

# Mechanical alloying process of Fe-Cr powders studied by magnetic measurements

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(Received 29 June 1992; accepted for publication 18 September 1992)

A mechanical alloying process for a mixture of elemental Fe and Cr powders with the Cr compositions 20–70 at. % was investigated through the measurements of x-ray diffraction, magnetization, and  $^{57}\text{Fe}$  Mössbauer spectrum. We show that magnetic studies provide more detailed information about the alloying process occurring during ball milling than the conventional diffraction techniques in this particular system. A final product after ball milling was identified as a high-temperature phase of the  $\alpha$  solid solution, regardless of compositions studied. Powders subjected to milling in Ar gas atmosphere for 200 h were further ball milled in  $\text{N}_2$  atmosphere. The presence of  $\text{N}_2$  gas has caused a partial amorphization. The amorphous phase thus produced is found to be paramagnetic at room temperature.

## I. INTRODUCTION

Mechanical alloying (MA) is capable of producing powders in a nonequilibrium state by either accumulating mechanical energy or accelerating the diffusion across the interface between unlike elements.<sup>1</sup> This technique is well suited to study a gradual structural change in the solid-state reactions, such as the transformation from a crystal into an amorphous phase.<sup>2</sup> A combination of the x-ray and neutron diffraction experiments has been recognized to be highly powerful for this purpose.<sup>3</sup> However, the diffraction technique becomes obviously unfavorable when two elemental powders possess nearly identical lattice constants in the same crystallographic structure and result in a homogeneous solid solution.

Both Fe and Cr possess the body-centered cubic (bcc) structure and the difference in their lattice parameters is only 0.5%. According to the equilibrium Fe-Cr phase diagram,<sup>4</sup> the disordered bcc solid solution ( $\alpha$  phase) exists at temperatures above the spinodal decomposition line. Though the diffraction lines of the respective elements can be resolved in the starting powders, line broadening owing to the accumulation of strains and defects in the course of the ball milling makes it almost impossible to pursue the structural change any further. Hence, other measurements should be combined to supplement the diffraction data.

The magnetic properties of Fe and Cr are quite different from each other. Fe is ferromagnetic below 770 °C, while Cr is nonmagnetic at room temperature. The  $\alpha$ -phase  $\text{Fe}_{100-x}\text{Cr}_x$  alloy, which can be obtained by quenching from temperatures above the spinodal decomposition line, exhibits ferromagnetism in the Cr concentration range  $0 < X < 70$ , while those with  $X > 76$  exhibit mictomagnetism at low temperatures.<sup>5</sup> The Curie temperature in the  $\alpha$  phase initially increases but begins to decrease with further increase in the Cr concentration. It is lowered to 0 °C at  $X = 70$ .<sup>4</sup> The magnetic moment almost linearly decreases with increasing the Cr concentration in conformity with the Slater-Pauling curve. Taking full advantage of this

strong composition dependence of the magnetic properties, one can extract valuable information on the mechanical alloying process in this system. Furthermore, the local structure around Fe atoms can be deduced by analyzing the  $^{57}\text{Fe}$  Mössbauer spectra.

In this article, we have analyzed the MA process for a mixture of elemental Fe and Cr powders on the basis of the data on magnetic properties and  $^{57}\text{Fe}$  Mössbauer spectroscopy. The formation of a homogeneous high-temperature  $\alpha$  phase has been confirmed as a final product. We also found that additional milling in  $\text{N}_2$  atmosphere resulted in the formation of an amorphous phase.<sup>6,7</sup> Changes in the magnetic properties due to nitrification are also reported.

