}Y_8Fe_4$ alloy. Crystallization did proceed more rapidly, indicating that that this glass is less stable to devitrification than $Al_{88}Gd_6La_2Ni_4$. Phase separation with a similar length scale to that observed in $Al_{88}Gd_6La_2Ni_4$ was observed in an $Al_{88}Y_8Ni_4$ amorphous alloy that was annealed for 1 hour at 140°C (60°C below T_x). Interestingly, a nearby alloy of composition $Al_{87.5}Y_{7.5}Ni_5$ did not show phase separation. This shows the extreme sensitivity of phase separation on alloy composition and could be a possible reason why phase separation was not observed in earlier studies on Al-Y-Fe and Al-Y-Ni amorphous alloys [5, 10].

CONCLUSIONS

The first evidence for possible phase separation prior to crystallization in Al-rich Al-RE-TM glasses was presented for a $Al_{88}Gd_6La_2Ni_4$ glass. Separation into Al-rich and Al-poor regions occurred with isothermal annealing below the crystallization onset temperature, measured in nonisothermal DSC studies. The precipitation of a high density of α-Al in the amorphous matrix occurred subsequently. The α-Al appeared to nucleate preferentially at the boundary between the phase-separated regions. The grain growth was initially rapid, likely due to a rapid diffusion coefficient near the boundary and the more favorable composition in the Al-rich region. After a cessation of growth of these heterogeneously nucleated grains, the phase transformation continued to completion by homogeneous nucleation and growth in the interiors of the Al-rich regions. Studies of glass formation near this compositional range suggest that the glasses crystallizing by this mechanism are more stable than adjacent compositions that do not appear to phase separate. More detailed work on the effect of composition on phase separation and the influence of phase separation on the nucleation and growth of Al-nanocrystals is in progress.

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