Synthesis of Amorphous Matrix Nano-composite in Al-Cu-Mg Alloy

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The microstructure of as-quenched $Al_{70}Cu_{18}Mg_{12}$ alloy has been investigated in detail using transmission electron microscopy. Al nano-crystals about 5 nm with a high density are distributed in the amorphous matrix, indicating amorphous matrix nano-composite can be synthesized in Al-Cu-Mg alloy. The high density of Al nano-crystals indicates very high nucleation rate and sluggish growth rate during crystallization possibly due to limited diffusion rate of solute atoms of Cu and Mg during solute partitioning. The result of hardness measurement shows that the mechanical properties can be improved by designing a nano-composite structure where nanometer scale crystals are embedded in the amorphous matrix.

Key Words: Metallic glass, Nano composite, Crystallization

INTRODUCTION

Recently, nano-composite materials in metallic alloy systems receive a great attention, since they provide unique properties such as high strength and hardness (Greer, 2001). For synthesis of nano-composites in metallic glass system, there are two typical methods which are phase separation in the liquid state before glass transition, and partial crystallization during cooling from the liquid state or during annealing in the solid state (Greer, 1994). It has been shown that phase separation can occur in many metallic glass forming systems, if one (or more than one) atom pair in the multi-component system has positive enthalpy of mixing in the liquid state, for example, in Zr-La-Al-Cu-Ni, Ti-Y-Al-Co, and Ni-Nb-Y, where Zr-La, Ti-Y and Nb-Y atom pairs have positive enthalpy of mixing, 13, 15, and 30 kJ/mol, respectively (Kündig et al., 2004; Park et al., 2004; Mattern et al., 2005). The resulting microstructure formed by phase separation consists of two amorphous phases with different compositions, and is categorized into two types: interconnected-type microstructure formed by spinodal decomposition and droplet-type formed by nucleation and growth mechanism (James, 1975). The phase diagram for phase separation can

be calculated if required thermodynamic data are available. In Ti-Y-Al-Co metallic glass system, it has been shown that a full spectrum of microstructure by phase separation can be obtained depending on the position of the alloy composition inside the miscibility gap, i.e., if the composition is located near the critical temperature, interconnected-type microstructure is obtained, while if the composition is located near the edge of the miscibility gap, droplet-type microstructure is obtained (Park et al., 2006). Depending on the glass forming ability of two different amorphous phases, the resulting nano-composite consists of amorphous-amorphous or amorphous-crystalline phases. The length scale of nano-composites by phase separation generally depends on the cooling rate.

Partial crystallization of the amorphous alloys is also one of the potential ways for obtaining nano-composites. Partial crystallization can occur during cooling from the melt if the glass forming ability is not good enough, and can also occur during heating the quenched-in amorphous alloy (Greer, 1994). One of the prerequisites for the formation of nano-composite by partial crystallization is the very high nucleation rate of the crystalline phase.

Recently, Al-based amorphous alloy receives an attention,

since it shows a good combination of functional properties such as good oxidation resistance and high conductivity when compared with other amorphous alloy systems (Kim et al., 2012). It has been shown that high density of quenched-in nuclei is present in some as-quenched Al-based amorphous alloys. Therefore, many results have been reported on the synthesis of Al-based nano-composites which consist of high density of nm scale fcc Al crystals embedded in the amorphous matrix. However, it is not clear yet whether Al crystals form by phase separation or nucleation and growth in the solid state. Although there have been a great amount of research on the formation of Al-based nano-composites during annealing of the as-quenched amorphous alloys, for example, Al-Ni-Y, Al-Ni-Co-Y, Al-Ni-La, Al-Ni-Gd alloys, there have been very few reports on the formation of Al-based nano-composites during cooling from the liquid state. It has been shown that high density of nm scale Al crystals form in the amorphous matrix during cooling from the liquid in Al-Y-Ni-Co-Pd alloy (Louzguine-Luzgin & Inoue, 2007). Here, it can be noticed that the formation of high density Al nano crystals has been reported in Al—transition metal—rare earth element (RE) alloys. Therefore, it is highly required to investigate the formation of high density Al nano crystals in Al-based alloys which do not contain RE. Previous study on Al-Cu-Mg alloy has shown that a fully amorphous phase with Al-Al and Al-Cu pair local short range ordering forms in the as-quenched sample, resulting in two halo peaks in the X-ray diffraction (XRD) pattern (Aburada et al., 2011). Since two halo peaks in the XRD pattern can also appear due to nano-crystallization or phase separation during cooling from the melt, a detailed study on the microstructure of as-quenched $Al_{70}Cu_{18}Mg_{12}$ alloy has been performed using transmission electron microscopy (TEM) in the present study.