## II. EXPERIMENTAL PROCEDURE

A mixture of appropriate amounts of Fe (99.9%,  $< 150 \mu\text{m}$  in size) and Cr (99.9%,  $< 74 \mu\text{m}$  in size) powders was ball milled in an Ar gas atmosphere in a vial (80  $\text{cm}^3$  in volume) with 20 balls (10 mm in diameter). Both the vial and balls were made of stainless steel. The compositions chosen were  $X = 20, 50,$  and  $70$  in the  $\text{Fe}_{100-x}\text{Cr}_x$  system. An average weight of the powders was 20 g. The milling was carried out with a planetary-type ball mill (Fritsch P-5) at the rotating speed of 430 rpm or intensity setting of 5. Milling was interrupted for 6 min every 30 min in order to minimize excessive temperature rise.

$^{57}\text{Fe}$  Mössbauer spectra were recorded at room temperature with a constant accelerating apparatus. A foil of natural iron at room temperature was used to calibrate its velocity scale. Magnetizations at room temperature were measured with a vibrating sample magnetometer (VSM) calibrated with reference to a Ni (99.99%) disk. X-ray diffraction experiments were carried out with a two-circle goniometer equipped with a graphite (00.2) counter monochromator and with  $\text{CuK}\alpha$  radiation.

Powders with an average composition  $X = 50$  were further ball milled in  $\text{N}_2$  gas atmosphere after ball milling in Ar gas for 200 h. A total content of N atoms in the sample

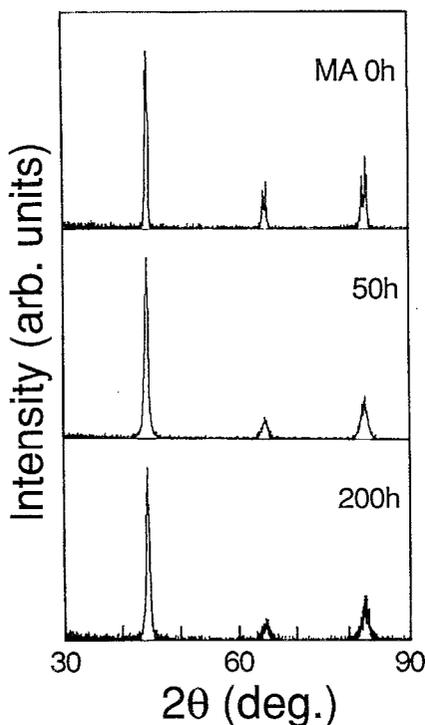


FIG. 1. X-ray diffraction spectra for the  $X=50$  powders subjected to MA for different milling times.

was determined with a nitrogen-oxygen analyzer (Horiba EMGA-650). The sample was heated up to 2800 °C in a carbon crucible and the nitrogen gas desorbed was quantitatively analyzed.

### III. RESULTS AND DISCUSSION

#### A. Structural studies by x-ray diffraction technique

X-ray diffraction spectra for the  $X=50$  powders are shown in Fig. 1 as a function of milling time. Diffraction lines of both Fe and Cr can be resolved before milling. However, they become broadened with increasing milling time and merge into a single one within 50 h of milling. The diffraction patterns indicate that the powders maintain the bcc structure throughout the course of milling. Any peaks associated with the  $\sigma$  (tetragonal) or  $\gamma$  face-centered cubic (fcc) phases present in the equilibrium phase diagram are not observed. The formation of the bcc single phase by milling was confirmed for all samples with  $X=20$ , 50, and 70. Evidently, information deduced from the x-ray diffraction technique is rather limited in the Fe-Cr system.

#### B. Magnetic studies for the $X=50$ powders

The Curie temperature for the  $\alpha$ -phase Fe<sub>50</sub>Cr<sub>50</sub> alloy is 330 °C<sup>4</sup> and its saturation magnetic moment at 0 K is 0.93  $\mu_B$ .<sup>8</sup> The saturation magnetization of the  $X=50$  powders is plotted as a function of milling time in Fig. 2. It is found that the value gradually decreases and levels off with increasing the milling time. <sup>57</sup>Fe Mössbauer spectra are

