

Structural and Magnetic Properties of Fe₅₀Cr₅₀ Alloys Prepared by Mechanical Alloying Method

Dong-Seok Yang^{1*}, Jiyeon Park¹, Yong-Goo Yoo², Kyeong-Sup Kim³, and Seong-Cho Yu⁴

¹Department of Physics Education, Chungbuk National University, Cheongju 361-763, Korea

²Chungbuk Technopark, Regional Innovation Agency, Choengwon 363-792, Korea

³School of Electrical & Computer Engineering, CBNU BK21 Chungbuk Information Technology Center, Chungbuk National University, Cheongju 361-763, Korea

⁴BK21 Physics Program and Department of Physics, Chungbuk National University, Cheongju 361-763, Korea

(Received 30 April 2010, Received in final form 23 June 2010, Accepted 5 July 2010)

Fe₅₀Cr₅₀ metastable alloys were prepared by the mechanical alloying method with milling periods of 1, 2, 4, 6, 12 and 24 hours, respectively. The structural evolution was analyzed by the extended x-ray absorption fine structure (EXAFS). In this work, the EXAFS analysis provided the local structural information around Fe central atom. The saturation magnetization was also measured by VSM. The magnetization decreased as the process mechanical alloying progressed. The magnetic property was related to the local structural variation as a function of processing time. The analysis showed that the diffusion Cr atoms into Fe clusters caused the reduction of magnetization. EXAFS analysis exhibited that the local ordering of magnetic atoms caused the magnetic ordering. Also, EXAFS analysis showed that the long range order of Fe atoms was destroyed completely in 24 hour milling.

Keywords : Fe₅₀Cr₅₀, mechanical alloy, magnetization, local structure

1. Introduction

The Fe-Cr alloy system has been widely investigated and much attention has been paid to the study of the structural characteristics and of the physical properties of final products. Especially, the Fe-Cr layered magnetic materials were extensively studied for the application of magnetic devices [1-5], and the stainless Fe-Cr alloy has been used in various applications of the structural materials of fuel cells and fusion reactors [6]. The peculiarity of the Fe-Cr system is the existence of a wide miscibility gap in the phase diagram where both Fe and Cr are insoluble at room temperature. Fe-Cr based alloys fabricated by the mechanical alloying techniques exhibited nanostructured characteristics in the X-ray diffraction analysis [7]. The mechanically alloyed nanocrystalline materials have a great attention to the field of new material fabrication because the mechanical alloying techniques provides practical alloys beyond the solubility limit of chemical elements for the industrial use. The anti-ferromagnetic

interaction between iron ions via a non-magnetic chromium ion in the layered structure plays an important role in the device mechanism. The magnetic interactions in these alloys are closely related to the local structure of magnetic atoms. Therefore, the aim of this work is to investigate the atomic interdiffusion phenomenon and the structural changes during mechanical alloying process of Fe₅₀Cr₅₀ metastable alloys. The magnetization was examined by using the vibrating sample magnetometer (VSM), and the local structure was analyzed by the synchrotron X-ray absorption fine structure (EXAFS) study [8-10].

2. Experiments

Fe₅₀Cr₅₀ metastable alloys were prepared by the mechanical alloying system using the SPEX 8000 mixer and mill with stainless steel balls, and the ball-to-powder ratio of the mixed powder was 6 : 1 in weight. The starting material was a mixture of pure Fe and Cr powders (~80 mesh, 99.9). The mechanical alloying (MA) process was performed for 1, 2, 4, 6, 12, and 24 hours in Ar atmosphere. Magnetic moments of the samples were measured by using the vibrating sample magnetometer (VSM) with

*Corresponding author: Tel: +82-43-261-2724

Fax: +82-43-273-2777, e-mail: dosyang@cbnu.ac.kr

the maximum field of 10 kOe. EXAFS experiments were carried out at the beam line, 3C1 EXAFS of the Pohang light source (PLS) synchrotron in the Pohang Acceleratory Laboratory (PAL) in Korea. PLS was operated with the electron energy of 2.5 GeV and the maximum current of 200 mA. The EXAFS spectra were obtained near Fe K edge (7112 eV) in the transmission mode at room temperature. The ion chambers were filled with the pure nitrogen gas.