MATERIALS AND METHODS

Al-Cu-Mg alloy ingot with the nominal compositions of $Al_{70}Cu_{18}Mg_{12}$ was produced by melting high purity elements (99.9% or higher) in two stages. First, Al and Cu alloy ingot were prepared by arc melting under a Ti-gettered argon atmosphere in a water cooled copper crucible. Then, the ingot and Mg were placed into induction furnace and melted under argon atmosphere. Rapidly solidified ribbons were prepared by re-melting the alloys in quartz nozzles, and ejecting with an over-pressure of 50 kPa onto a Cu wheel. To investigate the effect of cooling rate, the ribbon samples were prepared using different diameter of nozzles with the Cu wheel speed of 30 m/s. As a result, the thickness of the ribbon samples was ~37 and ~26 μm, respectively. The structure of the samples was examined preliminarily by XRD (Rigaku CN231; Rigaku, Japan) using monochromatic Cu K_{α} radiation. Thermal analysis of the samples was carried out using a differential scanning calorimeter (DSC, PerkinElmer DSC7; PerkinElmer, USA) with a constant heating rate of 0.667 K/s. The microstructures of the samples were examined using a TEM (200 kV, JEM 2100F; JEOL, Japan) linked with an energy dispersive X-ray spectrometer (EDS; Oxford Instruments INCA, UK). The thin foil specimens for TEM were prepared by Ar ion milling (PIPS 691; Gatan, USA) at 2.6 keV and 5 mA with liquid nitrogen cooling. Hardness of the sample was measured using Vickers hardness tester (MXT-ZX7E; Matsuzawa, Japan) under the load of 300 gf.

RESULTS AND DISCUSSION

Fig. 1A and B show the XRD patterns obtained from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloys with the thickness of ~26 and ~37 μm, respectively. The XRD pattern from ~26 μm thickness sample exhibits two diffuse halo peaks at $2\theta=38.6°$

A
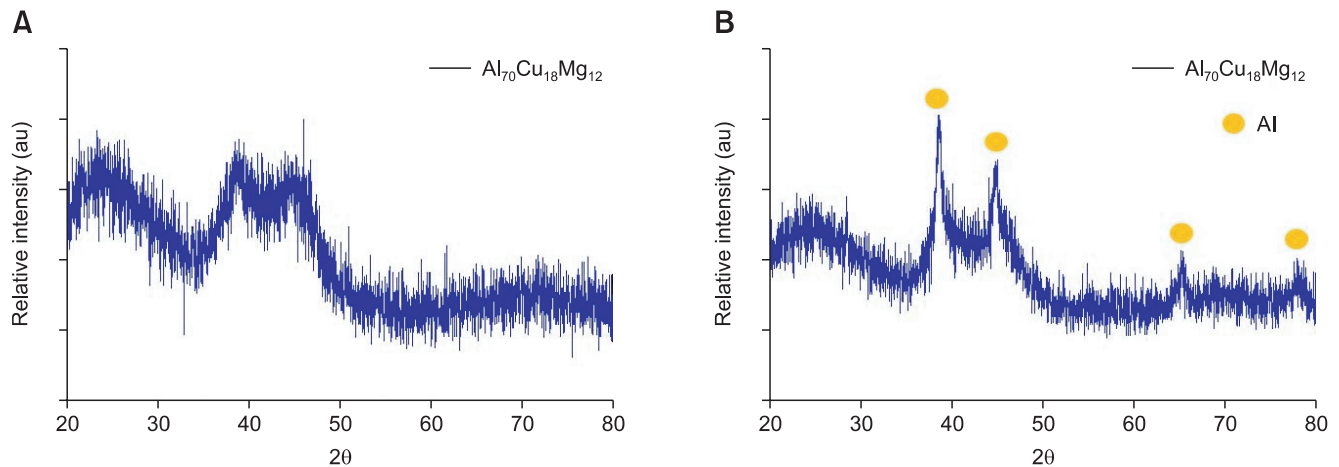
B

Fig. 1. The X-ray diffraction patterns obtained from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloys with the thickness of ~26 μm (A) and ~37 μm (B).

