Materials Science and Engineering A 485 (2008) 532–543

MATERIALS SCIENCE & ENGINEERING A

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Development of fcc-Al nanocrystals in Al–Ni–Gd metallic glasses during continuous heating DSC scan

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Received 31 July 2007; received in revised form 7 August 2007; accepted 8 August 2007

Abstract

This paper examines the *early* crystallization stages in Al–Ni–Gd glass-forming alloys, especially in $Al_{87}Ni_7Gd_6$, $Al_{85}Ni_7Gd_8$ and $Al_{90}Ni_5Gd_5$, to more thoroughly quantify the mechanisms responsible for two-step fcc-Al nanocrystal formation phenomenon observed in certain amorphous Al alloys. Alloys were systematically studied using differential scanning calorimetry (DSC), X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution TEM techniques. It was found that a confined range of chemistries for Al–Ni–Gd alloys partially devitrified into fcc-Al nanocrystals during both the *first* and *second* stages. The morphology of fcc-Al nanocrystals evolves gradually from spherical to irregular as the bulk Al content is decreased, consistent with an earlier report [M.C. Gao, G.J. Shiflet, Scripta Mater. 53 (2005) 1129–1134]. The current study reveals a close relationship among crystallization behavior during continuous heating DSC, isothermal annealing and plastic deformation, especially on the compositional dependence. For alloys of high Al contents such as $Al_{87}Ni_7Gd_6$ whose first crystallization peak during a DSC scan spans a wide temperature range with a long decaying tail, the presence of medium-range Al clustering in the amorphous solid is responsible for exclusive formation of fcc-Al nanocrystals when annealed at low temperatures or when plastically deformed at room temperature and the absence of an apparent glass transition event. The morphology of the initially spherical nanocrystals evolves into irregular shapes after passing the first stage peak temperature. The fact that both particle number density and volume fraction keeps rising throughout both stages suggests continuous nucleation and crystal growth. For alloys of low Al contents such as $Al_{85}Ni_7Gd_8$, there is no sign of medium range Al clustering in the as-quenched state, and they exhibit a well-defined glass transition and a supercooled liquid regime. It is noted that the particle number density drops while the volume fraction rises during the second stage.

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Keywords: Al-base glasses; Crystallization; Continuous-heating DSC; TEM; Phase transformations; Medium range Al clustering

1. Introduction

The Al-rich (containing 80–92 at.% Al) Al-TM-RE (TM = transition metals; RE = rare earth elements) glasses [1–3] are highlighted by their light-weight, tunable corrosion resistance and high fracture strength, greater than 800 MPa [1–5]. This set of properties make Al-based glasses very promising materials for potential aerospace applications. Because of the relatively weak metallic bonding in metallic glasses (compared to silicate glasses dominated by covalent bonds), they do often crystallize rapidly to reduce their total free energy for the system when the temperature is lower than or approaching the glass transition temperature (T_g). The mechanical properties of partially crystallized Al-glasses were first studied by Chen et al. [6], and by using TEM a quantitative density (10^{23} to 10^{20} m^{-3}) of the fcc-Al nanocrystals was reported. The fracture strength of the amorphous alloy containing fcc-Al increased by ∼20% (comparing to the glassy precusor) under optimal devitrification. Soon after this observation, a similar strategy has been applied to other glass-forming systems. For example, by tailoring the chemical components, bulk compositions and processing parameters, Johnson and coworkers [7,8] were able to successfully synthesize a novel composite with ductile crystalline bcc phase with a dendritic morphology embedded in a Zr-based amorphous matrix. They found the resulting composite exhibited significantly improved ductility and fracture toughness because the mechanically soft and ductile second phase stabilizes the composite against shear localization and critical crack propagation [7,8].

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doi:10.1016/j.msea.2007.08.009

