Magnetic properties of nano-crystalline Fe-Cr alloys prepared bymechanical alloying

著者	MURUGESAN M., KUWANO Hisashi
journal or publication title	IEEE transactions on magnetics
volume	35
number	5
page range	3499-3501
year	1999-09
URL	http://hdl.handle.net/10258/217

doi: info:doi/10.1109/20.800569

Magnetic Properties of Nano-crystalline Fe-Cr Alloys Prepared by Mechanical Alloying

M. Murugesan and H. Kuwano, Muroran Institute of Technology, 27-1 Mizumoto cho, Muroran – 050 8585, Japan.

***Abstract*—Fe-Cr powdered alloys synthesized via mechanical attrition have been examined by magnetization and ^{57}Fe Mössbauer spectroscopy. Mössbauer studies reveal that $Fe_{1-x}Cr_x$ becomes paramagnetic for $x \geq 0.46$ after 100 h milling. Magnetization results suggest that a significant reduction of Fe magnetic moment occurs in the nano-crystalline $Fe_{1-x}Cr_x$ alloys. Curie temperature for x = 0.46 and 0.69 lies below liquid N_2 and liquid He temperature, respectively.**

***Keywords*—Fe-Cr, ^{57}Fe Mössbauer spectroscopy, Magnetism, Mechanical alloying**

I. Introduction

Since the discovery of giant magneto resistance, magnetic materials having a random mixture of ferromagnetic and antiferromagnetic interactions have recently attracted a lot of attention [1]. Like Fe-V transition metal alloys, Fe-Cr alloy system also exhibits ferromagnetism over a wide range of Fe compositions [2]. At room temperature Fe is ferromagnetic while Cr is antiferromagnetic. Although extensive investigations carried out in a granular Fe-Cr alloy system, there are only very few reports available for amorphous/nano-crystalline $Fe_{1-x}Cr_x$ system [3],[4]. In this report, we discuss the results of ^{57}Fe Mössbauer spectroscopy and magnetization measurements in the nano-crystalline $Fe_{1-x}Cr_x$ samples for various x values prepared by mechanical alloying. Since both Fe and Cr crystallizes in body-centered cubic (bcc) structures and the difference in lattice parameters is only 0.5 %, it is very difficult to analyze the nano-crystalline $Fe_{1-x}Cr_x$ system alone with the diffraction techniques. This can be overcome with the help of ^{57}Fe Mössbauer spectroscopy where it discriminates the different local environments, even in the presence of a high density of defects or a high degree of disorder [5].

II. Experimental

Elemental Fe and Cr powders with 3N purity were mixed to a nominal composition of $Fe_{1-x}Cr_x$, where x varies from 0.00 to 0.75 and mechanically alloyed in a hardened steel vial with steel balls of 0.26 and 0.5 in diameter under an Ar atmosphere in a SPEX 8000 Mixer/Mill. The mean grain size, D was deduced from Transmission Electron Microscope (TEM) images and X-ray diffraction (XRD) data, details of which were written elsewhere [3]. Chemical compositions of alloyed powders were analyzed by LINK-EDS using a JEOL 2000FX TEM. ^{57}Fe Mössbauer spectra were recorded at both room temperature (RT) and 15 K with a ^{57}Co(Rh) source. Magnetization at RT as well as at 4 K was measured using superconducting quantum interference device (SQUID).

TABLE 1: Composition and grain size

Nominal $Fe_{1-x}Cr_x$	Analyzed (x)	Grain size D (nm) XRD	TEM	μ_{Fe} at 4 K (μ_B)
x = 0.00	0.000	9.8	10.2	1.984
x = 0.25	0.231	7.8	7.9	1.364
x = 0.50	0.465	4.1	5.3	0.136
x = 0.75	0.695	3.4	4.6	0.032

III. Results and Discussion

RT powder XRD patterns for $Fe_{1-x}Cr_x$ alloys milled for 100 h show a single phase composition for all values of x and none of the peaks corresponds to Fe and/or Cr oxides were observed. This confirms the non-existence of oxide phases in the milled samples. XRD results showed that the width of the peak increases with increasing milling time for all x values. It is common that the cold worked material exhibit broad diffraction peak owing to the reduction in the size of the diffracting domains and accumulation of microstrain within the domains. D becomes small with the increase in x value of $Fe_{1-x}Cr_x$, e.g., pure Fe has been reduced to only 9.8 nm in size while $Fe_{0.31}Cr_{0.69}$ yields the nano-crystalline size of as small as 3.4 nm after 100 h attrition. D values obtained from bright field TEM images (listed in Table 1) are nearly close to the values deduced from the XRD data. The diffuse electron diffraction ring (otherwise called halo pattern) observed in the $Fe_{0.31}Cr_{0.69}$ sample supports that the formation of amorphous/nano-crystalline material. The analyzed Cr content of the alloyed material is less than the nominal composition due to the Fe contamination from the steel balls and the vial wall (Table 1).

