Amorphous and nano-crystalline structures of mechanically-alloyed Al-24.4%Fe(mole fraction) powder mixture[①]

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Abstract: Elemental powders of Al-24.4%Fe (mole fraction) alloy were mechanically-alloyed using a conventional type ball-milling. Not only Fe particles gradually disperse in Al matrix but also Al and Fe crystal grains are refined to the order of ten nanometers after ball-milling for 180 h. The amorphization starts at the early stage of ball milling and proceeds gradually. Complete amorphization is confirmed by ball-milling for 720 h. The amorphization of the powders after ball-milled for 180 h can be promoted by heating up to 673 K, which suggests a possibility of producing amorphous material by appropriate ball-milling and subsequent heating.

Key words: crystal and amorphous structure; mechanical alloying; Al-Fe alloy   **Document code:** A

1　INTRODUCTION

Mechanical alloying (MA) is a ball-milling process related to repeated fracturing and rewelding of powder particles[1]. Koch et al reported for the first time the preparation of amorphous $Ni_{60}Nb_{40}$ powder by MA of elemental powders in 1983[2]. Since then, considerable studies on the preparation of non-equilibrium phases such as amorphous[3~5], supersaturated solid solutions[6] and metastable compounds[7] have been carried out. In the previous papers[8,9], nanometer order crystalline structures and metastable phases in Al-Fe alloys formed during MA were reported. It was found that the process of gradual refinement of crystal size and the formation of metastable phases take place concurrently. The results of further studies on the Al-24.4%Fe(mole fraction) alloy will be reported in this paper.

2　EXPERIMENTAL

The conventional ball-milling apparatus was used in this experiment. Both the pot and the balls were made of SUS304 stainless steel. The pot is about 1.7×10^{-3} m³ in volume and balls are 9 mm in diameter. 99.9% pure Al and Fe powders with the average particle size of about 50 μm were put into the pot containing the balls. The powder to ball ratio was kept to 1:90 (in mass). Powder was sealed in the pot in argon atmosphere with 3% methanol. X-ray powder diffractometry was performed using a Cu Kα target. Samples for the transmission electron microscope(TEM) were made by slicing the powder embedded in resin using a sapphire blade.

3　RESULTS AND DISCUSSION

Fig.1 shows the X-ray diffraction patterns of Al-24.4% Fe (mole fraction) samples ball-milled for various length of time. The diffraction peaks corresponding to (111) and (311) plane of the FCC aluminum became broad and weak with the increase of ball-milling time, and almost negligible after ball-milling for 180 h. The diffraction peak corresponding to (110) plane of the BCC iron, overlapped by (200) plane of the

FCC aluminum, became broad and slightly shifted to low angle side with the increase of ball-milling time, which indicates the formation of solid solution of larger Al into Fe. Halo-like broad peak can be seen between the first two diffraction peaks. For the sample ball-milled for 454 h, only halo pattern was observed. Prolonging the ball-milling time, there is almost no
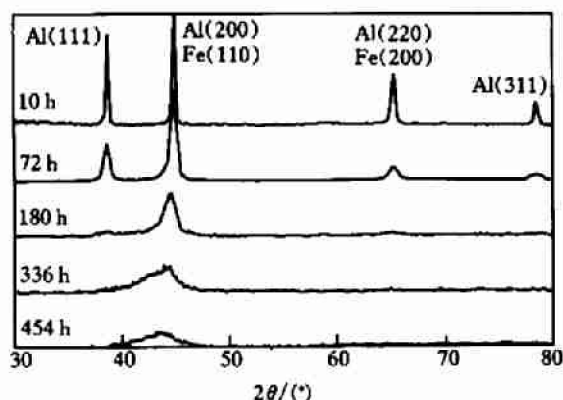
change in the XRD pattern.

Fig. 2 shows the SEM images of samples ball-milled for various times. Similar to those of Al-4 % Fe(mole fraction) samples[8], Fe particles finely dispersed in an equiaxed shape into the matrix with the increase in ball-milling time. The size of dispersed Fe particles became too small to be seen by the SEM after ball-milling for 180 h.