With the possibility to develop an optimal composite structure to improve the combination of strength and ductility for Al-glasses, the crystallization process has been studied since 1990, especially focusing on the formation mechanisms of such a high density of fcc-Al nanocrystals [9–22]. Although a few differing models have been proposed, there is still no agreement concerning the formation mechanism. For instance, it has been suggested that there is a high density of "quenched-in" fcc-Al nuclei in the "amorphous" state [9–13]. This approach is based upon heterogeneous nucleation theory and has gained further support from the fact that many Al glasses (generally with Al contents larger than 85 at.%) do not exhibit a well-defined glass transition temperature, and thus their amorphous nature has been called into question [15]. The other evidence to support such an argument is the absence of an incubation signal during isothermal annealing at a temperature slightly lower than the first crystallization onset using differential scanning calorimetry (DSC), first exercised in 1988 [23]. In addition, a new model based on time-dependent homogeneous nucleation theory has been developed by Kelton [16,24] that links the stochastic fluxes of diffusion and interfacial attachment, followed by a phase separation model [14,17], which argues that phase separation into an Al-rich region and a solute-rich region occurs prior to nanocrystallization of fcc-Al crystals based on experimental observation on alloy $Al_{88}Gd_6La_2Ni_4$ [14]. Such phase separation has also been observed in alloys $Al_{88}Y_7Fe_3Cu_2$ and $Al_{85}Y_9Ni_6$ but not in $Al_{88}Y_7Fe_5$ [17], demonstrating its strong composition and system dependence, whose physical origins are not clear. However, contradictory claim has been made on phase separation in Al glasses by Tian et al. [25] who demonstrated that there is no phase separation occurring in the $Al_{88}Gd_6Er_2Ni_4$ amorphous alloy. Instead they found surface crystallization prior to the primary crystallization[1] of fcc-Al nanocrystals caused uneven foil thickness in TEM specimens prepared by electropolishing, resulting in artificial phase separation like contrast in TEM images. Further, early chemistry studies using analytical TEM on the fcc-Al crystals and the interfaces by Csontos and Shiflet [26,27] showed that the fcc-Al crystals are almost pure Al crystals free of solutes within the experimental error, agreeing with Tian et al. [25]. This makes sense because the solubility of all RE and most TM in the first row in the periodic table such as Ni and Fe (except Cu, Zn, Mn and Ti) in Al is essentially negligible [28]. Therefore, the product of the primary crystallization is referred to fcc-Al crystals in this report rather than α-Al that emphasize a solid solution of Al in previous reports. To conform to nomenclature used in the literature, both devitrification and crystallization are used to describe the devitrification of metallic glasses, which refers to the same process. In summary, the mechanism of crystallization in Al glasses are far from reaching a general consensus of understanding, but it certainly appears to be very composition and system dependant. This report attempts to study the early stages of crystallization in Al–Ni–Gd metallic glasses and examine the effect of broadening compositions.

The hypothesis of "quenched-in" Al nuclei was also questioned by the current authors [29–33], in light of observations that the particle number density continues to increase during the first thermal stage (DSC event) in several alloys (namely, $Al_{90}Ni_5Gd_5$, $Al_{87}Ni_7Gd_6$ and $Al_{85}Ni_7Gd_8$) and that both of the first *two* stages refer to formation of the same product phase, fcc-Al [31–33]. Johnson and coworkers [18,20] first observed the two-stage fcc-Al precipitation in the binary amorphous $Al_{90}Y_{10}$ but not in the Al–Fe–Y glasses they studied. The current authors identified two-stage fcc-Al formation in a few Al–Ni–Gd glasses [33] and confirmed it again in many alloys in this study. The behavior is that only fcc-Al nanocrystals are formed in the first *two* well separated and distinctive exothermic stages during a continuous heating DSC scan. The size and the volume fraction of the Al crystals are apparently larger after the second stage than after the first stage. This interesting observation raises many challenging questions, such as, what is the intrinsic reaction associated with these two stages? Is the increase in particle size and volume fraction because of nucleation and growth of new particles, or just growth? Is the nucleation homogeneous or heterogeneous and if the latter, what are the nucleation sites? Why are there two distinctly different stages (e.g., temperature onset, enthalpy, etc.) for the same product phase to form in the same alloy during a continuous heating DSC scan? To answer, or at least contribute to answers to these questions, a detailed experimental investigation on the structural evolution in these alloys during DSC experiments of 17 amorphous Al–Ni–Gd alloys was undertaken, with a focus on the quantitative evolution of Al crystal number density, volume fraction, morphology, etc.

2. Experimental procedures

The alloys were synthesized from pieces of Al (99.999% purity), Gd (99.9%) and Ni (99.995%) totaling about 5 g in a Ti-gettered arc-melter under an argon atmosphere. The buttons were remelted 4–5 times to ensure chemical homogeneity, and the weight loss was less than 1.0 wt.%. The ingots were then ground using SiC paper to remove surface oxide followed by cutting into small pieces (less than 6 mm). These pieces were placed in a quartz tube and underwent melt-spinning employing a Cu wheel in a partial He atmosphere, creating ribbons of 1–3 mm in width and 15–30 μm in thickness. Techniques including XRD and TEM were used to verify a wholly amorphous state of the as-spun ribbons. The XRD analysis was performed on a diffractometer using Cu Kα radiation. Specimens for TEM studies were thinned by electropolishing in a solution of 1 part nitric acid to 3.5 parts methanol at 8–12 V and −30 °C. Conventional TEM was done on a 200 kV instrument. The devitrified microstructures were characterized using XRD, TEM and a 400 kV top-centered high-resolution TEM (HRTEM). The thermal stability of the amorphous alloys was measured using a differential scanning calorimeter (DSC) at a rate of 20 K/min under a flowing argon environment.

To determine the product phase(s) formed at a particular crystallization stage, the scanning was deliberately halted after this

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[1] Primary crystallization in Al glasses refers to the first thermal event observed during DSC scan, which results in formation of fcc-Al crystals and a more supersaturated amorphous matrix than the initial glass.

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