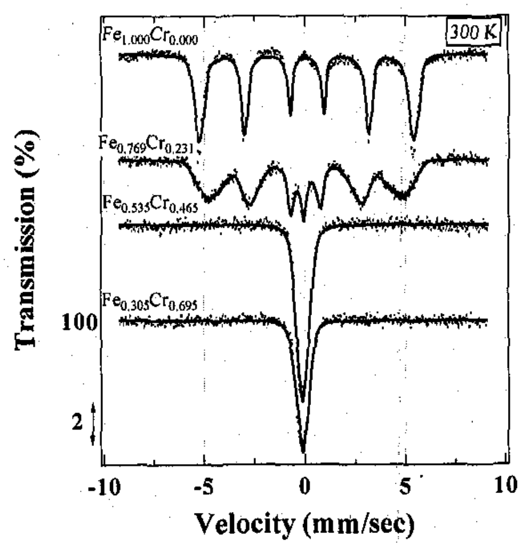

Figure 1: RT Mossbauer spectra of Fe-Cr powders for various x values after 100 h milling.

Shown in figure 1 are the RT Mössbauer spectra for $Fe_{1-x}Cr_x$ samples for various x values alloyed for 100 h. Irrespective of the x values, Mössbauer peak becomes broad after 100 h milling. We interpret this broadening is purely due to a finite hyperfine magnetic field (hmf) since the spectra were almost identical. A paramagnetic absorption line at –0.1 mm/s is observed in the samples for $0.23 \leq x \leq 0.43$. The absorption area of the paramagnetic peak grows at the expense of ferromagnetic peak up to $x = 0.43$. This paramagnetic peak belongs to the nonmagnetic Fe atom in the Fe-Cr alloy and not due to diffusion of Fe into Cr lattice. Because, the position of paramagnetic peak in the Mössbauer spectrum does not change with x. Finally, for $x \geq 0.46$ the ferromagnetic absorption almost vanishes leaving the paramagnetic peak alone at -0.1 mm/s.

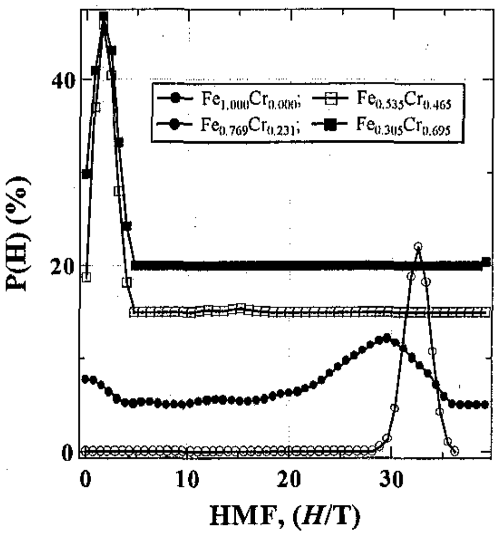

Figure 2: HMF distributions obtained from Mossbauer spectra

Figure 2 is the probability distributions (P(H) curves) of the hmf which were computed from the experimental Mössbauer spectrum using a program developed by Le Caer and Dubois [6]. As x increases the P(H) maximum shifts towards a low hmf followed by the increase in full width half maximum (FWHM). At the same time a peak near 2 T begin to grows with increasing x. We interpret that (i) the low field shift of P(H) maximum is attributed to the existence of Cr atom in the Fe lattice, and the increase in the FWHM is due to the number of Cr atom present in the Fe lattice increases with increasing x (ii) the peak at around 2 T (hereafter called as paramagnetic peak) is due to the nonmagnetic Fe in Fe-Cr alloys. Moreover, the alloys for x = 0.46 and above, the P(H) curves consist of mainly a paramagnetic peak.

