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Effect of Process-Control Agents on Characteristics of Amorphous Al-Y-Ni-Co Alloy Powder Produced by Mechanical Alloying

H. V. Nguyen, J. C. Kim, J. S. Kim, Y. J. Kwon, and Y. S. Kwon*
Research Center for Machine Parts and Materials Processing,
School of Materials Science and Engineering, University of Ulsan,
Namgu Mugeo 2-Dong, San 29, Ulsan 680-749, Korea
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Abstract In this work, effect of various process-control agents (PCAs) on the mechanical alloying of amorphous alloy of $Al_{85}Y_8Ni_5Co_2$ has been investigated. The dependence of the particle shape, size and crystallization behavior of the amorphous alloy powders on the type of PCAs and their concentrations was investigated by using X-ray diffraction, field-emission scanning electron microscopy and differential scanning calorimetry. It was found that the additive of toluene could affect positively the amorphization and thermally induced crystallization processes, as well as the size refinement, morphology and particle-size distribution of as-milled powders in comparison with alloy obtained without PCA.

Keywords : Amorphous alloy, Mechanical alloying, Process-control agent

1. Introduction

Amorphous alloy of Al-Y-Ni has received much attention because of their high tensile strength, good strength and ductility, high corrosion resistance and hardness [1-3]. Addition of Co to the Al-Y-Ni alloy increases mechanical strength and do not affect bending ductility [4]. Amorphous Al-Y-Ni-Co had been synthesized successfully by rapid quenching, such as melt-spinning technique [5]. However, this process has a limitation in the size and shape of glassy samples, i.e. thin ribbon [4-7]. Alternatively, attempts had been made to produce amorphous alloy of Al-Y-Ni-Co in solid state using mechanical alloying (MA) [8, 9]. This technique is a convenient and widely used one for the synthesis of amorphous powder, when combined with a suitable consolidation technique such as hot-pressing or extrusion [10-12]. Generally in the MA process, the properties of the milled powder are controlled by ball-to-powder weight ratio, temperature of milling, milling speed and process-control agent (PCA) [13]. Many researchers focused on the effect of milling parameter to the formation of amorphous Al-Y-Ni-Co [9, 11, 14, 15]. However, the effect of PCA on the amorphization process of the Al-Y-Ni-Co alloy has not been reported yet.

In this study, the effect of different PCAs on the phase transformations, particle size, thermal evolution of amorphous $Al_{85}Y_8Ni_5Co_2$ alloy powder produced by MA was investigated.

2. Experimental

Elemental Al, Co, Ni and Y powders (purity 99.8 %) were mixed to the desired nominal composition of $Al_{85}Y_8Ni_5Co_2$. Mechanical alloying was performed under protective Ar atmosphere of 4×10^5 Pa pressure using a Fritsch Pulverizette-7 planetary ball mill. Vials and balls were made of hardened bearing

*Corresponding Author : [Tel : +82-52-259-2238; E-mail : yskwon@ulsan.ac.kr]

steel. A ball-to-powder weight ratio was 14:1, where milling times were varied from 1 to 100 h. Forced air cooling was applied in order to prevent excessive heating of the vials in the course of milling. A set of liquid organic substances [16] was used as PCAs to accelerate the amorphization process as well as to reduce sticking of the powder to the milling tools: n-heptane ($CH_3(CH_2)_5CH_3$); n-dodecane ($CH_3(CH_2)_{10}CH_3$); toluene ($C_7H_8(C_6H_5CH_3)$); xylene; and isopropyl (C_3H_7OH) and n-butyl (C_4H_9OH) alcohols. Amount of 3-5 ml PCA was added to 5 g of initial powder mixture before milling, the residual volume of the milling vials was filled with Ar.

Structural characterization of milled samples was performed by X-ray diffraction (XRD) using CuK_α radiation. The thermal stability of the alloy powders was investigated by means of differential scanning calorimetry (DSC) at a heating rate of 10 K/min under constant He flow.

3. Results and Discussion

3.1. Amorphous $Al_{85}Y_8Ni_5Co_2$ obtained by MA without PCA

Structural and phase transformations of $Al_{85}Y_8Ni_5Co_2$ powder mixture during MA were observed by means of X-ray diffraction (Fig. 1). Amorphous phase started to appear after milling of 4h, and there existed a broadening of XRD peaks and increase in the background as the MA progressed, suggesting the formation of amorphous phase, fine crystalline grains and high density of defects. Peaks corresponding to pure initial metals (except Al element) disappeared. However, single-phase amorphous state could not be reached even after alloying for 100 h: some crystalline peaks can be seen on the diffraction pattern, which might be related to intermetallic compounds with the structure similar to Al_9Co_2.