3. Results and Discussion

The introduction of a large number of crystal defects upon mechanical milling of a mixture of powders provides the conditions required for the solid-state reactions which lead to alloying effect [11]. The mixed powder of iron and chromium partially undergoes some fracture and welding repeatedly as the milling progresses. Many works showed that the fracture and welding in mechanical alloying (MA) process caused the decrease of particle size and formation of alloy [12]. The materials fabricated by MA have significant fraction of atoms residing in defect environments such as grain boundary and lattice defects which might offer different unusual physical properties to the alloy. The analysis of magnetization and EXAFS spectra is one of good method for investigation of intrinsic properties of metastable materials. Fig. 1 shows the M-H curves for $\text{Fe}_{50}\text{Cr}_{50}$ metastable alloys at room temperature with increasing milling times. All curves exhibit a hysteretic behavior and magnetization of these samples almost saturates at $H=5$ kOe. H_c increases with increasing milling time. The implication of this is that new materials are produced during the mechanical alloying process. Fig. 2 shows the variation of saturation magnetization measured at room temperature in an external field of 10 kOe for the $\text{Fe}_{50}\text{Cr}_{50}$ metastable alloys with the increase of milling times. The values of magnetization were obtained from the M-H curves of the samples. The magnetization behavior is a physical property sensitive to the structural change. As seen the Fig. 2, the magnetization shows that there is a significant difference on milling time. The magnetization decreased rapidly before 6 hours milling, but it decreased slowly and linearly after 6 hours milling. This indicates that two possible steps exist in the alloying process. In the first step, the iron clusters decreased in size and the inter-diffusion of the iron and the chromium increased rapidly. In the second step, the magnetic interaction was changed gradually due to the creation of new alloys as the milling progressed. Iron and chromium have same BCC crystal structure, and the lattice parameters are similar to each other. We expected that the local structure of Fe-Cr would

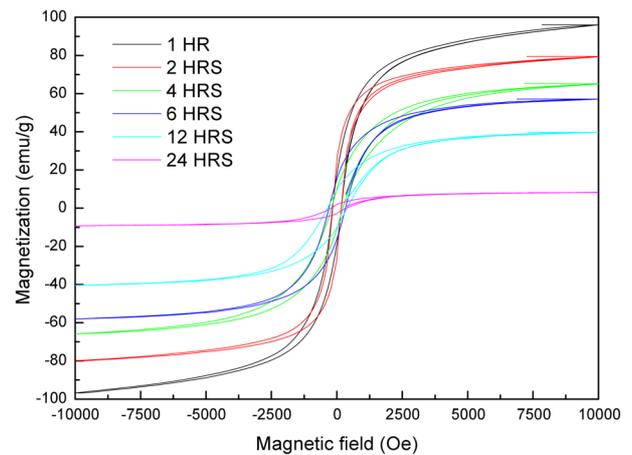


Fig. 1. M-H curves for $\text{Fe}_{50}\text{Cr}_{50}$ powders with increasing milling times.

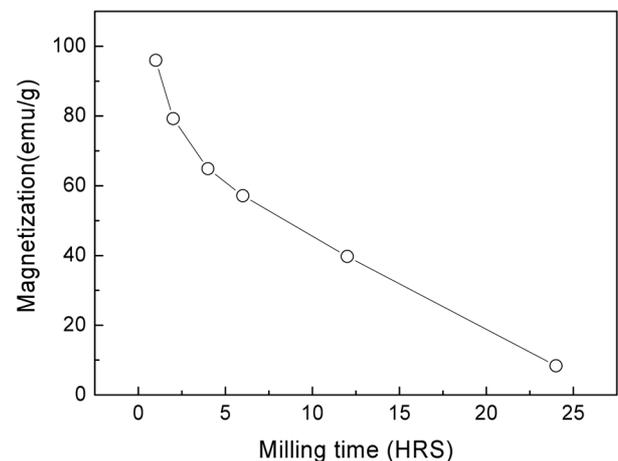


Fig. 2. Variation of magnetization for $\text{Fe}_{50}\text{Cr}_{50}$ powders with increasing milling times.

be unchanged. However, the local structures were seriously changed with milling time in MA process.