Fig. 3 shows the TEM images of the powders after ball-milled for 180 h. The refinement of grain size of the BCC Fe particles about several tens of nano-meters is shown. Halo-like broad ring which indicates the existence of amorphous phase is observed near the first diffraction ring. The TEM images of the sample which was ball-milled for 454 h revealed almost no images of crystal grains except for scattered grains of roughly ten nano-meters in size as shown in Fig. 4. The electron diffraction pattern shown in the same figure indicates that the matrix activates only the halo ring pattern, whose position matches with that of the broad halo-peak of X-ray diffraction shown in Fig. 1. The scattered grains of roughly ten nano-meter in size were identified to be BCC Fe crystal grains.
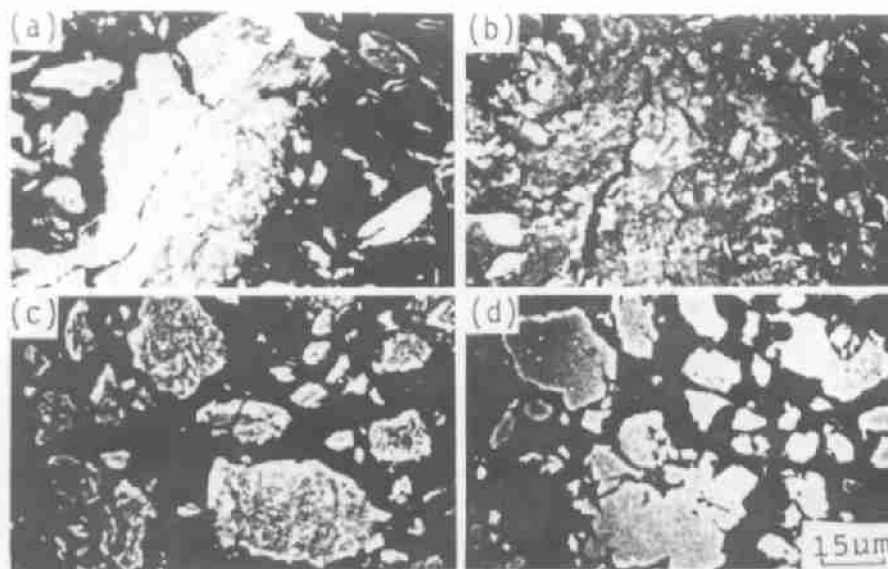
Fig.1 X-ray diffraction patterns of Al-24.4% Fe (mole fraction) samples after ball-milled for various times(Cu Kα)

Fig.2 SEM images of Al-24.4% Fe(mole fraction) powders after ball-milled for various times
(a)—20 h; (b)—36 h; (c)—72 h;(d)—180 h

Complete amorphization was confirmed by the TEM images of the sample which was ball-milled for 720 h as shown in Fig. 5. No images of crystal grains were observed from either the bright or dark field images. It is to be noted that the large amorphous forming tendency around Al-24.4% Fe(mole fraction) composition was also reported using the sputtering method[10].

Fig. 6 shows the mössbauer spectra of samples after ball-milled for various length of time. The spectrum (c) was obtained from the same sample as that shown in Fig. 4. Consequently, the paramagnetic doublet absorption peak can be attributed to the amorphous phase. The ferromagnetic component remained can be attributed to the scattered BCC Fe crystal grains as shown in Fig. 4. It should be noted that the doublet absorption peak exists even in the sample which was ball-milled for only 72 h. This result indicates that the amorphous phase starts to form at the early stages of ball-milling at the interface of the Fe particles and Al matrix. Using TEM,
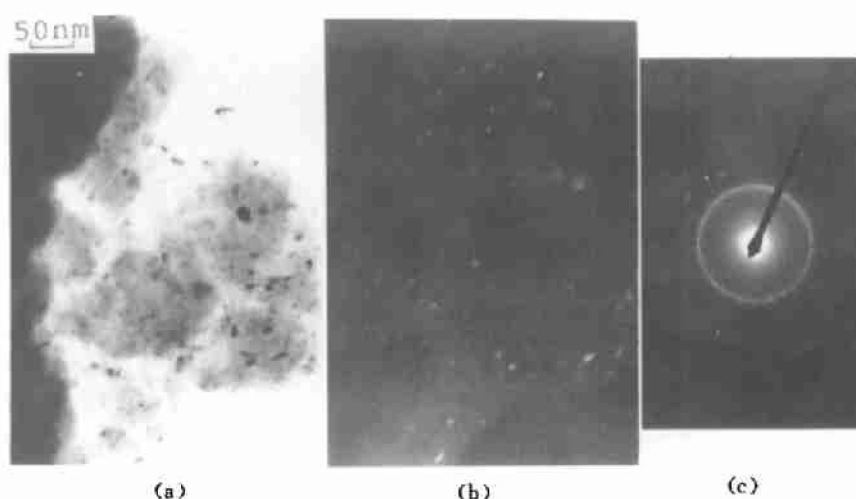