The average hmf (<*H*>) calculated from the high field component of P(H) curves for H > 5 T (Figure 3) does decrease monotonously with x. It has been well established that Fe atoms exhibit smaller hmf when Fe atom possesses Cr atoms as the nearest neighbor, and its reduction rate per Cr atom is about 3 T [7]. The decrease in <*H*> is attributed to the decrease in average moment of Fe. There are even reports available that the Fe atoms in the 85 at% Cr alloy are still

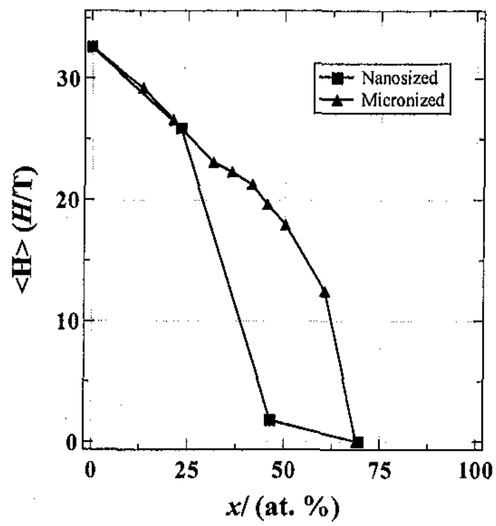

Figure 3: Average Field versus Cr concentration

magnetic, while the spontaneous magnetization almost disappears [8]. The calculated <*H*> values are nearly close to the values reported for the alloys whose *D* is in the μm range up to the Cr concentration of 0.23. For $x = 0.46$, the nano-crystalline materials are paramagnetic, while in the μm size samples the ferromagnetism was retained up to 0.70. However, it is common that when the sample consists of small particles (≤ 10 nm), the magnetization is no longer fixed to an easy direction at room temperature, but fluctuates in a random way results in superparamagnetic relaxation. In order to ascertain that the appearance of paramagnetic peak in $Fe_{1-x}Cr_x$ samples milled for 100 h is not pertained to the superparamagnetism, we have carried out low temperature Mössbauer studies on $Fe_{0.31}Cr_{0.69}$ sample at 15 K. It is well known that below the blocking temperature, T_B (is defined as the temperature below which the particles behave as magnetically ordered crystals) superparamangetic particles show a ferromagnetic behavior [9]. e.g., the spectrum of 7 nm Fe_2O_3 microcrystal contains only paramagnetic component at 440 K while the 83 K spectrum contains both strong Zeeman

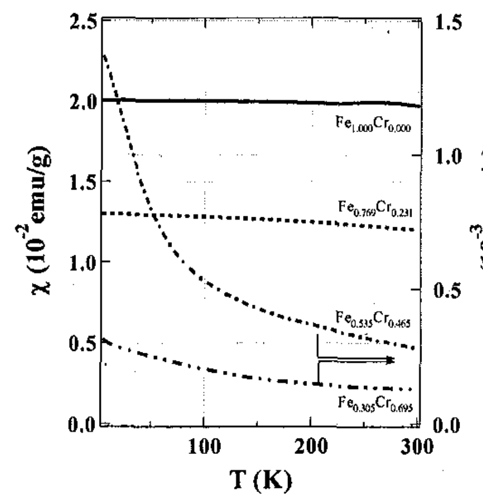

Figure 4: Magnetic susceptibility versus temperature for Fe-Cr alloys (milled for 100 h) for various x values.

split component and a weak paramagnetic component. On the other hand, in the present study we did not observe any ferromagnetic behavior even at 15 K. This confirms that the appearance of paramagnetic peak at around −0.1 mm/s in the Mössbauer spectrum is predominantly due to the non-magnetic Fe atoms present in the mechanically attrited $Fe_{1-x}Cr_x$ powdered alloys.

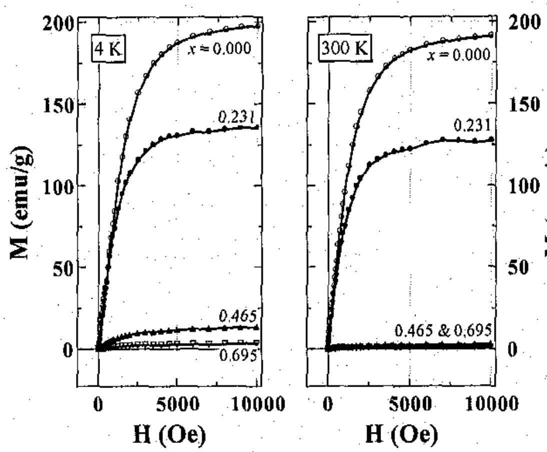

Figure 5: Magnetization curves for Fe-Cr alloys (milled for 100 h) for various x values.