The local structure of the mixed powder transformed to complex different structure from the initial structure due to the intermixing of chemical bonds. The variation of magnetization can be compared to the EXAFS spectra. Fig. 3 shows the EXAFS spectra of $\text{Fe}_{50}\text{Cr}_{50}$ metastable alloys with the indicated milling times. The significant difference of local structure before and after 6 hours milling is shown in the EXAFS spectra. The amplitudes decreased slowly before 6 hours milling time but decreased rapidly from 6 to 24 hours milling. The line shape near $k=5.0 \text{ \AA}^{-1}$ was changed significantly in 24 hours milling. This indicates that the Fe-Cr alloying began at 6 hours milling time, and new alloys were created in 24 hours milling. Also, this is consistent with the variation of magnetization with the milling time shown in Fig. 2.

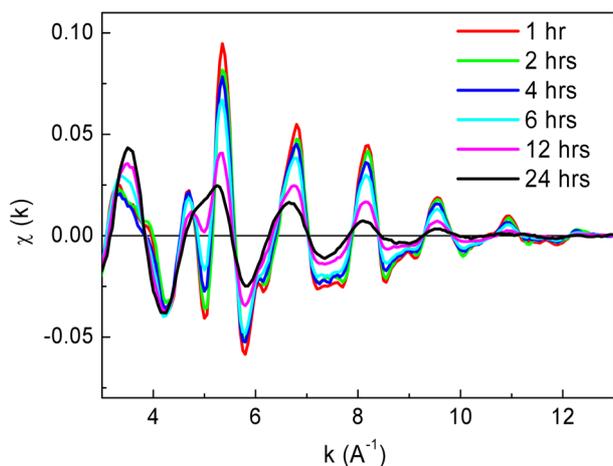


Fig. 3. EXAFS spectra of Fe₅₀Cr₅₀ alloys with indicated milling times.

Variations of EXAFS spectra are related to information on the structural changes of alloys at atomic scale. The reduction of the amplitude of EXAFS spectrum is mostly caused by the disorder in local structure. The phase shift of EXAFS spectrum is related to the change of chemical order.

As shown in Fig. 3, the amplitude decreased significantly as milling time increased. Also, the line shape was seriously deformed with the increase of milling time. Before 6 hours, the reduction of amplitude was dominant. This indicates that the fracture and cold-welding of both Fe and Cr were dominant. However variations of the phase were dominant after 6 hours. This indicates that new phases were created in this period. It seems that the amount of the new phases increased gradually as the milling time increased. Especially, the spectra near $k=3.5 \text{ \AA}^{-1}$ shows that there was no significant change before 6 hours but changed gradually in 6 to 24 hours. This means that no significant variation occurred in the local structure but the structure was changed gradually after 6 hours.

Fig. 4 shows the Fourier transform of EXAFS spectra measured at Fe K-edge with the indicated milling time. As shown in Fig. 4, the magnitude of the Fourier transformed spectra decreased gradually as the processing time increased. This suggests that the number of Fe-Fe bonds decreased due to the diffusion of Cr atoms in the unit shell of iron cluster. The reduction of Fe-Fe bond gives rise to the decrease of magnetization. The higher shell peaks showing the long range ordering in Fe-Fe in the Fourier transform of EXAFS spectra decreased gradually in up to 12 hour milling. However, the peak disappeared after 24 hours milling. This indicates that the long range

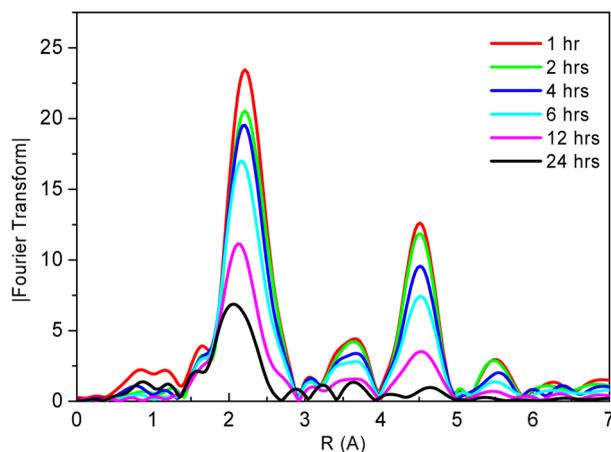


Fig. 4. Fourier transform of EXAFS spectra for Fe₅₀Cr₅₀ alloys measured at Fe K-edge with indicated milling times.

