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Mechanical alloying of aluminium and $Al_{13}Co_4$ to an amorphous phase

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Abstract

An amorphous phase with blend composition of $Al_{85}Co_{15}$ was fabricated by mechanical alloying (MA) from the mixture of pure Al and monoclinic $Al_{13}Co_4$, which cannot be obtained by MA for the Al and Co elemental powders. Use of the MA from the compound and element is a result of the enhancement of efficiency during milling by leaving out the welding and supressing the agglomeration of the powders in the process. Mechanism of the amorphization is discussed together with the mechanical grinding of the compound. We assert that the MA between the Al and compound is an available process to produce amorphous phases in Al-enriched (Al > 85 at.%) alloys.

Keywords: Mechanical alloying; Aluminum–cobalt system; Amorphization

1. Introduction

Since the work of Benjamin et al. [1], it has been realized that mechanical alloying (MA) by ball milling can provide the possibility of prepared non-equilibrium materials in various alloy systems. In the last few years, there has been an increasing fascination on the evidence that metastable and amorphous phases can be formed by mechanical alloying [2]. Following this, many works has recently been dedicated to clarifying the mechanism of amorphization in binary alloys [2]. Various mechanisms have been suggested for the amorphization process induced by MA. An assertion [3] of a high defect concentration which rises the free energy system up to the level of an amorphous phase, is accepted.

As mentioned above, amorphization in many alloys, which could not be achieved by liquid quenching, is identical in the MA process. Al-based alloys are one of the most useful for practical application as an industrial material because of their low density and high strength. Recently, a group of Al-based amorphous alloys with high strength was discovered in Al-transition metal (TM)-rare earth metal (RE) systems [4]. However, there is no report of an amorphous alloy prepared by liquid-quenching in Al-TM binary system, especially in an Al-enriched side. To date, only a few alloys have been identified to form an amorphous phase by the MA process in Al-based alloys performed for up to several hundred hours. A long milling time by MA is necessary because of the high ductility of the starting materials (elements) which cause the agglomeration in the earlier period during MA and reduce the interface between particles. To our knowledge, only an amorphous phase was achieved by the MA process in an $Al_{81.8}Co_{18.2}(Al_9Co_2)$ [5], $Al_{80}Cr_{20}$ [6], $Al_{80}Fe_{20}$ [7]. In this study, we employed the mechanical alloying of the mixture of pure Al and Al-based compounds with a brittle nature for preparation of an $Al_{85}Co_{15}$ amorphous phase. For comparison, MA with starting materials of the elements and mechanical grinding (MG) were performed.

2. Experimental details

The $Al_{13}Co_4$ compound was prepared from aluminum and cobalt powders by arc melting in an argon atmosphere and then annealed for homogenization in vacuum in a sealed tube at 1073 K for 48 h. Commercial Al and Co powders with a purity of 99.9% and grain

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size smaller than 100 μm were used. The mixtures of $Al_{13}Co_4$ and Al, Al and Co were designated to have the composition of $Al_{85}Co_{15}$. The powder of $Al_{13}Co_4$ was milled for one hour to have an average grain size smaller than 100 μm, subsequently mixed with Al powder and then transferred to a pot. The powder mixtures were then sealed in vacuum (1×10^{-4} Torr) in a cylindrical stainless steel (SUS304) container. The milling was performed in a planetary ball mill (Fritsch p5) at 150 rev min^{-1}. The ball to powder weight ratio was 10:1. The phase identification was examined by conventional X-ray diffractometery (CuKα) and transmission electron microscopy (TEM) (JOEL EX200). Thermal stability was examined by differential scanning calorimetry (DSC) and the morphology of the powders at various stages was observed by scanning electron microscopy (SEM) (HT-800).

3. Results and discussion

The analytical compositions after milling for 200 h by various processes are listed in Table 1. The blend composition was $Al_{85}Co_{15}$ and one can see that the deviation in composition was supressed below 1 at.%. Fig. 1 shows the evolution in the X-ray diffraction pattern for MA of the Al and Co powder mixture. As shown in Fig. 1, intensity of the diffraction peaks was reduced with milling time, but amorphization was not observed after milling for 200 h. Broad diffraction Al peaks still remained after milling for 200 h, whereas the formation of nanocrystalline or supersaturated f.c.c. by MA could be inferred. However, MA of the mixture of monoclinic $Al_{13}Co_4$ and Al (CE-MA) as starting materials revealed the amorphization as shown in Fig. 2. Evidence for the amorphization by CE-MA is shown in Fig. 3(a) and (b). However, the overmilling, in turn, stabilizes the Al_9Co_2 compound. A difference in evolution of the diffraction patterns between the two processes can be pointed out, that is, diffraction peaks of Al disappeared after being milled for 36 h in CE-MA, whereas those still remained even after milling for 200 h in the EE-MA. It should be noted that the pattern of 12 h in the CE-MA is very analogous to that of 200 h in the EE-MA, and we are able to speculate that the two states are similar. In short, the CE-MA shortens the formation time of the amorphous phase in the process.

