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Amorphization by Compound-Element Milling in Al-TM(TM=Mn,Fe,Co and Ni) Binary System*

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A compound-element milling process was employed to fabricate Al-based amorphous alloys. Amorphous phases with a blend composition of $\text{Al}_{85}\text{Co}_{15}$ and $\text{Al}_{85}\text{Mn}_{15}$ were obtained by mechanical alloying (MA) for the mixture of Al and monoclinic $\text{Al}_{13}\text{Co}_4$ powders and Al and orthorhombic $\text{Al}_{11}\text{Mn}_4$ powders which could not be obtained by milling Al and Co or Mn elemental powders. Avail of the MA from the compound and element is due to the enhancement of efficiency during milling by leaving out the welding and suppressing the agglomeration of the powders in the process. Mechanism of the amorphization were discussed together with mechanical grinding of the compound. We assert that the MA of Al and its compounds is a available process to produce amorphous phases in Al-enriched(Al>85 at%) alloys.

KEYWORDS: compound-element mechanical alloying, amorphization, aluminum- transition metal

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 to prepared non-equilibrium materials in various alloy systems. A lot of interest has been focussed on the formation of amorphous alloys by MA. In the last few years, there has been an increasing fascination on the evidence that metastable and amorphous phases formed by MA.²⁾ In general, MA is starting from elemental crystalline powders. During the early stages, ball milling produces powder particles with a characteristically layered microstructure due to cold welding and repeated mechanically deformation. Further milling leads to the formation of an ultrafine composite, and finally a true alloying by solid-state reaction occurs, leading to formation of a homogenous amorphous alloy. While the amorphization of intermetallic compounds by mechanical grinding is the introduction of defects and breaking down the crystalline size increases the free enthalpy of the alloy. When the free enthalpy exceeds the free enthalpy of the amorphous phase, the intermetallic compounds can transform into an amorphous phase. In general, the process of amorphization by solid-state reaction includes the mechanical alloying elemental powder mixture and mechanical grinding intermetallic compound.

Amorphization in many alloys which could not be achieved by liquid-quenching is identical in MA process. Al-based alloys are one of the most useful for practical application as an industrial materials because of its low density and high strength. Recently, a group of Al-based amorphous alloys with high strength had been discovered in Al-transition metal(TM)-rare earth metal(RE) systems.³⁾ However, there is no report of an amorphous prepared by liquid-quenching in Al-TM binary system especially, in Al-enriched side. To date, only a few alloys were identified to be formed amorphous phase by MA process in Al-based

alloys performed for long time up to several hundreds hours. A long milling time by MA is necessary because of the high ductility of 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 MA process in an $\text{Al}_{81.8}\text{Co}_{18.2}$,⁴⁾ $\text{Al}_{80}\text{Cr}_{20}$,⁵⁾ and $\text{Al}_{80}\text{Fe}_{20}$.⁶⁾ In this study, we employ the mechanical milling of the mixture of the Al and Al-based compounds powders to prepare an amorphous phase of $\text{Al}_{85}\text{TM}_{15}$ (TM=Mn, Fe, Co and Ni). For comparison, the MA with starting materials of elements and mechanical grinding(MG) were performed.

2. Experimental Details

Alloys with compositions of $\text{Al}_{11}\text{Mn}_4$, $\text{Al}_{13}\text{Fe}_4$, $\text{Al}_{13}\text{Co}_4$ and Al_3Ni were prepared from aluminum and pure elemental 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, Mn, Fe, Co and Ni powders with purity of 99.9% and grain size smaller than 100 μm were used. The mixtures of $\text{Al}_{13}\text{TM}_4$ and Al or Al and TM were desinated to have the composition of $\text{Al}_{85}\text{TM}_{15}$. The powder of compounds were 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 mixtures of the powder 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 diffractometry($\text{CuK}\alpha$) and transmission electron microscopy(TEM, JOEL EX200). Thermal stability was examined by differential calorimetry (DSC) and the morphology of the powders at various stages was observed by scanning electron microscopy (SEM, HT-800).

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3. Results

The analytical compositions after milled for 200 h by various processes in present study are listed in table 1. The blend composition was $\text{Al}_{85}\text{Co}_{15}$ and one can see that the deviation in composition was suppressed below 1 at %. In this study, five Al-based compounds, $\text{Al}_{13}\text{Co}_4$ ⁷⁾, Al_9Co_2 ⁸⁾, $\text{Al}_{13}\text{Fe}_4$ ⁹⁾, $\text{Al}_{11}\text{Mn}_4$ ¹⁰⁾ and $\text{Al}_3\text{Ni}_{11}$ ¹¹⁾ were used. Their structures have been determined as indicated in references.