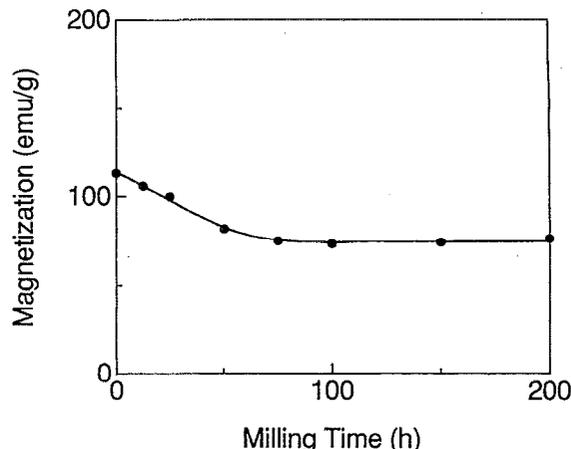


FIG. 2. Saturation magnetization as a function of milling time for the  $X=50$  powders.

shown in Fig. 3. It has been reported that Fe atoms, which possess Cr atoms as the nearest neighbor, exhibit a smaller hyperfine field than that of pure Fe, and its reduction rate per Cr atom is about 30 kOe.<sup>9</sup> The spectrum for powders before milling represents that for pure Fe. The first and sixth absorption lines after 25 h of milling become asymmetric, and a component having a hyperfine field smaller than pure Fe apparently emerges. Therefore, it is inferred from the Mössbauer spectra that Cr atoms begin to diffuse into Fe within 25 h. The absorption area of this component indicates that Fe atoms surrounded by Cr atoms in the Fe

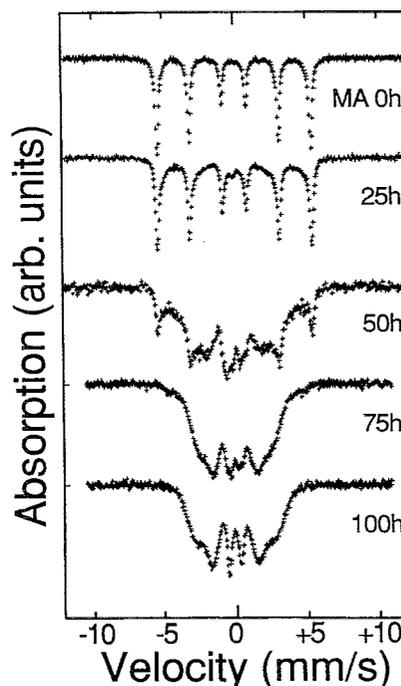


FIG. 3. <sup>57</sup>Fe Mössbauer spectra for the  $X=50$  powders subjected to MA for different milling times.

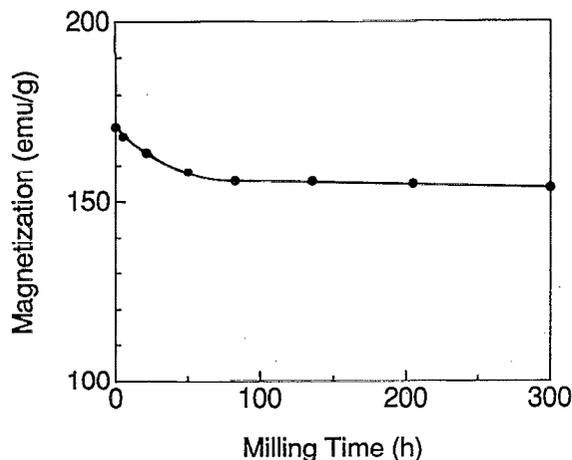


FIG. 4. Saturation magnetization as a function of milling time for the  $X=20$  powders.

matrix is estimated to be about 40%. A paramagnetic absorption line is observed at  $-0.1$  mm/s in this Mössbauer spectrum. The absorption area of this component indicates that about 4% of Fe atoms is also diffused into the Cr matrix. A comparison of the spectra for the samples milled for 75 and 100 h indicates that the absorption of the paramagnetic Fe and that of the hyperfine field of about 270 kOe have almost disappeared in the latter. This suggests that a homogeneous alloy is formed at this stage. Indeed, the Mössbauer spectrum after 200 h of milling is found to be identical to that of 100 h. By combining the x-ray diffraction data shown in Fig. 1, we conclude that the  $\alpha$  phase is produced by the MA process at the equiatomic composition. This is different from the formation of the  $\sigma$  and  $A15$  phases due to the sputtering method.<sup>10</sup>