(a)   (b)   (c)

Fig. 3   TEM images of Al-24.4% Fe(mole fraction) powders after ball-milled for 180 h
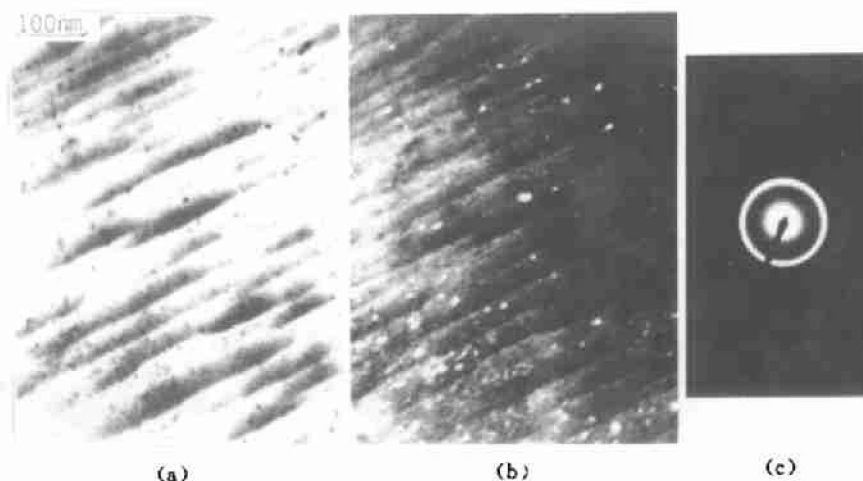(a)—Bright field TEM; (b)—Dark field TEM; (c)—Electron diffraction pattern

(a)   (b)   (c)

Fig. 4   TEM images of Al-24.4% Fe(mole fraction) powders after ball-milled for 454 h
(a)—Bright field TEM; (b)—Dark field TEM; (c)—Electron diffraction pattern
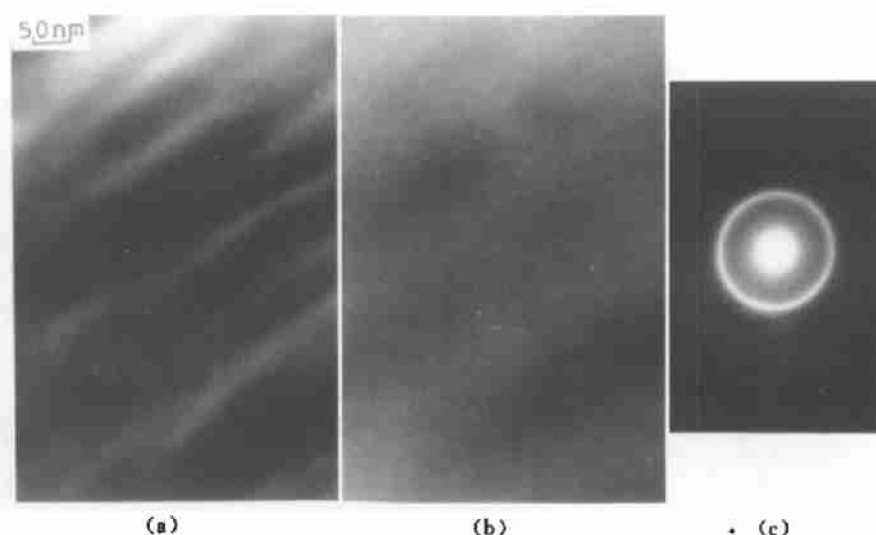
Fig.5   TEM images of Al-24.4%Fe(mole fraction) powders after ball-milled for 720 h
(a)—Bright field TEM; (b)—Dark field TEM; (c)—Electron diffraction pattern

however, the identification of the amorphous phase was difficult even in the 180 h ball-milled sample, whose major part (60%) of Fe atoms were in the amorphous phase as calculated from the absorption peak area of the spectrum in Fig.6 (b).

