The Effect of Minor Addition of Insoluble Elements on Transformation Kinetics in Amorphous Al Alloys

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Abstract

Nanocrystalline metallic materials based on partial devitrification of amorphous aluminum alloys show an attractive combination of high strength and low density. A key feature concerning the improved mechanical properties is the high number density of Al nanocrystals ($10^{22} \sim 10^{23} \text{ m}^{-3}$) that precipitate within the amorphous precursor structure upon low temperature annealing. For $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$, the melt-spun ribbons consisted of an amorphous matrix with a dispersion of Pb nanoparticles (10nm diameter). HRTEM images of the Pb-Al interface revealed a good wetting behavior between the Al and the Pb nanoparticles. Isothermal annealing for $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ showed no transient stage even though the crystallization onset, T_x , was at a much lower temperature (247°C) compared with $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ (267°C). For $\text{Al}_{(88-x)}\text{Y}_7\text{Fe}_5\text{In}_x$ ($x=0.5, 1.0$,

1.5, 2.0), the DSC results indicated that T_x continuously decreased from 232°C to 220°C as the indium level increases from 0.5 at.% to 2.0 at.%. Under STEM, the image showed a coherent interface between Al and In particles. In the analysis of the transformation kinetics, the addition of minor elements can effectively promote additional nucleation of Al nanocrystals by providing heterogeneous nucleation sites. These developments offer new opportunities for the control of nanoscale microstructures.

1. Introduction

Nanocrystalline phases formed within an amorphous matrix during the primary crystallization have attracted a continued interest [1,2]. This is also the basis for the FINEMET formation where a dispersed iron phase with nanometer-sized grains is formed that enables superior magnetic properties [3]. For the Al-based amorphous alloys with transition metal and rare earth element additions, it has been reported that the Al dispersions within an amorphous matrix may enhance the fracture strength to 1300-1500 MPa [4]. This property enhancement may benefit from the high density of the well-dispersed Al nanocrystals, which can be achieved due to the growth kinetic limitations arising from the redistribution of the solute during the annealing process that results in a rapid diffusion field impingement [5].

It was recently discovered that a small amount of doping with 1.0 at.% Pb has a catalyzing effect for the primary crystallization of the Al-based amorphous alloy and yields a higher density of the Al nanophase [6]. In order to understand the mechanism of the catalyzing effect due to Pb doping, it is important to identify the nucleation site of the nanocrystalline Al phase and its relationship with the quenched-in Pb particles. Though Pb and Al are immiscible

even in the liquid state at equilibrium state, it is reported that a nano-sized Pb particle may have good contact with a crystalline Al matrix [7]. By studying the melting behavior of the Pb nanoparticles within an Al matrix, Sheng et al [8] stated that the contacting angle between Pb and Al was estimated to be only 35° based upon a calorimetric analysis. While some work has been reported on the thermal behaviors of Al-based amorphous alloys bearing In particles [8], there is limited information on the potential catalytic effect of In.

2. Experimental Methods

Ingots made of Al-Y-Fe following the composition ratio of $\text{Al}_{88}\text{Y}_7\text{Fe}_5$, $\text{Al}_{(88-x)}\text{Y}_7\text{Fe}_5\text{In}_x$ ($x=0.5, 1.0, 1.5, 2.0$) and $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}_1$ were produced by arc melting of pure components five times to ensure homogeneity. In or Pb, which has a melting point far below the other three elements, was added to the ingot just before the melting spinning process to avoid excessive weight loss. Ribbons were formed by single roller melt spinning on a copper wheel with a tangential speed of 55m/s. Both arc melting and melt spinning were performed in an inert argon atmosphere. X-ray diffraction measurements were performed on a Philips STOE high resolution X-ray diffractometer. A PerkinElmer DiamondDSC was used for both isothermal heat treatment and thermal analysis with a heating rate of 20K/min. TEM specimens were made by electropolishing ribbon samples in a 25/75vol.% nitric/methanol mixture at -40°C. Microscopy observations and EDS compositional analysis were made with a Philips CM200 UltraTwin transmission electron microscope and a spherical aberration corrected Titan STEM. Thickness of the sample was measured through electron energy loss spectroscopy (EELS).

3. Results

The continuous heating DSC trace in Fig.1 showed the onset temperature (T_x) for primary nucleation peak decreased from 267°C for $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ to 247°C for $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$. For AlYFe-In system, T_x continuously decreased from 232°C to 220°C as the indium level increases from 0.5 at.% to 2.0 at.%.