Table 1 Analytical composition 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

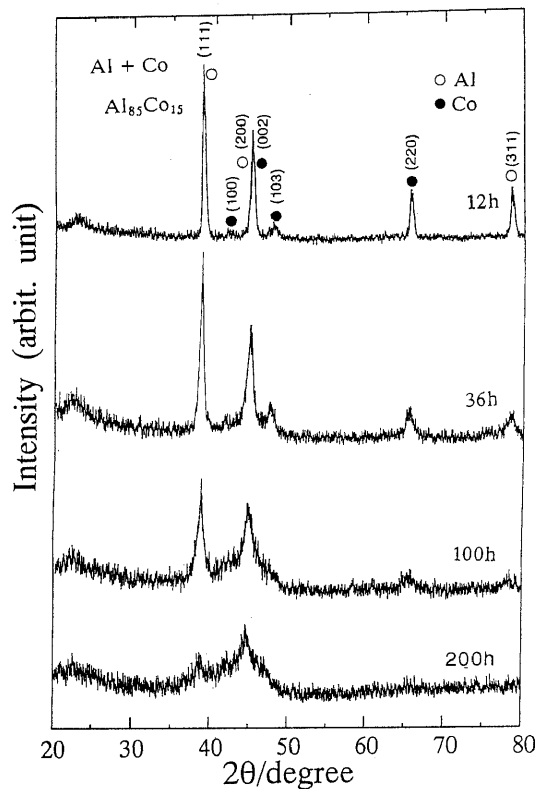


Fig.1. X-ray diffraction patterns of the MA powders of Al and Co with a blend composition of $\text{Al}_{85}\text{Co}_{15}$ milled for various times.

Figure 1 shows the evolution in X-ray diffraction pattern for MA of the mixture of Al and Co powders. As shown in the figure 1, intensity of the diffraction peaks gradually reduced with milling time but amorphization was not observed after milling for 200 h. Broad diffraction peaks of fcc-Al still remained after milling for 200 h, whereas could be inferred the formation of nanocrystalline or supersaturated f.c.c. by MA. On the other hand, the MA

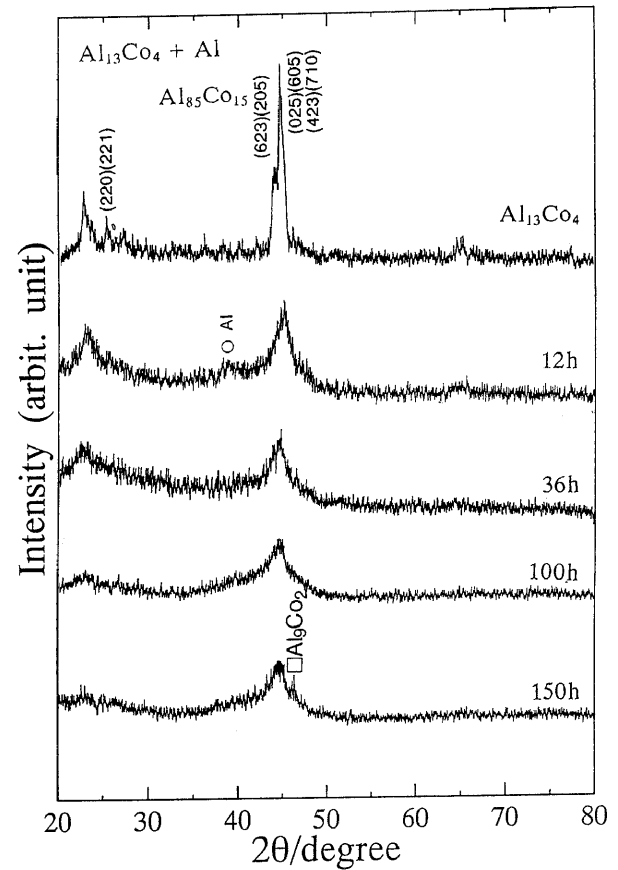


Fig.2. X-ray diffraction patterns of MA powders of Al and monoclinic $\text{Al}_{13}\text{Co}_4$ with a blend composition of $\text{Al}_{85}\text{Co}_{15}$ milled for various times.