After mechanical alloying for 100 h, a final product consisting of Al nanograins and new intermetallic phases distributed over the amorphous matrix forms. Fully amorphous state was not reached. Possible reasons can be given as follows: the first is the formation of local heating of powder during ball milling resulting in sticking of Al onto balls and walls of the milling media; and the other is the contamination of powder from milling tools.

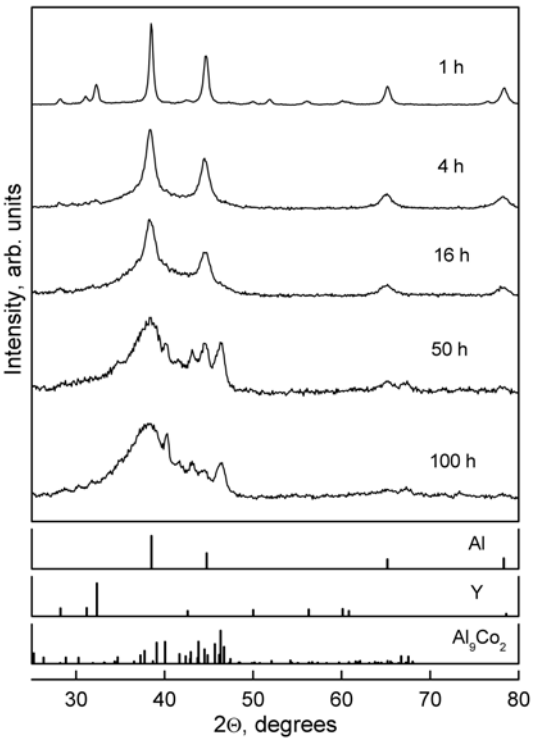

Fig. 1. X-ray diffraction patterns of $Al_{85}Y_8Ni_5Co_2$ samples dry-milled for various times.

3.2. Effect of PCA on the formation of amorphous $Al_{85}Y_8Ni_5Co_2$ powder alloy

XRD patterns of the samples milled for 32 h in presence of liquid organic compounds are presented in Fig. 2.

It can be clearly seen that additives of saturated hydrocarbons (n-heptane and n-dodecane) give almost no acceleration of the amorphization process with respect to dry milling. They also poorly prevent sticking of the powder to the milling tools.

However, an additive of toluene resulted in full amorphization of the powder already after 32 h of MA, i.e. toluene considerably accelerates amorphiza-

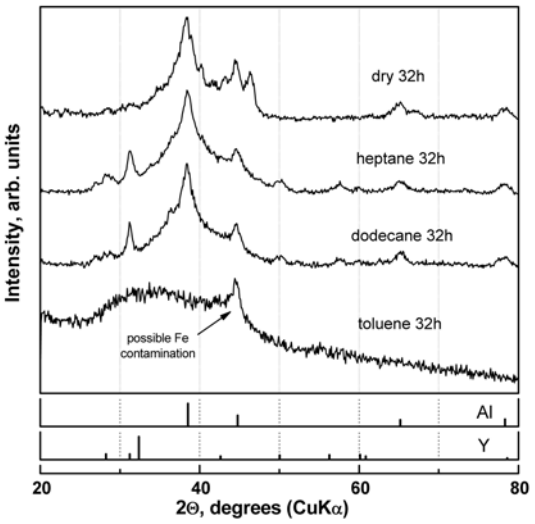

Fig. 2. X-ray diffraction patterns of $Al_{85}Y_8Ni_5Co_2$ wet-milled samples.