Table 1
Analytical compositions by chemical analysis for the powders used

at.%	Al	Co	Fe	O2
Al + Co	84.2	15.0	0.33	0.43
Al13Co4 + Al	84.0	14.8	0.61	0.57

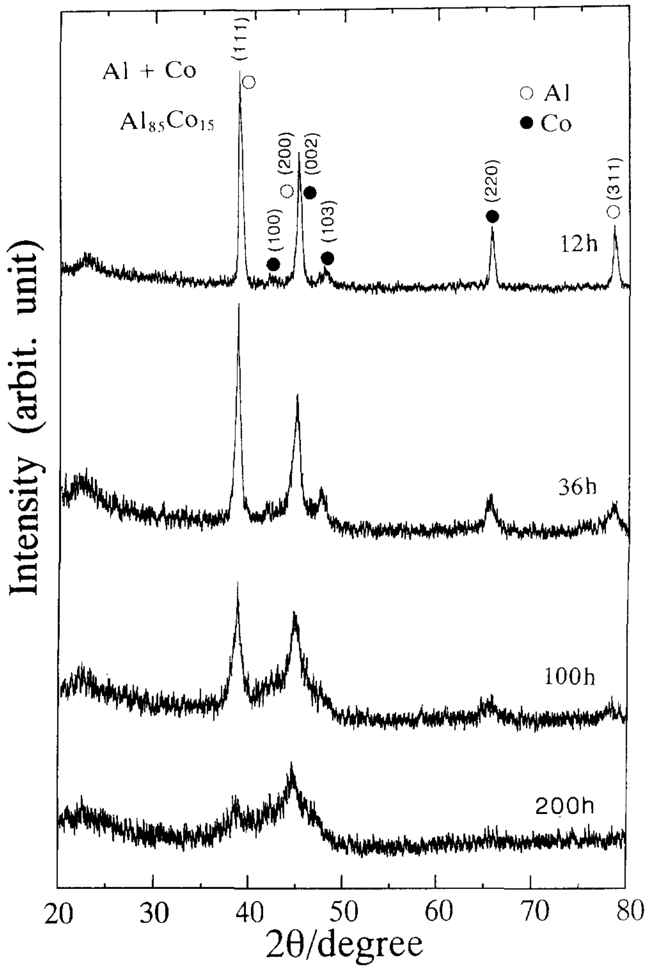

Fig. 1. Powder X-ray diffraction patterns of the MA powders of Al and Co with a blend composition of $Al_{85}Co_{15}$ milled for various times.

Fig. 4 shows the X-ray diffraction patterns of MG for $Al_{13}Co_4$ at different milling times. In a fully annealed state most of the intensive diffraction peaks can be indexed as a monoclinic $Al_{13}Co_4$. The pattern varies quickly in one initial stage, even for a short milling time, and changes to an amorphous phase after 200 h milling. The formation of the amorphous phase was also confirmed by TEM observation as shown in Fig. 5 which revealed no contrast in (a) a bright-field image and (b) a diffuse halo in diffraction pattern. Amorphization of stoichiometric compound with a large negative mixing enthalpy has been interpreted by its drastic change of free energy with composition. That is, accumulation of strains and defects during MG leads to local defect fluctuations which causes a rapid increase in Gibbs energy and stabilizes the amorphous structure. MG of the Al_9Co_2 compound could not form an amorphous phase although it has a similar mixing enthalpy to the monoclinic $Al_{13}Co_4$. However, the results are quite contrary in the MA for the two compound compositions reported by Sui et al. [5]. For these results, an intermetallic compound AlCo was obtained by the