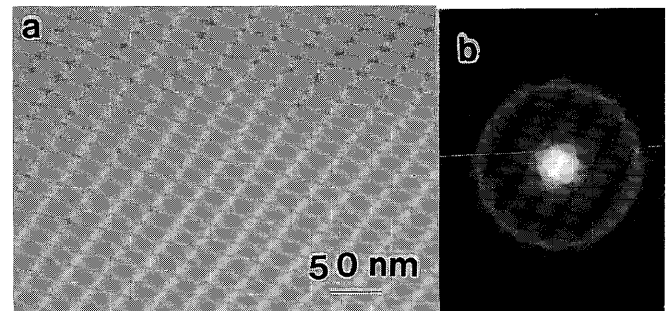


Fig.3. Bright-field image(a) and electron diffraction pattern (b) for 100h-milled sample in Fig.2.

with starting materials of the mixture of monoclinic $\text{Al}_{13}\text{Co}_4$ and Al powders (CE-MA) revealed the amorphization as shown in Fig.2. An evidence for the amorphization by CE-MA was shown in a set of TEM micrographs; bright-field image(a) and electron diffraction pattern(b) in Fig.3. 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 had disappeared after milled for 36 h in the CE-MA, whereas those still remained even after milling for 200h in the EE-MA. We should note that the pattern of 12h in the CE-MA is very analogous to that of 200h in the EE-MA, being able to speculate that the two states are similar. In

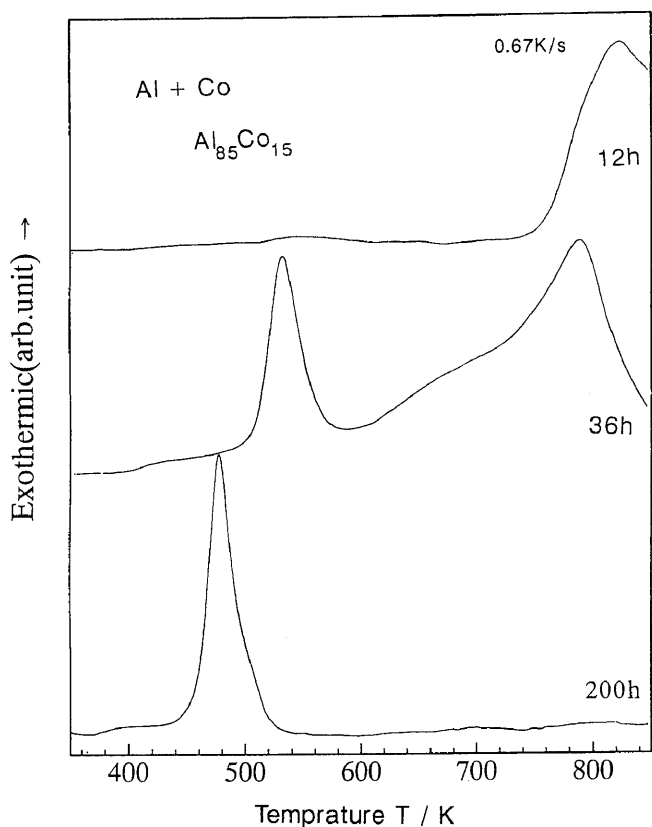


Fig.4. DSC curves for the EE-MA powder milled at various times.

from the DSC curves in Figs. 4 and 5. Fig.4 and Fig.5 show the DSC curves of the powders milled at various time in Fig.1 and Fig.2 respectively. An exothermic peak near 500K appeared after milled for 12h in CE-MA while it was observed after milled for 36h in EE-MA.

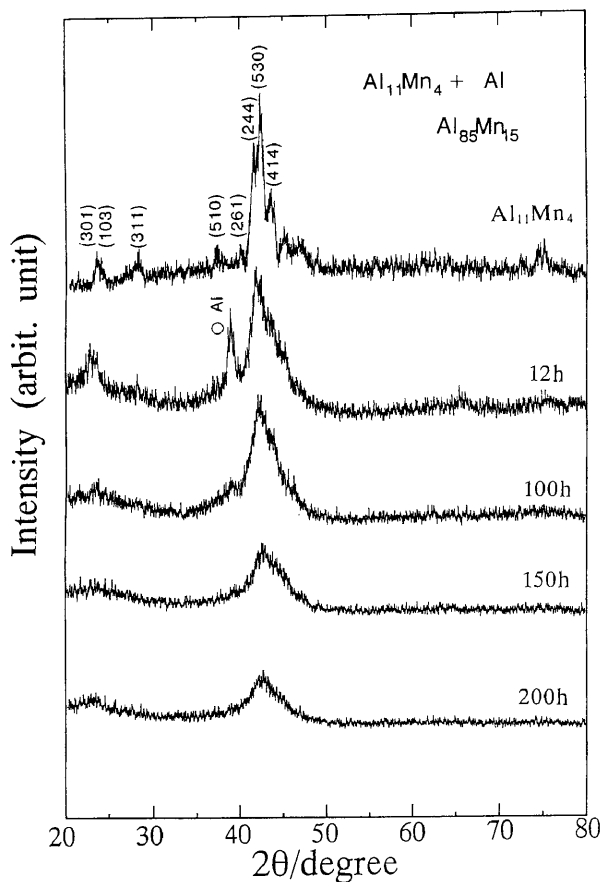


Fig.6. X-ray diffraction patterns of the CE-MA powder with a blend composition of $Al_{85}Mn_{15}$ milled for various times.