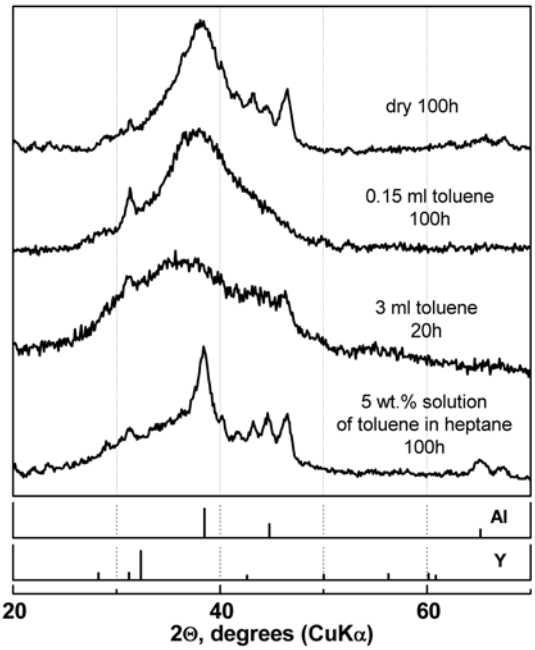

Fig. 3. X-ray diffraction patterns of $Al_{85}Y_8Ni_5Co_2$ samples wet-milled in presence of toluene additives.

tion process. Additionally, even though the data was not shown here, from the gravimetric analysis a slight increase in weight was confirmed. This might be resulted from a contamination with Fe from milling tools which is indicated by the peak at 44.5° on the XRD pattern in Fig. 2 and 3. The sample after preparation was self-inflammable when loaded out from mill to the open air, so it was wetted with solution of dodecane in heptane in order to prevent oxidation.

Xylene additive acted in a similar way as toluene did, but gave even stronger contamination of the final alloy with Fe. Milling in presence of isopropyl and n-butyl alcohols resulted in quick polymerization of organic substances, and alloying process terminated, as metal particles become covered with polymerized organic coating (data were not shown).

Thus, based on the results obtained, saturated hydrocarbons, xylene and alcohols were found to be unsuitable for mechanical alloying of $Al_{85}Y_8Ni_5Co_2$. On the other hand, toluene additive appeared to have a positive effect on MA process. It also prevented sticking of the powder to the milling tools.

The following conditions were applied in further milling experiments: (1) MA with small amount of 0.15 ml additive of toluene; (2) MA with additive of solution of toluene in heptane (3 ml of 5 wt.% toluene solution); and (3) MA with large amount of 3 ml additive of toluene;

Milling time of 100h was required in the first two cases to reach close-to-amorphous state, while only 20h of milling was needed in the third case. Fig. 3 shows XRD patterns of the final products milled in presence of various toluene additives. The best improvement in amorphization of $Al_{85}Y_8Ni_5Co_2$ could be achieved using small amount of 0.15 ml additive of toluene: the sample after milling for 100h was almost amorphous, the only weak crystalline peak was observed at 31.5° (being possibly related to residual Y or some Y-based solid solution) together with almost no contamination of Fe from milling media. Milling with large amount of toluene gave a similar degree of amorphization after 20 h of milling, but the halo peak shifted strongly towards lower angles, indicating significant changes in the amorphous phase composition [17]. No improvement in amorphization after 100 h of sample milling using