The XRD patterns for the as-spun $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ and the $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ sample annealed at the end temperature for primary nucleation (290°C) are shown in Fig. 2 (a). For the as-spun sample, the diffuse peak around $2\theta = 39^\circ$ can be identified, confirming that the as-spun samples are amorphous. Also, the wide Pb peaks indicated Pb existed in the sample as insoluble small crystalline particles. After annealing, the amorphous peak decreased and the crystalline Al peaks developed, indicating the nucleation of crystalline primary Al. For the as-spun AlYFe-In samples shown in Fig.2 (b), with a low amount of indium doping (0.5 at.%~1.5 at.%), In diffraction peaks cannot be detected and the TEM images do not show any In crystals. Mu et.al have found the similar phenomenon.[9] However, there are obvious In peaks after the In amount reached 2.0 at.% and In nanocrystals are observed in the TEM.

The relationship between Al particle density and isothermal annealing time for $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ at 227°C is shown in Fig.3. For $\text{Al}_{88}\text{Y}_7\text{Fe}_5$, annealed at 237°C to 247°C, the curve undergoes three stages: transient stage, steady state nucleation stage and growth stage [10-12]. In contrast with the nucleation behavior of $\text{Al}_{88}\text{Y}_7\text{Fe}_5$, $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ showed no transient stage even though it was annealed at a much lower temperature 227°C. The particle density was constant with the increase of annealing time.

The bright field TEM images (Fig.4 (a) to (e)) showed the evolution of Al and Pb particles with the increase of annealing time. According to the EDS result, the bright particles are Al and the dark particles are Pb. For the as-spun $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ sample (Fig.4 (a)), spherical Pb particles with a diameter of about 10nm were distributed uniformly in the matrix. With an annealing time as short as 2min at 227°C, small Al particles with an average diameter of 7 nm nucleated on the surface of Pb. In this stage, the interface between Pb and Al was curved (Fig.4 (b)). After the annealing time increased to 5min (Fig.4 (c)), the Al nanocrystals grew and some of the interfaces between Al and Pb became planar. With an annealing time of 15min (Fig.4 (d)), Al particles had an average diameter of 20nm and almost all of the particle pairs have a planar interface. Even with a long annealing time such as 40min (Fig.4 (e)), the size of Pb did not increase as the Al nanocrystals grew. Also, all of the nucleation sites for Al were at the surface of Pb, rather than in the matrix. To show the catalytic effect of Pb on nucleation, a comparison could be made between Fig.4 (b) and (f). Both of those samples were annealed at the same temperature 227°C, however, at a short annealing time (2min), the Pb doped sample already showed Al crystallization and with an even longer annealing time (20min), the undoped sample demonstrated no crystallization at all. Because at 227°C, 20min is shorter than the delay time and within the transient stage, no crystallization occurs under such heat treatment condition.

The wetting behavior between the two phases is confirmed by a dynamic observation that shows a contacting evolution between them. The evolution is caused by exposing one particle to the electron beam. A series of the TEM images were taken at different times and shown in Fig.5. The electron irradiation activated a diffusion process of the Pb atoms so that the Pb particle developed around the Al particle. This may be related to the low melting temperature of the Pb

phase, and due to the size effect, the melting temperature for the nano-Pb particle is lower than its equilibrium melting temperature [13]. The process shown in Fig.5 takes about 10 minutes. The initial and the final states of the particle pair is shown in Fig.5 (a) and (b) respectively. For the contacting behavior between In and Al, the STEM image (Fig.6) taken by the BF-DF detector showed a coherent interface between the Al and In and the STEM image taken by the HAADF detector with a Z contrast shows the bright particle to be In and the dark particle to be Al. The nano-diffraction pattern shows that the In particle is in a $\{110\}$ orientation.

4. Discussion

Adding Pb can greatly promote the nucleation of Al. There are four evidences for this catalytic behavior. First, as shown in Fig.1, T_x is shifted from 267°C to a lower temperature 247°C by adding one atom percent of Pb. Secondly, after annealing at 227°C for 20min, the $Al_{88}Y_7Fe_5$ sample showed no crystallization, however, after annealing at the same temperature for a shorter time, 2min, the $Al_{87}Y_7Fe_5Pb$ sample already exhibited the crystallization of Al. Thirdly, the doped sample demonstrated no transient and steady state nucleation stages at 227°C, however, for the undoped sample, the transient stage still existed at a much higher temperature 247°C. Fourth, according to the literature [6, 14], after annealing at 245°C for 10min, the Pb-doped sample showed that the number of Al crystals increased by a factor of 10 compared with the Pb-free sample.