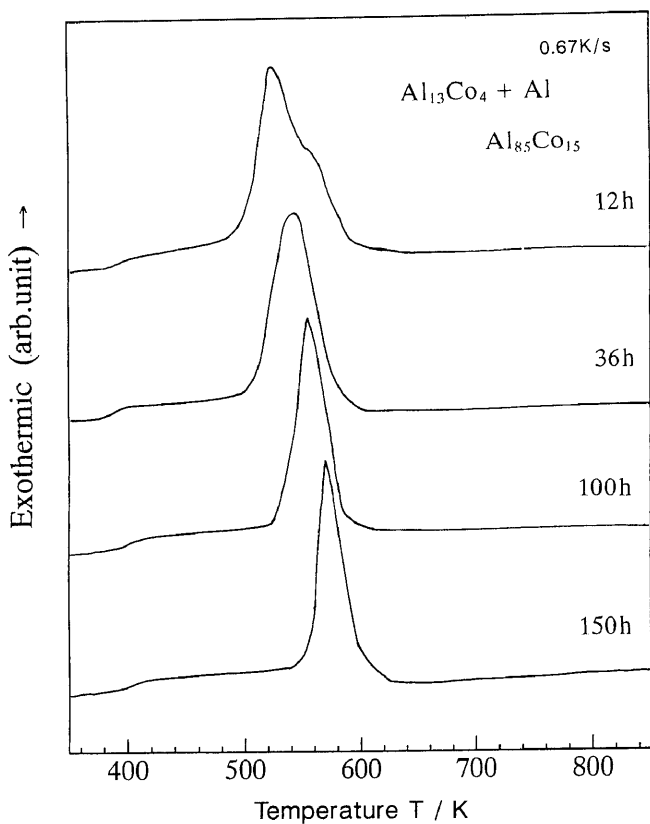


Fig.5. DSC curves for the CE-MA powder milled at various times.

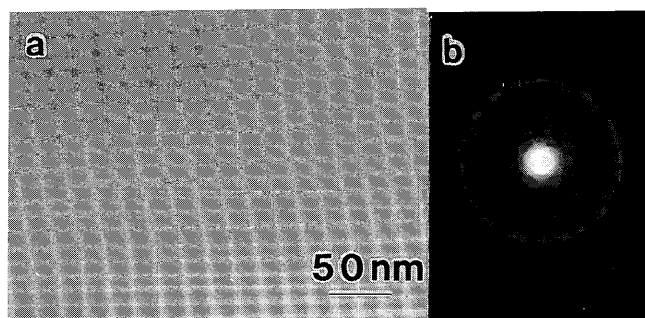


Fig.7. Bright-field image(a) and diffraction pattern(b) for the 200-milled sample in Fig.6.

short, the CE-MA shortens the time for the formation of amorphous phase in the process. This also could be inferred

Full amorphization for the alloy with blend composition of $Al_{85}Mn_{15}$ was completed by CE-MA for $Al_{11}Mn_4$ and Al powders. Figure 6 exhibits the evolution in the CE-MA process for $Al_{11}Mn_4$ and Al powders. The amorphous phase also identified by TEM as shown in Fig.7. On the other hand, figure 8 shows X-ray diffraction patterns for CE-MA of $Al_{13}Fe_4$ and Al powders milled at various time. In view of the pattern after milled for 300h, full amorphous phase seems to be formed. However, in TEM observations, it