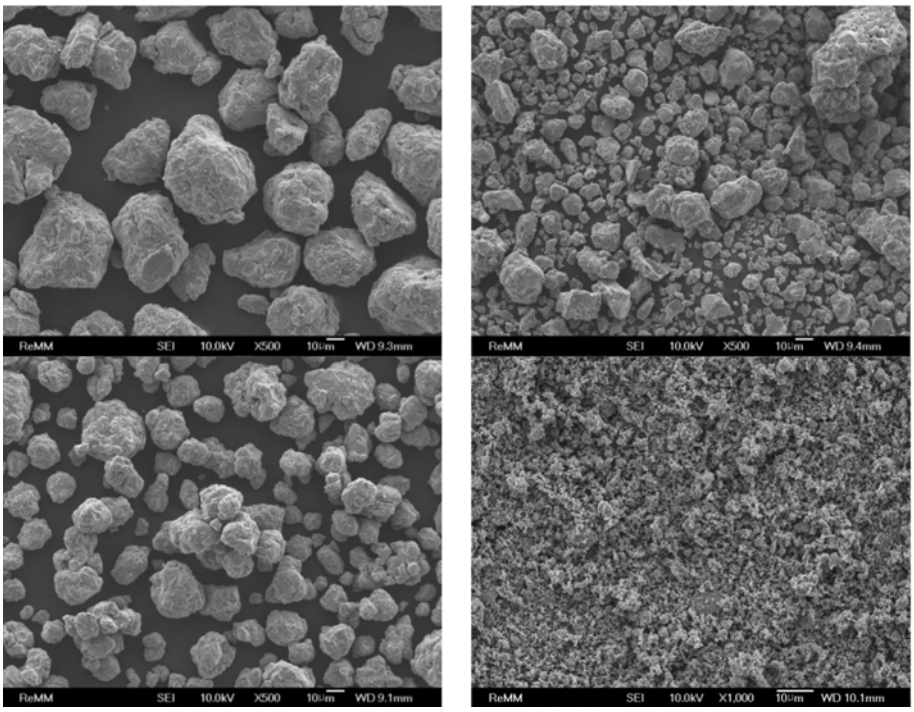

Fig. 4. FE-SEM images of amorphous $Al_{85}Y_8Ni_5Co_2$ powders with milling condition: (a) dry milling, (b) 3 ml heptane + 5% toluene, (c) 0.15 ml toluene and (d) 3 ml toluene.

the solution of toluene in heptane was observed with respect to dry-milled samples.

3.3. SEM observation and particle size distribution

Fig. 4 shows SEM micrographs of powders which were milled under the following conditions: (a) dry milling for 100h, (b) 5wt% solution of toluene in heptane for 100h, (c) 0.15 ml toluene for 100h, and (d) 3 ml toluene for 32h, respectively. It can be seen that fine powders were agglomerated to form large particles in dry-milled sample. The particle shape of powder, milled in the solution of toluene in heptanes, appears plate-like. Sample milled using small amount of 0.15 ml additive of toluene has finer structure compared to the dry-milled one. The sample milled with large amount of toluene exhibits the finest particle size.

Particle size distributions of the as-milled powder samples were measured by means of laser scattering granulometry and shown in Fig. 5. The 100 h dry-milled sample has an average particle size of about

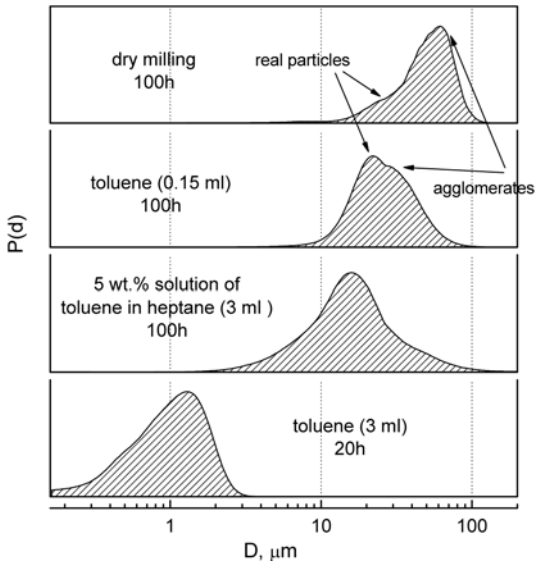

Fig. 5. Particle size distribution curves of $Al_{85}Y_8Ni_5Co_2$ powder alloys.

25 μm (weak peak on the left side of the distribution function, marked with arrow), but a considerable part of the powder was agglomerated. The agglomerates have sizes of 50-70 μm and are not easily breakable under ultrasonic treatment during the measurements. The size of particle and agglomerate was smaller for the sample milled with small additive of toluene. The sample milled in solution of toluene in heptane showed even smaller particle size and almost no agglomeration. The finest particle size of about 1 μm was observed for the sample milled with a large additive of toluene, which may explain the self-inflammable behavior of the sample.

3.4. DSC analysis of $Al_{85}Y_8Ni_5Co_2$ powder alloys

Fig. 6 shows the DSC curves of the Al-Y-Ni-Co powder alloys with a heating rate of 10 K/min. The sample milled with small toluene additive shows the first crystallization onset peak starting at 605 K which is about 50 K higher than that of dry-milled sample. The crystallization onset temperature becomes even more shifted to higher temperature when milling in solution of toluene in heptane was applied: the crystallization starts only above 640 K because of a relatively high volume fraction of crystalline phases in the sample, that is, a decrease in driving force for crystallization.

Good DSC curves could not be obtained for the sample milled with large additive of toluene, possibly due to evaporation of organic coating from the powder under heating. However, it can be concluded from the curves obtained that thermal crystallization of this sample might start already at 500 K.