The Curie temperature (T_C) of the μm size α–phase $Fe_{1-x}Cr_x$ alloy is 943K for $x = 0.20$, 603 K for $x = 0.50$ and 273 K for $x = 0.70$ [2]. However, it is inferred from our Mössbauer results that T_C for the nano-crystalline $Fe_{1-x}Cr_x$ alloy lies well below the T_C value of the μm size samples. To confirm this, susceptibility measurements were carried out. The results of magnetization versus temperature (Figure 4) showed that the T_C values for $x = 0.46$ and 0.69 samples lie respectively near 70 K and below 4 K. Figure 6 shows the Fe magnetic moment (μ_{Fe}) deduced from the saturation magnetization values (from Figure 5) both at 300 K as well as 4 K for nano-crystalline $Fe_{1-x}Cr_x$ materials. For comparison, μ_{Fe} in μm size

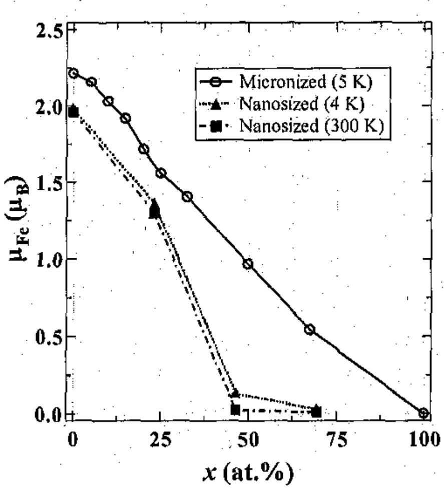

Figure 6: Average moment of Fe deduced from saturation magnetization for Fe-Cr alloys milled for 100 h.

samples taken from [9] is also incorporated. It is clear from figure 6 that irrespective of x the μ_{Fe} in the nano-crystalline materials are always lower than the μm size samples. The extremely low value of T_C in nano-crystalline materials may be presumed to be the low μ_{Fe} in the ball milled materials. In addition, the x dependence of μ_{Fe} in μm size $Fe_{1-x}Cr_x$ sample is almost linear for all x values. However, in the nano-crystalline samples the variation of μ_{Fe} is linear only up to $x = 0.23$. Beyond $x = 0.23$, the μ_{Fe} suddenly drops to near zero value. This sudden drop coincides with the Mössbauer spectrometry observations. The lower value of μ_{Fe} at 4 K than at 300 K is largely due to the reduction in thermal scattering.

IV. CONCLUSION

We have studied the magnetic properties of nano-crystalline $Fe_{1-x}Cr_x$ materials by Mössbauer spectrometry and SQUID measurements. Mössbauer studies showed that hmf in nano-crystalline materials are very close to the values of μm size samples for $x \leq 0.23$. The nano-crystalline material becomes paramagnetic even for $x = 0.46$ while the μm size samples retain ferromagnetism up to $x = 0.70$. It is found that μ_{Fe} of the nano-crystalline materials is highly reduced than in the μm size materials.

ACKNOWLEDGMENT

M.M. thanks Monbusho for providing financial assistance.

REFERENCES

[1] A. K. Majumdar and P. V. Blanckenhagen, "Magnetic Phase diagram of (10 < x < 30) alloys," *Phys. Rev. B.*, vol. 29, pp. 4079-4085, April 1984.

[2] M. V. Nevitt and A. T. Aldred, "Ferromagnetism in V-Fe and Cr-Fe Alloys," *J. Appl. Phys.*, vol. 34, pp. 463-468, March 1963.

[3] H. Kuwano, H. Ouyang and B. Fultz, "A Mössbauer spectroscopy study of nano-phase Cr-Fe synthesized by mechanical alloying: A measurement of grain boundary width," *Nanostruct. Mater.*, vol. 1, pp. 143-148, 1992.

[4] T. Koyano, T. Takizawa, T. Fukunaga, U. Mizutani, S. Kamizuru, E. Kita and A. Tasaki, "Mechanical alloying process of Fe-Cr powders studied by magnetic measurements," *J. Appl. Phys.*, Vol. 73, pp. 429-433, January 1993.

[5] C. Michaelsen and E. Hellstern, "Mössbauer effect on mechanically alloyed Fe-Zr glasses," *J. Appl. Phys.*, vol. 62, pp. 117-119, July 1987.

[6] G. Le Caer and J. M. Dubois, "Evaluation of hyperfine parameter distributions from overlapped Mössbauer spectra of amorphous alloys," *J. Phys.: Sci. Instrum..*, vol. 12, 1083-1089, 1979.

[7] S. M. Dubiel and J. Zukrowski, "Mössbauer effect study of charge and spin transfer in Fe-Cr," *J. Magn. Magn. Mater.*, **23**, 214 (1981).

[8] M. Shiga and Y. Nakamura, "Effect of local environment on formation of local moments in bcc Fe-Cr alloys – Mössbauer study," *J. Phys. Soc. Jpn.*, vol. 49, pp. 528-534, August 1980 and relevant references therein.

[9] R. L. Cohen, *Applications of Mössbauer Spectroscopy*, vol. 2, Academic Press: New York, 1980, pp. 1-48.