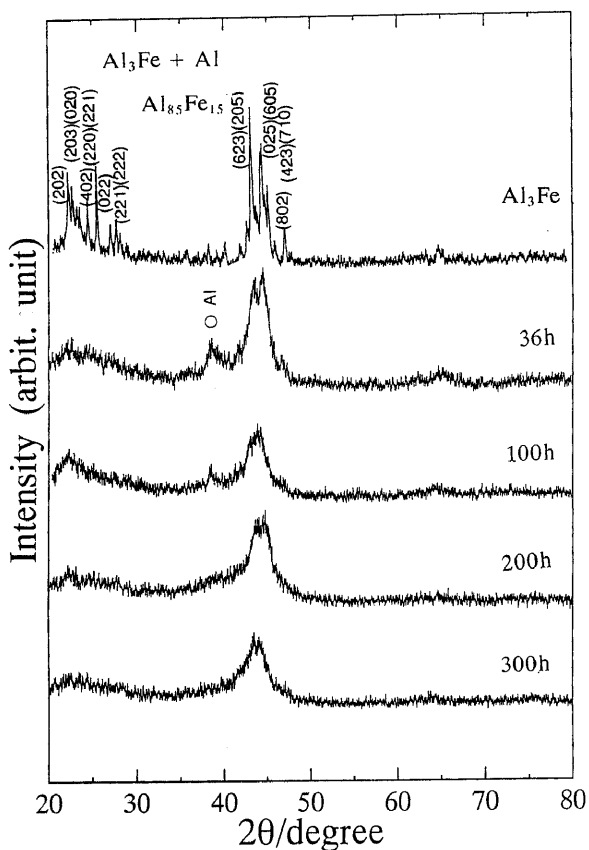


Fig.8. X-ray diffraction patterns of the CE-MA powder with a blend composition of $Al_{85}Fe_{15}$ milled at various times.

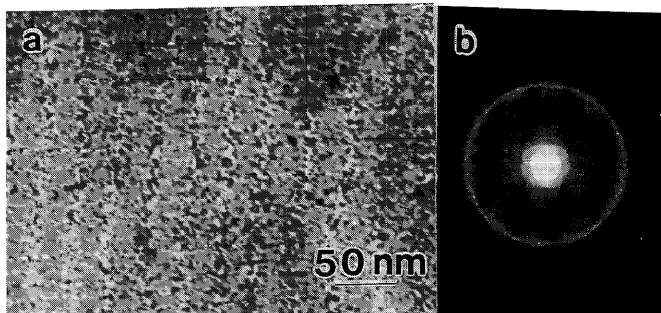


Fig.9. Bright-field image(a) and electron diffraction pattern (b) of the 300-milled sample in Fig.8.

revealed a nano-crystalline phase as shown in Fig.9. Similarly, as shown in Fig.10, amorphization was not achieved in CE-MA process for Al_3Ni and Al powders.

4. Discussion

It was reported that an intermetallic compound $AlCo$ was obtained by the MA for the $Al_{13}Co_4$ milled for 70 h and an amorphous phase was formed in the MA for the Al_9Co_2 milled for 80h, both started from the elements (EE-MA) of Al and Co. ⁹ It is difficult to discuss the difference in the results because milling condition is different from one to another. In order to realize the amorphization mechanism of the CE-MA, the MG for the

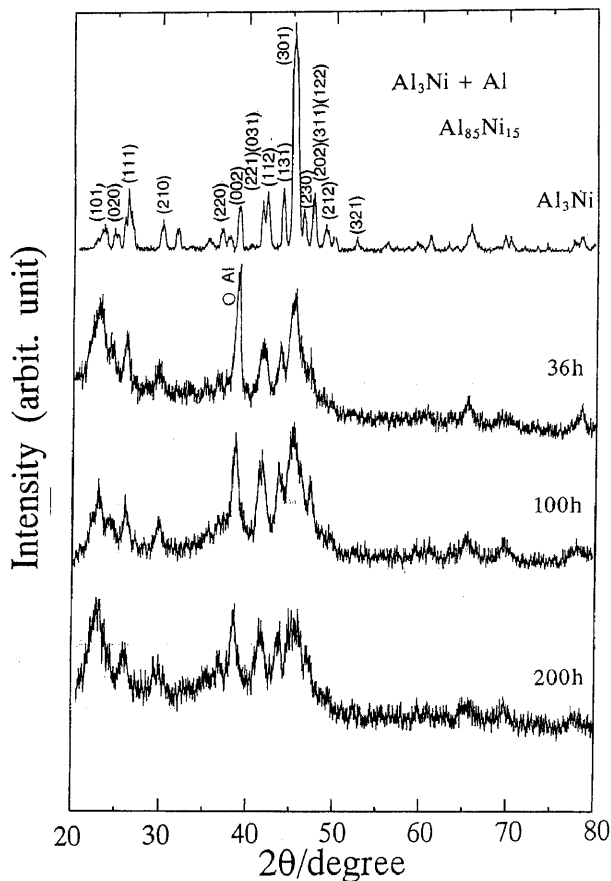


Fig.10. X-ray diffraction patterns of the CE-MA powder with a blend composition of $Al_{85}Ni_{15}$ milled at various times.