The three crystallization stages of dry-milled samples are well-matched with the DSC profile obtained on arc-melted $Al_{85}Y_8Ni_5Co_2$ alloy [18-19]. However, lower peak temperature was observed for $Al_{85}Y_5Ni_8Co_2$ alloy [20], indicating that an increase

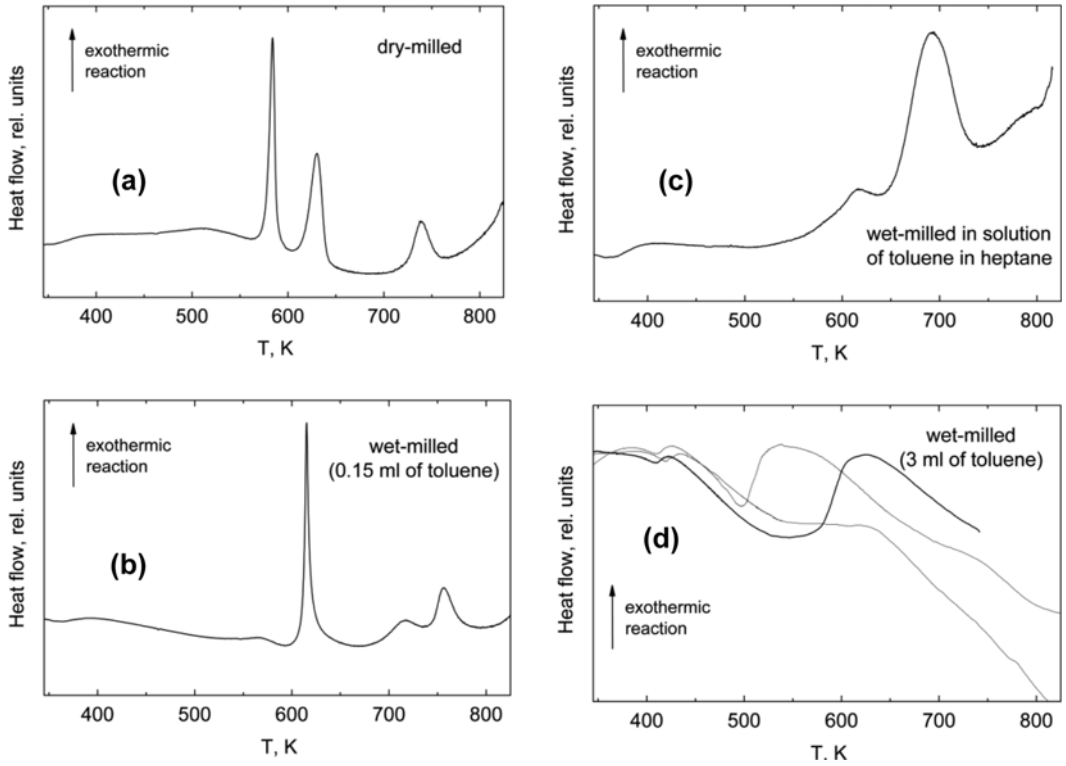

Fig. 6. Continuous heating DSC curves of amorphous $Al_{85}Y_8Ni_5Co_2$ powder alloys at a heating rate of 10 K/min. (a) dry-milling, (b) 0.15 ml toluene solution, (c) solution of toluene in heptane and (d) 3 ml toluene solution.

in Y content leads to an increase of the thermal stability [21]. The crystallization peak temperatures of the two stages in sample milled with the solution of toluene in heptane are in agreement with the data obtained on the $Al_{84}Y_9Ni_5Co_2$ alloy [22]. Crystallization peak temperatures of the four stages in sample milled using small amount additive of 0.15 ml toluene are different with the data obtained on the $Al_{85}Y_5Ni_8Co_2$ alloy [20].

4. Conclusions

A set of $Al_{85}Y_8Ni_5Co_2$ powder samples with close-to-amorphous structure was synthesized by means of mechanical alloying with various PCAs. Toluene was found to have a positive effect on the amorphization process as well as on the powder structure, particle size and thermal evolution. XRD patterns of the final samples milled in presence of various toluene additives showed that the best improvement in amorphization of $Al_{85}Y_8Ni_5Co_2$ powder alloy could be achieved using small amount of 0.15 ml additive of toluene. No improvement in amorphization after milling of 100 h with solution of toluene in heptane was observed in comparison with the dry-milled sample. Large additive of toluene gave nearly complete amorphization after milling 20 h.

The alloy powders under dry- and wet- milling using small amount of 0.15 ml additive of toluene were crystallized through three and four stages, respectively. The crystallization of sample with solution of toluene in heptane occurred through two stages. The thermal analysis showed that the thermal stability increases in the order of samples milled (1) without PCA and wet-milling (2) using small additive of toluene and (3) solution of toluene in heptane.

Acknowledgments

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