### C. Magnetic studies for $X=20$ powders

The Curie temperature of the  $\alpha$ -phase  $\text{Fe}_{30}\text{Cr}_{70}$  alloy is  $670^\circ\text{C}$ .<sup>4</sup> The saturation magnetization for the  $X=20$  powders is plotted against milling time in Fig. 4. The magnetization monotonically decreases with increasing the milling time, and levels off at the value of 150 emu/g. It is clear from Fig. 4 that milling time, at least, beyond 100 h is necessary to complete the reaction in the MA process.

$^{57}\text{Fe}$  Mössbauer spectra for the  $X=20$  powders are presented in Fig. 5. In the spectrum for the sample milled for 21 h, the number of Fe atoms surrounded by the Cr atoms is estimated to be about 20% from the ratio of the absorption area. It is noted that neither an isolated Fe atom in Cr matrix nor the nonmagnetic  $\sigma$  phase could exist, since no paramagnetic absorption near zero velocity was observed. In the spectrum for the sample milled for 50 h, two distinct absorptions can be observed inside of those of pure Fe. Their hyperfine fields turn out to be about 300 and 270 kOe. We believe that they correspond to the absorption of Fe atom surrounded by nearest neighbors involving one and two Cr atoms, respectively. The spectrum for the sample milled for 83 h is essentially the same as that

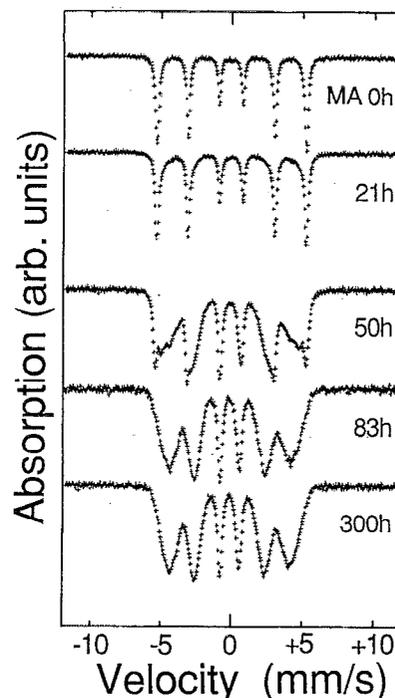


FIG. 5.  $^{57}\text{Fe}$  Mössbauer spectra for the  $X=20$  powders subjected to MA for different milling times.

after 300 h of milling. Judging from both x-ray diffraction and Mössbauer spectroscopy data, we conclude that the MA process for the  $X=20$  powders results in the formation of the ferromagnetic  $\alpha$  single phase.

### D. Magnetic studies for the $X=70$ powders

The Curie temperature of the  $\alpha$ -phase  $\text{Fe}_{30}\text{Cr}_{70}$  is  $0^\circ\text{C}$ .<sup>4</sup> As shown in Fig. 6, a prominent paramagnetic absorption is observed already in the Mössbauer spectrum for the  $X=70$  sample milled for 25 h, and its intensity increases with increasing milling time. The Mössbauer spectrum after 100 h of milling seemingly represents only the paramagnetic component. The magnetization curves were measured on the samples milled longer than 200 h. The results are shown in Fig. 7. In spite of the presence of only the paramagnetic component in the Mössbauer spectrum for the 100 h sample, the coercive force and residual magnetization still remain finite. They decrease further with a further increase in the milling time, and eventually disappear after 400 h of milling. The measurement of the magnetization curves slightly above the Curie temperature is so sensitive that the presence of nonreacted Fe of only 0.05 at. % can be readily detected. Therefore, sensitive magnetic measurement for this particular composition powders allowed us to conclude that the ball milling of 400 h is at least needed to reach a homogeneous  $\alpha$ -phase solid solution of  $X=70$ . The composition dependence of the Curie temperature ensures that the fluctuation in the Fe concentration in this powder is within  $\pm 2$  at. %.