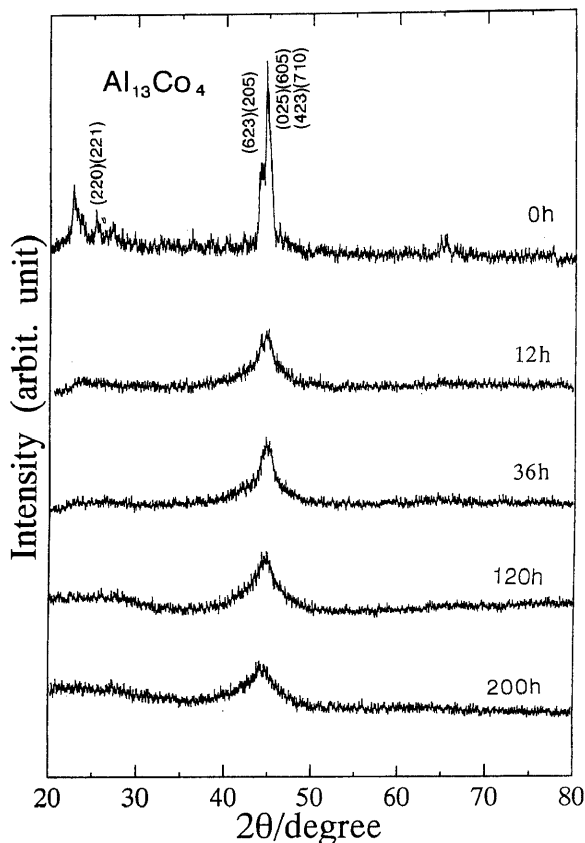


Fig.11. X-ray diffraction patterns of MG powder of $Al_{13}Co_4$ milled for various times.

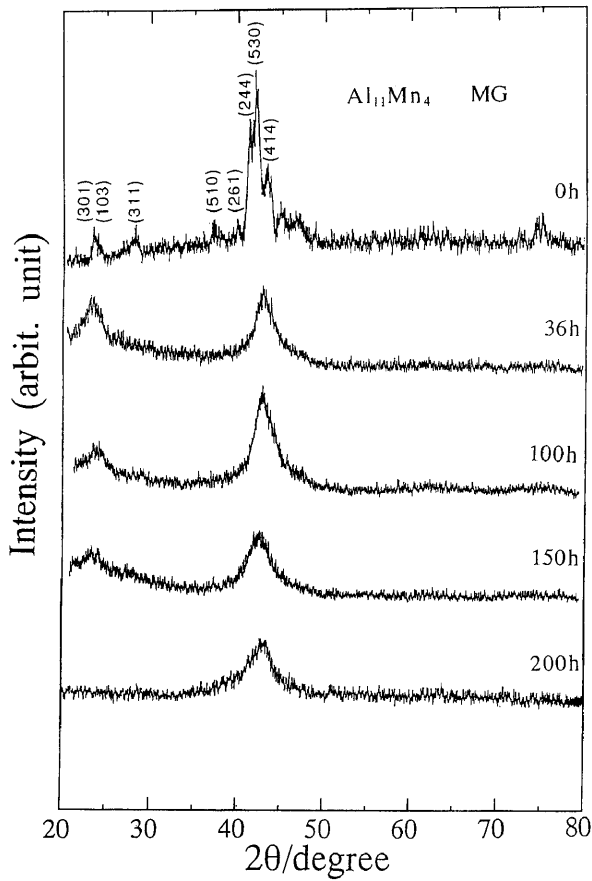


Fig.12. X-ray diffraction patterns of MG powder of $Al_{11}Mn_4$ milled for various times.