and 44.8°. The result is similar to that in the previous report (Aburada et al., 2011). However, with the decrease of cooling rate, i.e., in ~37 μm thickness sample, sharp diffraction peaks which were indexed as fcc Al were superimposed on a diffuse halo peak with 2θ range of 35°~50°, indicating that Al crystals are embedded in the amorphous matrix. Based on the XRD result, the structure of the ~26 μm thickness sample has been investigated by TEM. The bright field TEM image and selected area diffraction pattern (SADP) in Fig. 2A and B show that the microstructure consists of high density of Al crystals with the size of ~5 nm embedded in the amorphous matrix. The SADP shows two continuous spotty rings corresponding to (111) and (200) of fcc Al. The broad diffraction ring from the amorphous phase is superimposed on the (200) of fcc Al. Fig. 3 shows the high resolution TEM image obtained from the ~26 μm thickness sample. From the lattice fringes of Al crystal, defects such as dislocations are not observed. Al nano-crystals formed during annealing of the as-quenched Al-based amorphous alloy generally exhibit defect-free structure, as observed in the present study. However, the previous report on Al-Y-Ni-Co-Pd alloy has shown that Al nano-crystals formed in as-quenched sample, i.e., during solidification contain micro-strain and defects such as dislocations (Louzguine-Luzgin & Inoue, 2007). The origin of the micro-strain and the dislocations has been suggested to be due to impingement of the growing particles and the difference in thermal expansion coefficients between Al nano-crystals and the surrounding amorphous matrix. These two factors can lead to the development of stress during cooling in the solid state. In the present study, no defects are present
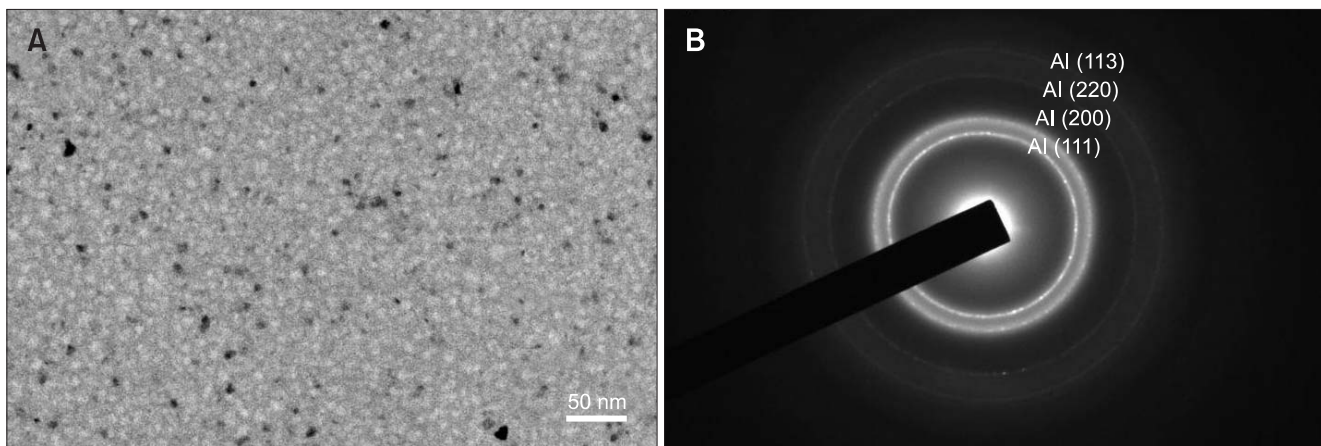