order disappeared after 24 hours milling. Also, the peak near $R=4.5 \text{ \AA}$ in Fig. 4 decreased gradually as the milling time increased until 12 hours milling but disappeared in 24 hours milling. This indicates that the amount of Fe in the metastable alloys decreased until 12 hour milling but pure Fe does not exist in 24 hour milling. From this, we see that the mixture of Fe and Cr was dominant in the beginning of the MA process and new alloys began to be formed after 4 to 6 hour milling time. It will be expected that some mixture of Fe, Cr, Fe-Cr alloy exists in 12 hours milling and Fe-Cr alloy was dominant in 24 hours milling.

According to the mean field theory, magnetization is proportional to the average magnetic moment of unit cell in crystalline solids. The average magnetic moment increases as the number of magnetic atom in unit cell increases. The decrease of magnetization shown in Fig. 2 is compared with the reduction of Fe atoms in the first shell shown in Fig. 4. The first shell in Fig. 4 contains the information of Fe-Fe and Fe-Cr bonds. It is expected that the Fe-Cr bond length is shorter than Fe-Fe bond length. The peak position of the sample milled for 24 hour was moved to lower position than those of other samples. This indicates that Fe-Cr pairing is dominant in 24 hours milling. This means that there is no magnetic ordering in the sample milled for 24 hours.

4. Conclusion

In this work, we fabricated Fe₅₀Cr₅₀ metastable alloys with mechanical alloying. From the analysis of magnetization and local structure, we found that the alloying was activated in 6 hour milling and completed in 24 hour milling. The analysis showed that the diffusion Cr atoms

into Fe clusters caused the reduction of magnetization. EXAFS analysis exhibited that the local ordering of magnetic atoms gives rise to the magnetic ordering in these alloys.

Acknowledgments

This study was supported by the research grant of Chungbuk National University in 2008.

References

- [1] G. Binasch, P. Grunberg, F. Saurenbach, and W. Zinn, *Phys. Rev. B* **39**, 4828 (1989).
- [2] M. Kubik, B. Handke, W. Karas, N. Spirdis, T. Slezak, and J. Korechi, *Phys. Stat. Sol. (a)* **189**, 705 (2002).
- [3] P. Khatua, A. K. Majumdar, A. F. Hebard, and D. Temple, *Phys. Rev. B* **68**, 144405 (2003).
- [4] R. S. Patel, A. K. Majumdar, and A. K. Nigam, *J. Magn. Mater.* **309**, 256 (2007).
- [5] K. Inomata, S. Okamura, and N. Tezuka, *J. Magn. Mater.* **282**, 269 (2007).
- [6] T. Horita, Y. Xiong, H. Kishimoto, K. Yamaji, N. Sakai, and H. Yokokawa, *Journal of Power Source* **131**, 293 (2004).
- [7] F. Z. Bentayeb, S. Alleg, and J. M. Greneche, *J. Alloy Compd.* **434-435**, 477 (2007).
- [8] D. E. Sayers, E. A. Stern, and F. W. Lytle, *Phys. Rev. Lett.* **27**, 1204 (1971).
- [9] D. C. Koningsberger and R. Prins, *X-ray Absorption: Principles, Application, Techniques of EXAFS, SEXAFS and XANES*, Wiley-Interscience, New York (1988) pp. 87-211.
- [10] D. S. Yang, J. M. Lee, *Phys. Scripta* **T115**, 200 (2005).
- [11] F. Z. Bentayeb, S. Alleg, and B. Bouzabata, *J. Magn. Mater.* **288**, 282 (2005).
- [12] J. I. Lee, H. W. Kwon, and Y. S. Kang, *J. Magnetism* **13**, 102 (2008).