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Novel deformation-induced polymorphic crystallization and softening of Al-based amorphous alloys

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ABSTRACT

Melt-spun amorphous ribbons of $Al_{90}Y_{10}$ (at.%) (90Al) and $Al_{84}Y_{8.5}Ni_4Co_2Pd_1Fe_{0.5}$ (84Al) are cold-rolled at near to liquid-nitrogen temperature or at room temperature, inducing partial crystallization to nanoscale fcc-Al (α-Al). The crystallization is characterized and contrasted with the distinct sequences of reactions on annealing 90Al and 84Al amorphous alloys. Rolling-induced crystallization leads to softening, opposite to the effect of nanocrystallization induced by annealing. The origins of the hardness changes are analyzed. The rolling induces novel polymorphic crystallization to α-Al with extended solid solubility. This transformation, which occurs equally in 84Al and 90Al, despite the much greater thermal stability of the former, allows the ribbons to retain good bending ductility, and delays the onset of embrittlement on subsequent annealing. Partial crystallization induced by cold-rolling is useful in avoiding the formation of compound phases associated with brittleness, and is a promising process for high-solute Al-based amorphous alloys to be further developed as structural materials.

1. Introduction

Aluminum-based amorphous alloys were first made in the system Al-Si-TM (TM = Fe, Co, Ni, Cu) [1,2], then in Al-Ln-(Ni,Co) (Ln = lanthanide metal) and Al-TM-(Ce,Y) (TM = Fe, Co, Ni) ternary alloys [3,4], and Al-Y-Ni-Co quaternary alloys [5]. Amorphous Al-Ln-TM alloys show tensile strengths above 980 MPa [3], with a maximum of >1500 MPa for Al-Y-Ni-Co-Sc [6]. On heating Al-based amorphous [am] alloys, in some cases, there is a glass transition followed by a supercooled-liquid (SL) region before crystallization which proceeds in stages. Above ~88 at.% Al, there is no detectable glass transition, and crystallization starts with the formation of fcc-Al (α-Al) nanocrystals: [am] → [am + α-Al] → [α-Al + compounds]. With 85–88 at.% Al, the sequence is [am] → SL → [am + α-Al] → [α-Al + compounds]. Below 84 at.% Al, the sequence is: [am] → SL → [α-Al + compounds] [7–10]. As recently shown [11] for the multicomponent alloy $Al_{84}Y_9Ni_4(Co,Fe,Pd)_3$ (at.%), the sequence is: [am] → SL → [am + α-Al + cubic Al_xM_y (M = Y, Fe, Co, Ni, Pd)] → [am + α-Al] → [α-Al + Al_3Y + $Al_9(Ni,Co)_2$ + unknown phase]. Here, the key observation is the novel reverse transformation [am + α-Al + Al_xM_y] → [am + α-Al], in which the volume fraction of amorphous phase increases on heating. The applications of Al-based amorphous alloys to date are mainly due to the exploitation of [am + α-Al] mixtures with high strength and good warm formability. The reverse transformation is of interest in expanding the composition and temperature ranges of the [am + α-Al] mixture. Importantly, the possibilities for achieving this phase mixture are extended in the present work.

Cold-rolling of Al-based amorphous alloys with 8–15 at.% solute causes the precipitation of α-Al nanocrystals in shear bands, and leads to a decrease in the onset temperature of crystallization on heating [12,13]. However, there has been no systematic study of compositional effects on these phenomena. The present work explores structural stability and mechanical properties for two Al-

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based amorphous alloys subjected to cold-rolling. The alloys are chosen from composition ranges with very different thermal stabilities. The $Al_{90}Y_{10}$ alloy [14] shows the onset of crystallization at 485 K. The $Al_{84}Y_{8.5}Ni_4Co_2Pd_1Fe_{0.5}$ alloy is similar to the $Al_{84}Y_{9}Ni_4(Co,Fe,Pd)_3$ alloys that show crystallization onset at ~576 K [11]. Upon cold-rolling, melt-spun amorphous ribbons of these alloys show a type of nanocrystallization not previously reported. Contrary to the hardening effect of thermally induced crystallization, the mechanically induced crystallization is associated with softening. We characterize the changes in structure, crystallization behavior, hardness and plasticity induced by cold-rolling, and explore the mechanisms of hardening and softening.

2. Experimental methods

The two alloys have nominal compositions (in at.%) of $Al_{90}Y_{10}$ (90Al) and $Al_{84}Y_{8.5}Ni_4Co_2Pd_1Fe_{0.5}$ (84Al). Ingots were prepared by arc-melting mixtures of elemental metals with purities above 99.8 wt% under an argon atmosphere. Alloy ribbons with a thickness of 35–45 μm and a width of 1.2 mm were prepared by melt spinning under an argon atmosphere. The structure of the as-spun ribbons was confirmed to be amorphous by X-ray diffractometry (XRD) (Suppl. Info., Fig. S1).

For cold-rolling, the ribbon samples were sandwiched between two type-304 stainless-steel plates, each with an initial thickness of 2 mm. The sandwich structures were passed through a twin-roller machine to obtain a thickness reduction of ~5% in each pass. Several passes were used to obtain ribbons with total thickness reductions in the range 20–85%. Rolling was conducted mostly close to liquid-nitrogen temperature (LNT, 77 K); for this, the sandwich structure was immersed in liquid nitrogen for 10 min before being taken out and immediately rolled. In some cases, for comparison, rolling was conducted at room temperature (RT). The initial Vickers hardness of the stainless steel sheet is 270 and this ultimately rises to ~600 as a result of the rolling.