Fig. 2. (A) The bright field transmission electron microscopy image. (B) Selected area diffraction pattern obtained from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloys with the thickness of ~26 μm.
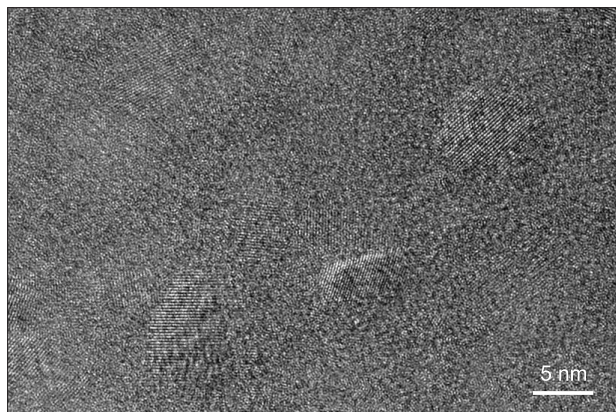

Fig. 3. The high resolution transmission electron microscopy image obtained from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloys with the thickness of ~26 μm.

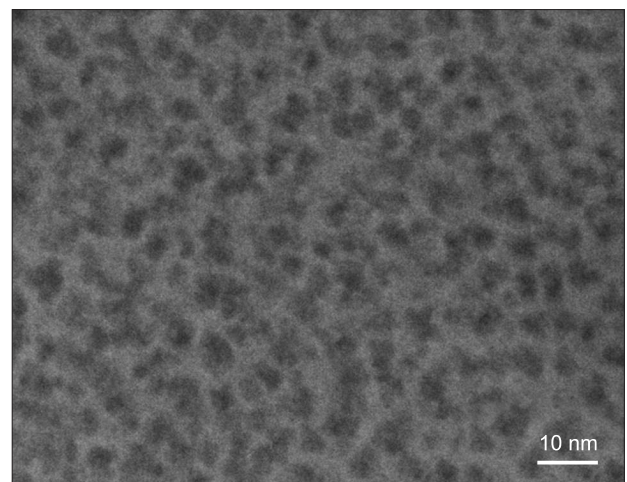**Fig. 4.** The high-angle annular dark-field scanning transmission electron microscopy image from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloys with the thickness of ~26 μm.
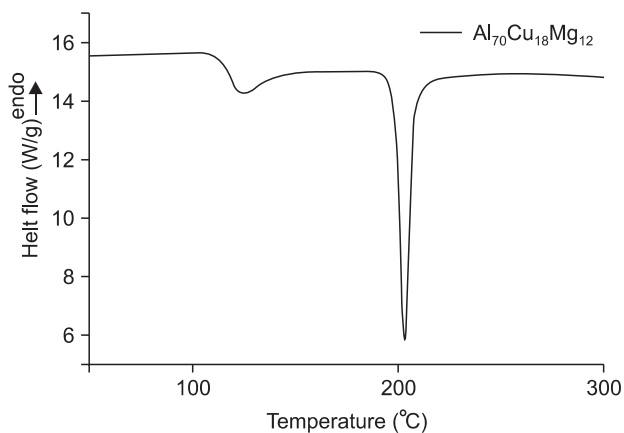
Fig. 5. A differential scanning calorimeter trace obtained from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloys with the thickness of ~26 μm.

in Al nano-crystals possibly because the difference in thermal expansion coefficients is not too large to induce strain field, or the dislocations are annihilate at the particle boundary during solidification. Fig. 4 shows the high-angle annular dark-field scanning TEM image obtained from the ~26 μm thickness sample. The darker particles of ~5 nm are embedded in the brighter matrix. The Al nano-crystals in the present study are formed by solute partitioning of Cu and Mg during solidification; therefore, the amorphous matrix is enriched with Cu and Mg, resulting in the brighter matrix.

Fig. 5 shows the DSC trace obtained from the as-melt-spun $Al_{70}Cu_{18}Mg_{12}$ alloy, exhibiting two exothermic peaks with onset temperature of 386 and 471 K. The two exothermic reactions indicate that the amorphous matrix exhibits a two-step crystallization behavior. From the DSC trace, no endothermic reaction of glass transition was observed.