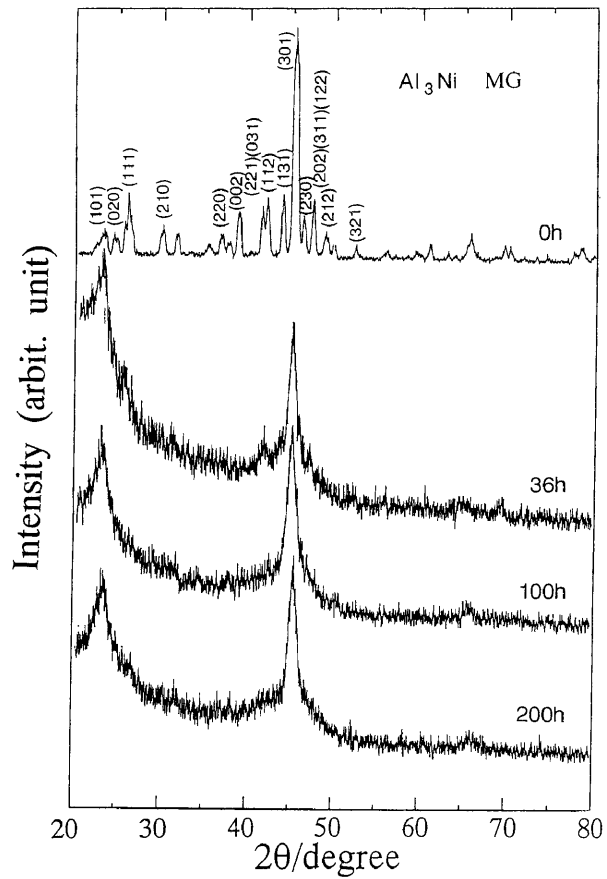


Fig.14. X-ray diffraction patterns of MG powder of Al_3Ni milled for various times.

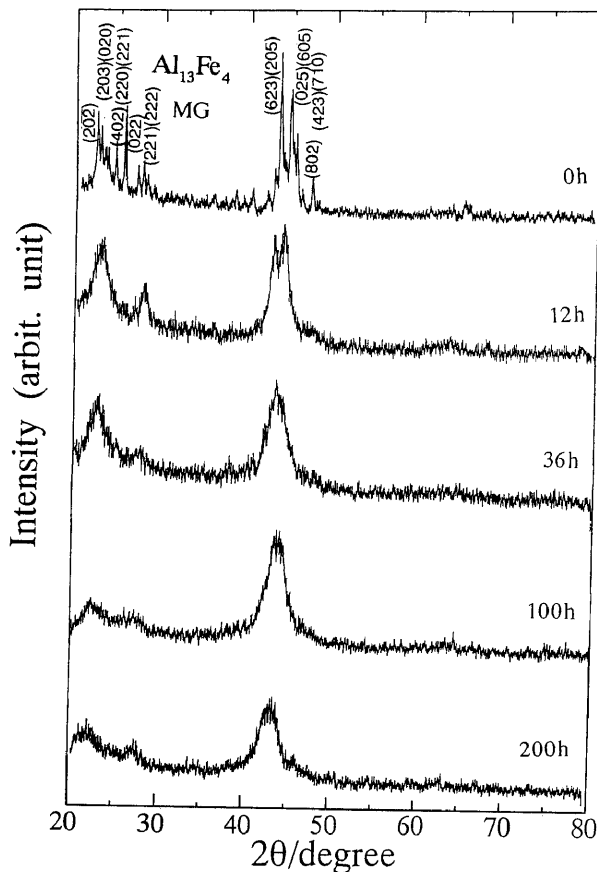


Fig.13. X-ray diffraction patterns of MG powder of $Al_{13}Fe_4$ milled for various times.

compounds in previous four system was performed. Figure 11 shows the X-ray diffraction patterns with milling time of MG for $Al_{13}Co_4$. In a fully annealed state most of intensive diffraction peaks can be indexed as a monoclinic $Al_{13}Co_4$. The pattern varies quickly at initial stage even in a short time milling and evolves to an amorphous phase after 200h milling. Amorphization of stoichiometric compound with a large negative mixing enthalpy had been interpreted by its drastic change of free energy with composition. That is, accumulation of strains and defects during MG leads to local defects fluctuations which causes a rapid increase in Gibbs energy and stabilizes the amorphous structure. Whereas, the MG of the Al_9Co_2 compound could not be formed an amorphous phase although it has the similar mixing enthalpy to the monoclinic $Al_{13}Co_4$. Unlike the mixture of Al and $Al_{13}Co_4$, amorphization was not observed in the CE-MA of Al and Al_9Co_2 even milled for 200 h(not shown). Amorphization of an $Al_{11}Mn_4$ compound was obtained by MG as shown in Fig. 12. However, amorphization for compounds of $Al_{13}Fe_4$ and Al_3Ni could not be achieved by MG process as shown in Fig.13 and Fig.14. According to the previous results, it is clear that amorphization of the compound in MG seems to be a necessary condition for the amorphization in the CE-MA. Amorphization of such compound will occur firstly and then be a nuclei site of amorphization during CE-MA process.