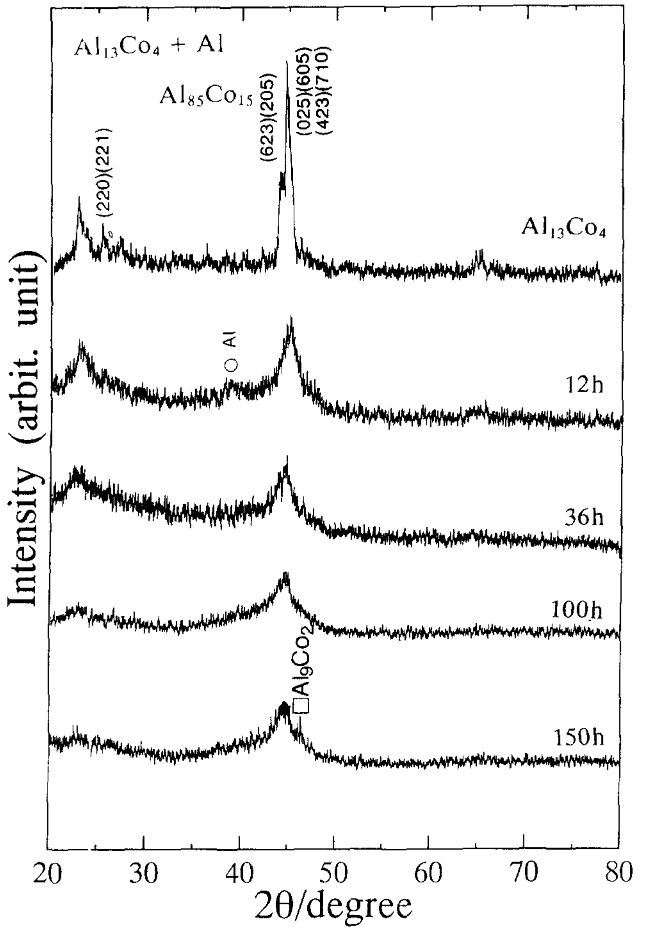

Fig. 2. Powder X-ray diffraction patterns of the MA powders of Al and monoclinic $Al_{13}Co_4$ with a blend composition of $Al_{85}Co_{15}$ milled at various times.

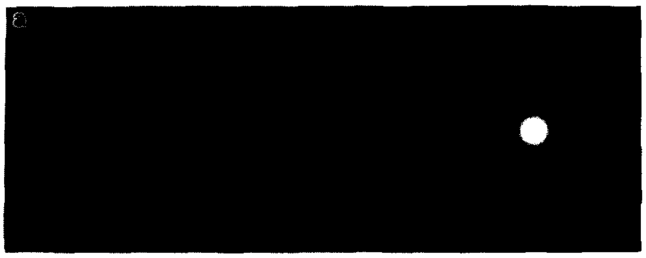

Fig. 3. TEM images of the amorphous phase with a blend composition of $Al_{85}Co_{15}$ obtained by the MA of Al and monoclinic $Al_{13}Co_4$ milled for 100 h. (a) Bright-field image, (b) typical electron diffraction pattern.

MA for $Al_{13}Co_4$, milled for 70 h, and an amorphous phase was formed in the MA for Al_9Co_2, milled for 80 h; both started from the Al and Co elements (EE-MA). It seems that factors such as the milling process and milling condition beyond the enthalpy should be considered. Interestingly, unlike the Al and $Al_{13}Co_4$ mixture, amorphization was not observed in the CE-MA of Al and Al_9Co_2, even milled for 200 h (not shown). Amorphization of the compound in MG seems to be a necessary condition for the amorphization in the CEMA. However, the reason that the amorphization of Al_9Co_2 in MG cannot be achieved is unknown.

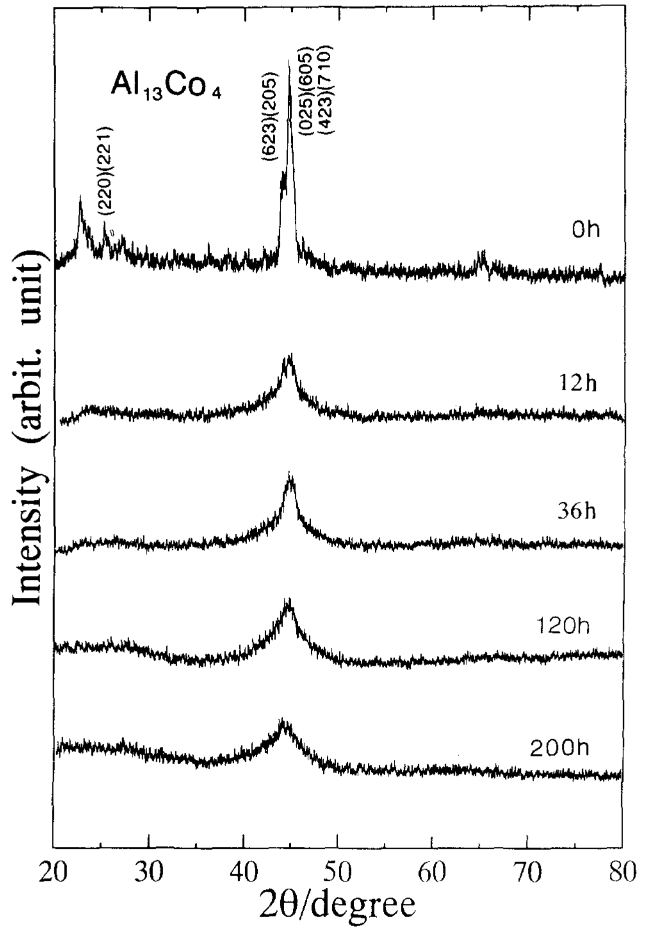

Fig. 4. Powder X-ray diffraction patterns of the MG powder of $Al_{13}Co_4$ milled for various times.