The present results show that Al nano-crystals form in the amorphous matrix during solidification of $Al_{70}Cu_{18}Mg_{12}$ alloy. TEM study shows that the size of Al nano-crystals is ~5 nm, and its density is 10^{24} m^{-3} assuming interparticle distance is 5 nm similarly to the previous result in Al-Y-Ni-Co-Pd system (Louzguine-Luzgin & Inoue, 2007). Such a high density of Al

nano-crystals indicates that the nucleation rate is very high and the growth rate is very sluggish during crystallization. In order to form nano-crystals, solute partitioning is required, and limited diffusion rate of solute atoms of Cu and Mg may probibit the growth of Al crystals significantly. Considering these TEM results, the two halo peaks observed in the XRD pattern excludes the possibility of phase separation in the liquid state. From the point of view of enthalpy of mixing in the liquid state which are −1, −2 and −3 kJ/mol for Al-Cu, Al-Mg, and Cu-Mg, respectively, it is highly unlike that phase separation occurs during solidification. The Vickers hardness measured from ~37 and ~26 μm samples are 150 Hv and 230 Hv, respectively, indicating that the mechanical properties can be improved by designing nano-composite structure where nanometer scale crystals are embedded in the amorphous matrix.

SUMMARY

Al nano-crystals form in the amorphous matrix during solidification of $Al_{70}Cu_{18}Mg_{12}$ alloy. The size of Al nano-crystals is ~5 nm, and its density is 10^{24} m^{-3}. Such a high density of Al nano-crystals can form when the nucleation rate is high and the growth rate is limited. During solute partitioning, slow diffusion of Cu and Mg may limit the growth rate of the crystals. The possibility of phase separation in $Al_{70}Cu_{18}Mg_{12}$ alloy is excluded from the XRD and TEM results. The result of hardness measurement indicates that the mechanical properties can be improved by designing such a nano-composite structure where nanometer scale crystals are embedded in the amorphous matrix. The present study shows that nano-composite can be synthesized in non RE containing Al-based alloys.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

REFERENCES

Aburada T, Fitz-Gerald J M, and Scully J R (2011) Pitting and dealloying of solute-rich Al-Cu-Mg-based amorphous alloys: effect of alloying with minor concentrations of nickel. *J. Electrochem. Soc.* **158**, C253-C265.

Greer A L (1994) Crystallization of metallic glasses. *Mat. Sci. Eng. A-Struct.* **179**, 41-45.

Greer A L (2001) Partially or fully devitrified alloys for mechanical properties. *Mat. Sci. Eng. A-Struct.* **304**, 68-72.

James P F (1975) Liquid-phase separation in glass-forming systems. *J.*

Mater. Sci. **10**, 1802-1825.

Kim S J, Kim S Y, Park J M, Heo J N, Lee J H, Lee S M, Kim D H, Kim W T, Lim K R, and Kim D (2012) Exploiting metallic glasses for 19.6% efficient back contact solar cell. *Appl. Phys. Lett.* **101**, 064106.

Kündig A A, Ohnuma M, Ping D H, Ohkubo T, and Hono K (2004) In situ formed two-phase metallic glass with surface fractal microstructure. *Acta Mater.* **52**, 2441-2448.

Louzguine-Luzgin D V and Inoue A (2007) Investigation of a rapidly solidified Al-based nanocomposite with extremely high number

density of precipitates. *Mat. Sci. Eng. A-Struct.* **449**, 1026-1028.

Mattern N, Kühn U, Gebert A, Gemming T, Zinkevich M, Wendrock H, and Schultz L (2005) Microstructure and thermal behavior of two-phase amorphous Ni–Nb–Y alloy. *Scr. Mater*. **53**, 271-274.

Park B J, Chang H J, Kim D H, and Kim W T (2004) In situ formation of two amorphous phases by liquid phase separation in Y–Ti–Al–Co alloy. *Appl. Phys. Lett*. **85**, 6353-6355.

Park B J, Chang H J, Kim D H, Kim W T, Chattopadhyay K, Abinandanan T A, and Bhattacharyya S (2006) Phase separating bulk metallic glass: a hierarchical composite. *Phys. Rev. Lett*. **96**, 245503.