When it comes to the avail of CE-MA, the mechanical process should be considered. The morphology of the

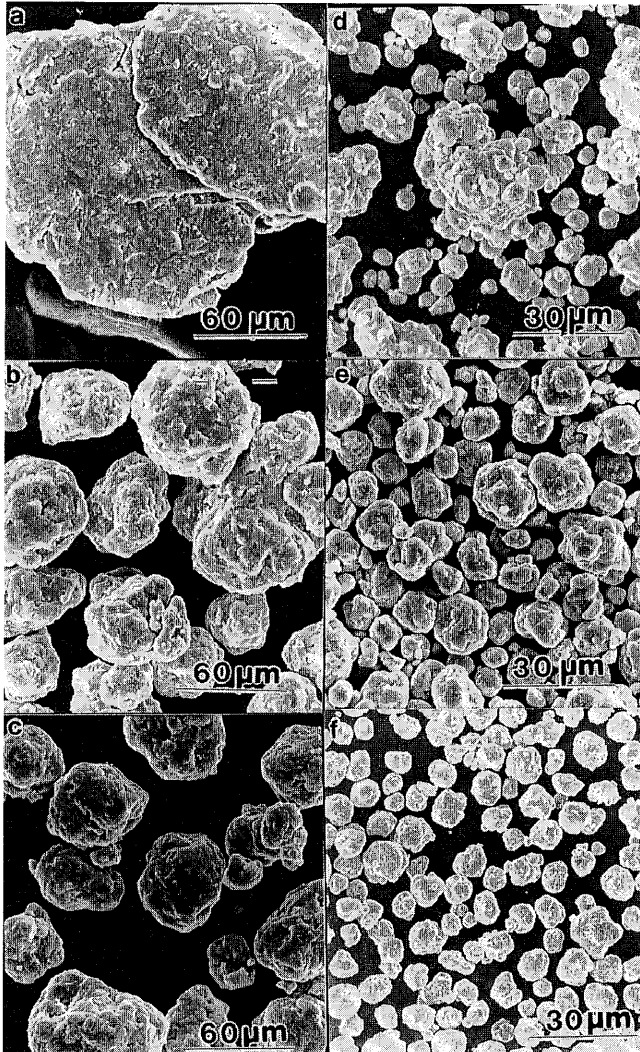


Fig.15. SEM images, morphology of EE-MA powders (a,c,e) and CE-MA(b,d,f) powders milled for 3h(a,d), (b,e)36h and (c,f)100h.

powders under various milling time for EE-MA (a,b,c) and CE-MA(d,e,f) was followed by SEM shown in figure 15. For the EE-MA, it can be seen that the agglomerates having an average size of about $\sim 200 \mu\text{m}$ with layered structure are formed after milling for 3 h, and particle size remained about $\sim 50 \mu\text{m}$ after milling up to 36 h and 100 h. On the other hand, only the agglomerates of the small particle were observed in the early stage and the particle size decrease with milling time and attain $\sim 5 \mu\text{m}$ after milled for 100h in the CE-MA process. The mechanical alloying process generally consists of repeated welding, fracturing and rewelding of powder particles. The process can be considered to evolve in four distinct stages.¹¹⁾ (1) Initially, during an intense cold welding period layered composite particulates of the starting constituents form. (2) then 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 get 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 prominent and leads to agglomeration of particles in early stage as shown in Fig.6(a). Thus, the fracturing will not be attained in early stage for the EE-MA. Because high volume fraction of the $\text{Al}_{13}\text{Co}_4$ (70 vol%) of the mixture in 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 leaves out the first stage of cold welding in the four MA processes e.g., enhances the efficiency of the milling. Secondary, in CE-MA the concentration difference between the powders was much smaller than in EE-MA, which shortens the time for atomic diffusion to a homogenous composition. It is widely accepted that two chemical conditions are necessary for the formation of the amorphous phase: the alloying elements must have a large negative heat of mixing and one of them should have an anomalously fast diffusion rate in the matrix element of the other.⁽²⁾⁽¹²⁾ However, although fulfilled, these conditions were not sufficient for the formation of the amorphous phase in the case of Al-Ni.¹³⁾ In addition, we could not observe any trace of amorphization in the CE-MA of the mixture of Al and Al_9Co_2 compound (blend composition $\sim\text{Al}_{85}\text{Co}_{15}$) although the $\text{Al}_{13}\text{Co}_4$ has the similar heat of mixing as that of Al_9Co_2 . This implies that some factors in milling prior to chemical reactions such as alloying or atomic diffusion, should not be neglected. Most important one of the factors is the area of the interface (A_i) during the MA. If A_i were 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 small size and prevented from agglomeration, are the key factors to promote the amorphization.

In conclusion, amorphous phase was formed in $\text{Al}_{85}\text{Co}_{15}$ and $\text{Al}_{85}\text{Mn}_{15}$ alloys by means of compound-element MA (CE-MA), which amorphization could not be achieved either by liquid quenching or by element-element MA. The avail of the CE-MA is thought to be due to enhancement of efficiency during milling by omitting the welding and suppressing the agglomeration of the powders in the process. Amorphization by MG for the compounds which were used as a starting materials in the CE-MA process, plays a crucial role in the amorphization by CE-MA.

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