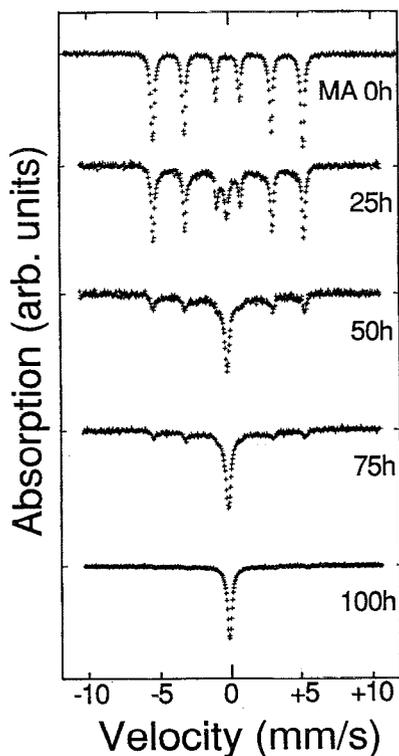


FIG. 6.  $^{57}\text{Fe}$  Mössbauer spectra for the  $X=70$  powders subjected to MA for different milling times.

The  $^{57}\text{Fe}$  Mössbauer spectroscopy and magnetic measurements for the  $X=20$  and  $50$  powders indicated that the formation of the  $\alpha$  phase has completed within the milling time of about  $100$  h. This is much shorter than the milling time required for the  $X=70$  powders. This difference

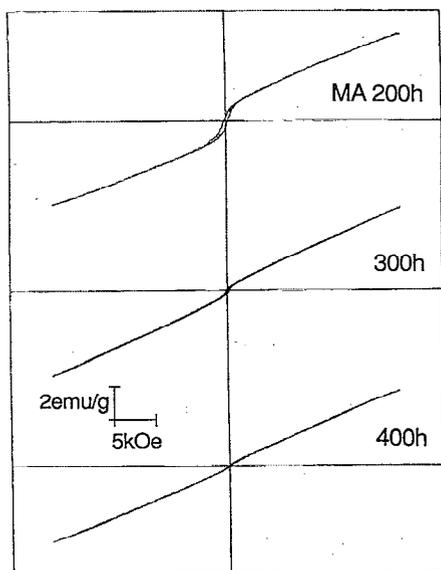


FIG. 7. Magnetization curves for the  $X=70$  powders subjected to MA for different milling times.