Fig.7 shows the DSC curves of Al-24.4% Fe(mole fraction) samples ball-milled for various times. For the sample ball-milled for 72 h, composite exothermic reactions to the equilibrium phases occur at about 673 K. The very sharp exothermic peak for the powders ball-milled for 454 h and longer may be attributed to the crystallization of the amorphous phase. For the samples after ball-milled for 95 and 180 h, the two exothermic peaks near 673 K are overlapping each other. The total heat of the exothermic peaks for samples after ball-milled for 72, 95, 180 and 454 h are measured to be 727, 387, 320 and 183 J/g, respectively, decreasing with increasing the ball-milling time. This result indicates that the amorphous phase which increases with increasing the ball-milling time (as shown in Fig. 6) is a thermodynamicly metastable phase, which can be confirmed by free energy versus composition diagram of Al-Fe system[9].

Fig. 8 shows the X-ray diffraction patterns taken from the 180 h ball-milled samples which were respectively heated up to 673 K (between the first and second peak in Fig.8(b)) and 773 K (after the second peak in Fig.8(c)) together with the corresponding as-ball-milled sample in Fig.8(a). In comparison with the as-ball-milled sample, the diffraction pattern of the sample heated up to 673 K and naturally cooled became much broader and slightly shifted to low angle side, which corresponds to formation of amorphous phase. The diffraction pattern of the sample heated up to 773 K shows the formation of compound Al_5Fe_2 in which Al_3Fe isn't formed probably because of contamination of iron coming from the stainless ball and pot. The sample heated up to 673 K was also observed by TEM. The electron diffraction pattern shows almost only the halo-like ring, while corresponding as-ball-milled sample shown in Fig. 3 clearly shows the second and third diffraction ring in addition to the first ring. These results indicate that the amorphization of the sample after ball-milled for 180 h can be promoted by heating up to 673 K, which suggests a possibility of producing amorphous material by appropriate ball-milling and subsequent heating. Unfortunately, the exothermic reaction due to the amorphization is
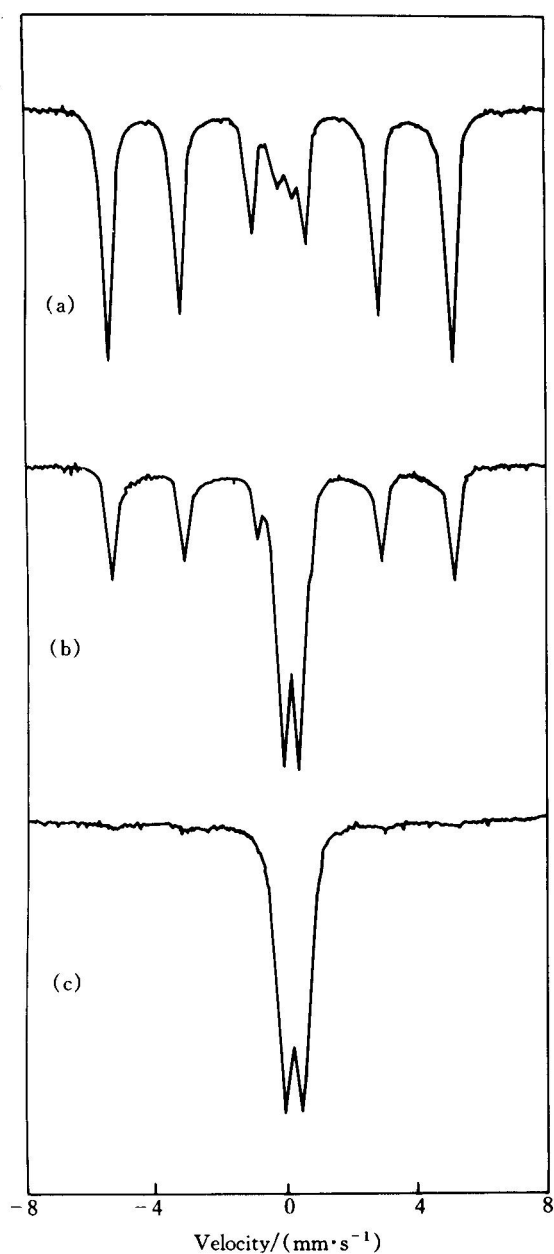
Fig.7 DSC curves of Al-24.4%Fe (mole fraction) samples ball-milled for various times