The structure of the cold-rolled ribbons was examined by XRD, scanning electron microscopy (SEM), standard transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) including nanobeam diffraction. The spatial distribution of the component elements was examined by atom-probe field-ion microscopy (APFIM, Cameca LEAP 3000HR time-of-flight atom probe). The samples for this were prepared by grinding ribbons down to square rods of about 20 μm × 20 μm × 5 mm and then polishing by ion milling. The field-ion microscopy (FIM) images were obtained using Ne as the imaging gas at 25–40 K. The atom probe analysis was performed at 35 K under a vacuum of ~1×10^{-8} Pa with a pulse fraction (V_p/V_{dc}) of 0.15 and a pulse repetition rate of 100 Hz.

The thermal stability of the as-spun and cold-rolled ribbons was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Microhardness (H_v, kgf mm^{-2}) was measured using a Vickers diamond indenter, applying a load of 0.49 N and a dwell time of 10 s. Bending ductility was evaluated by a simple bend test. Slip markings around Vickers microhardness indents and on the surface of bend-test samples were examined by optical microscopy (OM) and SEM.

3. Results

3.1. Structural effects of cold-rolling

The effects of cold-rolling were characterized using TEM and HRTEM (Fig. 1). After rolling at LNT, both 90Al and 84Al consist of α-Al crystallites in an amorphous matrix. In 90Al, the crystallite diameter is 2–25 nm and in 84Al it is 2–12 nm. For 90Al, the nanostructure induced by cold-rolling appears nearly the same as that induced by annealing [15]. For 84Al the phase mixture is different; in particular cold-rolling avoids the Al_xM_y compound formed on heating [11].

Based on the HRTEM images, the lattice parameter of the α-Al is ~0.407 nm in both 90Al and 84Al after rolling at LNT; this is significantly larger than the value of 0.405 nm for pure α-Al. The difference in the lattice parameters suggests that the cold-rolling-induced α-Al phase includes solutes, in particular Y with much larger atomic size. The lattice parameter of α-Al in cold-rolled 90Al and 84Al is also larger than those (0.405–0.406 nm) for α-Al obtained in similar alloys upon annealing [11,16]. Although difficult to quantify from the lattice parameter measurements, it seems that α-Al induced by cold-rolling contains more solute Y than when induced by annealing.

The TEM image of cold-rolled 90Al (Fig. 1a) reveals elongated regions (arrowed), suggesting that deformation occurs inhomogeneously through shear bands. The precipitation density of nanoscale α-Al appears higher in the bands, reminiscent of shear-deformation-induced precipitation previously reported for 90Al [17,18] and 92Al [19] amorphous alloys. In cold-rolled 84Al, in contrast, the micrograph (Fig. 1d) shows no evidence for shear bands, nor for heterogeneity of the precipitation density of α-Al. Despite higher solute content, 84Al shows deformation that is more homogeneous than in 90Al.

APFIM analysis was applied to 84Al after rolling at LNT to $R = 86\%$. The distribution profiles of the elements at a spot on the FIM tip as it is eroded by 150 nm (Fig. 2) show no significant variation with depth. This distance is much longer than the diameter (2–12 nm) of the α-Al crystallites and the spacing between them, and thus any solute partitioning associated with the precipitation should be detected. There appears to be no significant solute partitioning between the α-Al and amorphous phases, and no segregation or accumulation/depletion of solute at the α-Al/amorphous interfaces. That the formation of the α-Al solid solution is thus *polymorphic*, is reinforced by the distribution maps for the elements in the tip (Fig. 3). These results sharply contrast with the effects of annealing-induced crystallization which is associated with solute partitioning. To distinguish, we henceforth use α-Al to refer to the thermally induced phase, and SSSS-Al to refer to the supersaturated solid solution induced by cold-rolling.

The TEM, HRTEM and AP-FIM studies have been used to characterize the structural changes induced by heaviest deformation (cold-rolling to reductions in thickness $R = 75\%–86\%$). The trends in structure with progressively increasing R are more readily followed using XRD and DSC. In XRD, the amorphous haloes for both 90Al and 84Al show only slight, progressive changes (Fig. S1) on rolling at LNT (77 K) up to 80% reduction in thickness ($R = 80\%$). The Bragg angle of the halo maximum decreases slightly and the halo width increases, suggesting that the deformation leads to a decrease in the density of the samples and to an increase in their heterogeneity. The (200) reflection of fcc-Al becomes detectable in heavily rolled 90Al. More importantly, however, at around the same Bragg angle (in the boxed areas in Figs. S1a and b), the XRD patterns for both 90Al and 84Al show a broad shoulder on the side of the amorphous halo. This is consistent with the cold-rolling generating a fine dispersion of SSSS-Al nanocrystals. Similar effects have been seen in mechanical milling [20] and mechanical alloying [21] of Al alloys in which mixed structures consisting of amorphous + nanoscale crystalline phases are obtained. As in the present work, these structures can be observed in high-resolution TEM images, yet there are no distinct crystalline peaks in the corresponding XRD patterns.

DSC on heating shows no glass transition for as-spun ribbons of 90Al (Fig. 4a); for 84Al there is a clear glass transition followed by a very limited temperature range of supercooled liquid (Fig. 4b). For