The catalytic mechanism for Pb is probably related to the good wetting behavior between the nanoscale Pb and Al. The observations clearly showed that Pb provides the heterogeneous nucleation sites for Al. As is shown in Fig.4, all Al nanocrystals nucleated on the surface of Pb and no Al particles nucleated directly in the matrix. This is because 227°C is a too low temperature for Al nucleate independently within the matrix. Since the density of Pb particles is fixed in the matrix, Fig.3 shows there is no change in Al particle density with the increase of time.

Indium shows an even stronger catalytic effect than Pb. By doping 0.5 at% of In, T_x decreased by 35°C and this T_x decreases even further with the increase amount of In doping (Fig.1). Also, with the increase of In amount, T_x gets lower and the catalytic effect becomes stronger. The HR STEM images showed a coherent interface which proved that the contacting behavior between In and Al is also good. The mechanism behind this catalytic effect is more complicated for In doping than doping with Pb. First, the solubility of In in the matrix is larger than that of the Pb. At a low concentration (0.5 at.% to 1.5 at.%), the as-spun sample shows no In particles (Fig.2), which means In dissolves into the matrix. However, for Pb, with 1.0 at.% doping, Pb exists in the as-spun samples as nanocrystals. Second, the melting point of Pb is higher than the T_x , however, the melting point of In is lower than the T_x . In the case of Pb, Al nucleated on the surface of solid Pb particles. However, for In, during annealing, In melted and Al particles nucleate on the surface of liquid In particles in contact with the amorphous matrix. After the temperature decreased, liquid In solidified on the surface of Al crystals. These differences might explain why In has a stronger catalytic effect than Pb. There is a two-fold catalytic mechanism for In: the part of In that dissolves into the matrix can destabilize the glass

due to the positive heat of mixing [15] between In and Al; the part of In that precipitates as nanocrystals in the matrix can provide heterogeneous nucleation sites. Moreover, during the heating, the solidification of In leads to a volume change in the rigid matrix well below T_g and a stress field near the In particle, which can act to catalyze the Al crystallization.

5. Conclusion.

By doping one atom percent of Pb, the onset of primary crystallization temperature was shifted to a temperature 20 degrees lower than that of the Al-Y-Fe alloys. Also, after annealing at the same temperature, the doped sample showed crystallization, however, the undoped one showed no nucleation even with longer annealing time. Therefore, Pb can promote the nucleation of Al. The TEM results show that the catalytic effect of Pb is based on the good wetting behavior between Al and Pb as well as the role of Pb as heterogeneous nucleation sites. Through doping 0.5 at.% to 2.0 at.% of In, T_x decreased by 35°C to 47°C. Therefore, In has a stronger catalytic effect than Pb. The catalytic mechanism is complicated due to the fact that In has some solubility in the matrix and Al nucleates on the interface between the liquid In and the amorphous matrix. However, the coherent interface in the HR STEM image showed a good contacting behavior between Al and In.

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Fig. 1: DSC traces (20°C/min) of melt spun ribbons of three alloys. Substitution of 1.0 at.% Pb or 0.5-2.0 at.% In for Al results in a shift of the primary crystallization onset to lower temperatures. Doping with In has a stronger effect than doping with Pb. Also, the catalytic effect for AlYFe-In system increased with the increase of In amount.

Fig. 2. (a) XRD patterns for as-spun $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ sample and annealed at 290°C $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ sample. (b) XRD patterns and the corresponding TEM images for as-spun $\text{Al}_{88-x}\text{Y}_7\text{Fe}_5\text{In}_x$ ($x=0.5, 1.0, 1.5, 2.0$)

Fig. 3: Al crystal number density vs. annealing time for $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ annealed at 227°C and $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ annealed within the temperature range from 237°C to 247°C.

Fig. 4: TEM BF images (from (a) to (e)) for $\text{Al}_{87}\text{Y}_7\text{Fe}_5\text{Pb}$ annealed at 227°C for 0min, 2min, 5min, 15min and 40min. (f) is $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ annealed at 227°C for 20min.

Fig. 5: The dynamic observation of the contacting process between the Pb and Al phase. From (a) to (b) takes about 10 minutes. (a) is the initial state and (b) is the final state.

Fig. 6: AlYFe-0.5%In sample annealed at 223°C for 15min. (a): STEM image from BF-DF detector with both the Z contrast and strain contrast. (b): STEM image from HAADF detector with only Z contrast. The diffraction pattern show the indium {110} plane orientation.

Captions

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