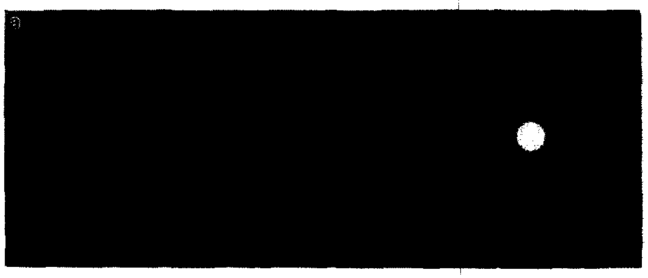

Fig. 5. TEM images of the amorphous phase for the MG of $Al_{13}Co_4$. (a) Bright-field image, (b) typical electron diffraction pattern.

Fig. 6 shows the morphology of the powders with milling time for EE-MA and CE-MA followed by SEM. For the EE-MA, it can be seen that the agglomerates with an average size of ~200 μm with layered structure are formed after milling for 3 h, and particle size remained ~50 μm after milling for up to 36 h and 100 h. On the contrary, only the agglomerates of the small particle were observed in the early stage and the particle size decrease with milling time and attain ~5 μm after milling for 100 h in the CE-MA. The MA process generally consists of repeated welding, fracturing

Fig. 6. SEM images, morphology of EE-MA powders and CE-MA powders milled for (a, d) 3 h, (b, e) 36 h and (c, f) 100 h.

and rewelding of powder particles. The process can be considered to evolve in four distinct stages [8]. Initially, during an intense cold welding period layered composite particulates of the starting constituents form; (2) during a rapid fracturing period the fracturing and cold welding leads to finer composite particle along with the beginning of dissolution and solid solution formation; (3) a moderate cold welding period lamellae gets finer and the composition of individual particles converge to the blend composition; (4) the final stage is a steady state period. By the time the processing has been completed, the particles have an extremely deformed metastable structure. Thus, the reaction rate of the process depends on how fast the repeat of welding and fracturing is. However, the welding is prominant and leads to agglomeration of particles in the early stage as shown in Fig. 6 (a). Thus, the fracturing will not be attained in the early stage for EE-MA. Because of a high volume fraction of $Al_{13}Co_4$ (70 vol.%) of the mixture in the CE-MA process, welding and fracturing have repeated in turn in early milling stage. In view of the results, it is clear that the CE-MA is beneficial for amorphization in comparison with EE-MA in two ways – process and chemistry. Firstly, as described previously the CE-MA omits the first stage of cold welding in the four MA processes e.g., the efficiency of the milling. Secondly, in CE-MA the concentration gradient between the two kinds of powders was small which shortens the time for atomic diffusion to a homogenous composition. Nevertheless, we could not observe any trace of amorphization in the CE-MA of the Al and Al_9Co_2 compound mixture (blend composition $\sim Al_{85}Co_{15}$), ruling out the effect of the second points. On the contrary, it is accepted that two chemical conditions are necessary for the formation of the amorphous phase: the alloying elements must have a large negative mixing heat and one of them should have an anomalously fast diffusion rate in the matrix element of the other [2,9]. However, although fulfilled, these conditions were not sufficient for the formation of the amorphous phase in the case of Al-Ni [10]. this implies that some factors in milling prior to chemical reactions, such as alloying or atomic diffusion, should not be neglected. Most importantly, one of the factors is the area of the interface (A_λ) during MA. If A_λ was large, the grain size of the powders would be small and the chemical reaction would be active. Thus, in the CE-MA process, powders were kept at a small size and prevented from agglomeration, being the key factor to promote the amorphization. Besides the Al-Co system, we have identified the amorphization in Al-Mn ($Al + Al_{11}Mn_4$) system but failed to see the amorphization in Al-Ni and Al-Fe systems, by the CE-MA process with a blend composition of $Al_{85}TM_{15}$. Difference in formation tendency for various TM elements remains unknown. The details will be published in the next report.

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