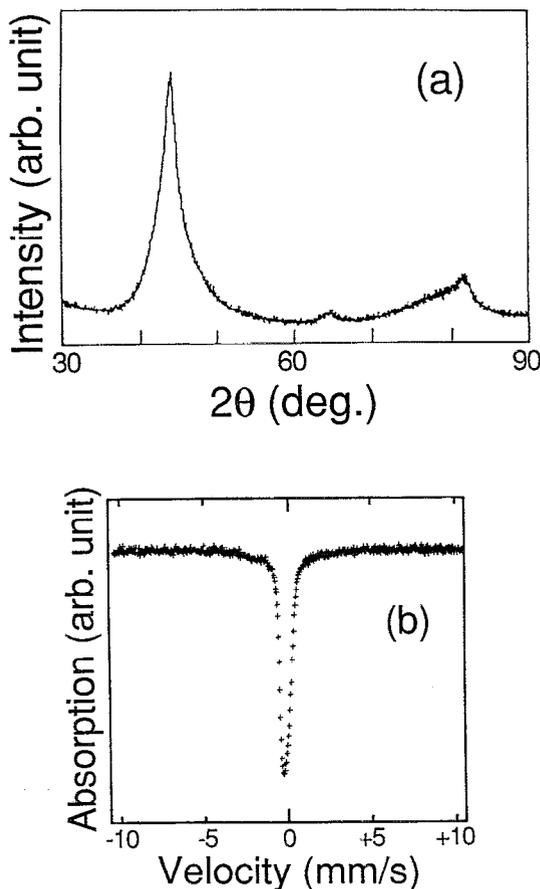


FIG. 8. (a) X-ray diffraction spectrum and (b)  $^{57}\text{Fe}$  Mössbauer spectrum for the  $X=50$  powders ball milled in Ar gas for  $200$  h and further milled in  $\text{N}_2$  gas atmosphere. Nitrogen content is  $5.8$  at. %.

might be ascribed to that in the activation energy for the diffusion<sup>11</sup> of one to the other: Cr in Fe diffuses faster than Fe in Cr. However, we must admit that  $^{57}\text{Fe}$  Mössbauer spectroscopy and magnetic measurements well below the Curie temperature are less sensitive than those slightly above that temperature. Unfortunately, the  $X=20$  and  $50$  samples cannot be heated above the Curie temperature, since the elevation of temperatures for the mechanically alloyed powders would assist the interdiffusion of remaining unreacted phases involved and no longer represent the as-milled state.

#### E. Formation of the amorphous phase by additional MA in $\text{N}_2$ atmosphere

As shown in Fig. 1, the  $\alpha$ -phase  $\text{Fe}_{50}\text{Cr}_{50}$  crystalline phase has been formed after  $200$  h of milling in Ar gas atmosphere. Further milling did not change the diffraction pattern, indicating that the  $\alpha$  phase is a final product. However, additional milling was carried out in  $\text{N}_2$  gas atmosphere. As shown in Fig. 8(a), a halo pattern characteristic of an amorphous phase was observed in spite of the presence of the remaining  $\alpha$  phase. An average nitrogen concentration turned out to be  $5.8$  at. %. The saturation magnetization for the  $\alpha$ -phase powders obtained after  $200$

h of milling in Ar gas was 76.3 emu/g. It decreases to 10.3 emu/g after nitrification. The Mössbauer spectrum for the Fe<sub>50</sub>Cr<sub>50</sub> sample containing 5.8 at. % nitrogen is shown in Fig. 8(b). The spectrum is found to consist of an intense paramagnetic component in the background due to broad ferromagnetic absorptions. A comparison with the data shown in Fig. 3 suggests that a decrease in the magnetization is caused by an increase in the paramagnetic component at the expense of ferromagnetic one. Therefore, we believe that the amorphous phase of (Fe<sub>50</sub>Cr<sub>50</sub>)<sub>94.2</sub>N<sub>5.8</sub> is paramagnetic at room temperature. The observed magnetization is due most likely to the remaining  $\alpha$  phase.

Finally, it may be worthwhile mentioning that the  $X=50$  powders become ductile when further nitrogen atoms are introduced. The nitrification beyond 5.8 at. % N had to be terminated, since the powders adhered to the bottom of the vial and effective ball milling could not be continued any further.

More detailed structural analysis on the formation of an amorphous phase in the Fe-Cr powders ball milled in the N<sub>2</sub> gas atmosphere will be reported elsewhere.<sup>7</sup>

#### IV. CONCLUSION

The MA process for a mixture of elemental Fe and Cr powders was investigated through measurements of x-ray diffraction, magnetic properties, and <sup>57</sup>Fe Mössbauer spectra. It is found that the magnetic studies are indispensable in this particular system to elucidate the alloying process in

detail. The results confirmed that the MA is capable of producing the homogeneous  $\alpha$  phase from respective elemental powders. Ball milling of the  $X=50$  powders in N<sub>2</sub> gas atmosphere results in the formation of the paramagnetic amorphous phase.

#### ACKNOWLEDGMENTS

The authors would like to thank K. Matsuda and Professor Ch. Yamauchi of Nagoya University for nitrogen gas analysis.

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