Fig.6 Mössbauer spectra of Al-24.4%Fe (mole fraction) samples after ball-milled for various times
(a)—72 h; (b)—180 h; (c)—454 h

overlapped in part with the subsequent crystallization reaction so that complete amorphization by heating can not be achieved.
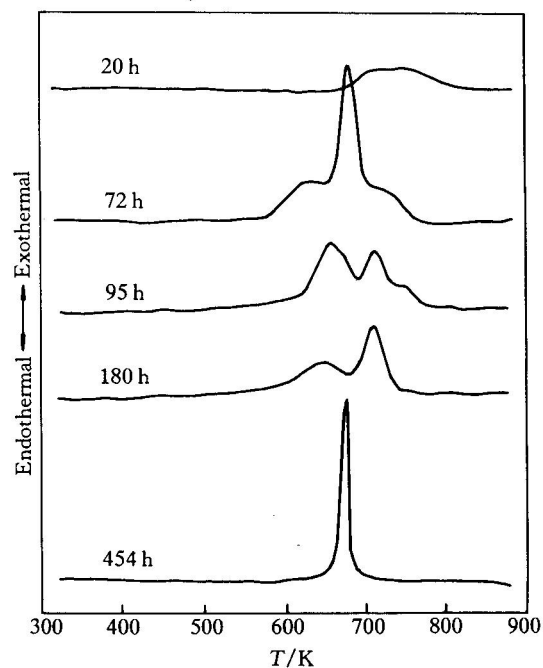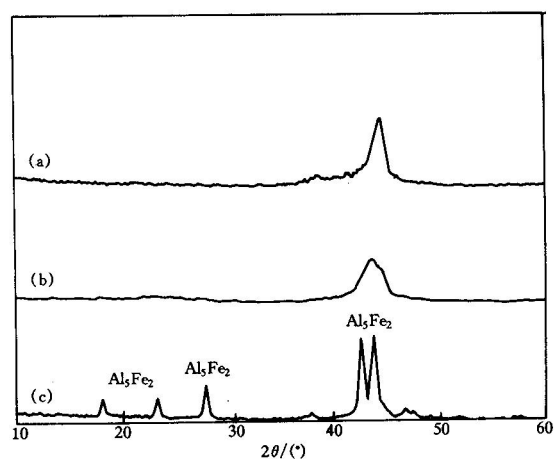

Fig.8 X-ray diffraction patterns of Al-24.4%Fe (mole fraction) samples after ball-milled for 180 h
(a)—As ball-milled;
(b)—Continuously heated up to 673 K and cooled;
(c)—Continuously heated up to 773 K and cooled

Free energies of the phases in Al-Fe system can be calculated by CALPHAD method. The

calculated results show that the amorphous alloy which is considered to be a undercooled liquid has a lower free energy than that of mixture of the two crystalline elements around Al-25% Fe composition at 400 K[9]. This difference in free energy (about 10 kJ/mol) is the driving force to form amorphous material by MA of Al and Fe crystalline elements.

Schwarz and Johnson first obtained the amorphous Au-La alloy by heating a thin multi-layered configuration of 6 to 16 alternating layers (10～60 nm) of crystalline gold and lanthanum for several hours at temperatures of 323 ～ 353 K[11]. At that temperature the amorphization takes place because the time necessary for nucleation and growth of crystalline phases is longer than the time for amorphization. A fast diffusion would lead to high mobility in the amorphous phase.

4　CONCLUSION

A successive dispersion of Fe particles into Al matrix occurs as the ball-milling time increases. The matrix crystal grain is also gradually refined to the order of ten nanometers after ball-milling for 180 h. The formation of amorphous phase begins at early stages of ball-milling at the interface of the Fe particles and Al matrix, and proceeds gradually. Complete amorphization is achieved by ball-milling for 720 h. For the 180 h ball-milled sample, the formation of amorphous phase can be promoted by heating up to 673 K, which suggests a possibility of producing amorphous material by appropriate ball-milling and subsequent heating.

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(**Edited by Huang Jinsong**)