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Local Structure and Magnetic Properties of Fe-Mn Nanocrystalline Alloys Fabricated by Mechanical Alloying Technique as a Function of Milling Time

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Structural and magnetic properties of $Fe_{50}Mn_{50}$ nanocrystalline alloys prepared by the mechanical alloying technique (using commercial Fe and Mn powders as the precursors) are studied as a function of milling time, 1 hr to 48 hrs. The nano-crystallite size and shape are examined by using scanning electron microscopy (SEM). The effect of milling time on structural characterization was investigated using X-ray diffractometer (XRD) and extended X-ray absorption fine structure spectroscopy (EXAFS). Both XRD and EXAFS studies showed that the alloying process should be completed after 36 hrs milling. Concerning the magnetic behavior, the data obtained from superconducting quantum interference devices (SQUID) exhibited both magnetic saturation (M_s) and coercivity (H_c) depend strongly on the milling time, which are related to the changes in the crystallite size and magnetic dilution.

Keywords : mechanical alloying, $Fe_{50}Mn_{50}$ nanocrystalline alloys, structure and magnetic properties

1. Introduction

Mechanical Alloying (MA) has been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or pre-alloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, meta-stable crystalline and quasi-crystalline phases, nanostructures, and amorphous alloys. MA produces nanostructured materials by the structural disintegration of coarser-grained structure as a result of severe plastic deformation. MA is able to produce nanostructure materials with unique chemical, structural, electrical and magnetic properties, due to type of disorder created by the high density of defects and the small supersaturated solid solution, amorphous phases and nano powders, starting from a crystal size. Nowadays, MA has been used to prepare metastable phases such as mixture of elemental components or inter-metallic compounds [1-5].

In fact, MA process is an effective way to fabricate nanocrystalline alloys [6], and their physical properties are related to structural variations. Some regularity in atomic arrangement in solids can be classified by the short-range order (SRO) and long-range order (LRO). Among these, LRO is frequently examined by X-ray diffraction studies while SRO could be examined by extended X-ray absorption fine structure (EXAFS). EXAFS give useful information related to the local structure around specific atoms [4].

So far anti-ferromagnetic FeMn alloys have been extensively studied for many magnetic applications. Various phenomena such as spin transition and shape-memory effect in Fe-Mn alloys have been reported [4, 7]. In this work, we present preparation and characterization of the structure and magnetic behavior of $Fe_{50}Mn_{50}$ alloys as changing the milling time.

2. Experimental Method

$Fe_{50}Mn_{50}$ metastable alloys were prepared by mechanical alloying using SPEX 8000 mixer with stainless steel balls and vial. The starting material was a mixture of pure Fe and Mn powders (used commercial Fe and Mn powders as the precursors). The weight ratio of balls-to-powder mixture was 5:1. $Fe_{50}Mn_{50}$ alloys were mixed and ground for different times 1-, 6-, 12-, 24-, 36- and 48 hrs.

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This process was performed in Ar ambient to prevent oxidation during the alloying process. After the preparation, the particle size and their shape were checked using scanning electron microscope (SEM). Magnetic measurements were carried out on SQUID. Structure data were obtained by X-ray diffractometer (XRD) using the Cu-K_α radiation. The data were analyzed using Material Data Inc. (MDI) software. Based on these data, crystallite size of the samples were estimated in terms of the Scherrer formula. EXAFS data were collected from the 3C1 EXAFS beam line of the Pohang Light Source (PLS). The PLS was operated with an energy of 2.5 GeV, and a maximum current of 200 mA. EXAFS spectra were obtained at Fe K-edge (7112 eV) in the transmission mode at room temperature. The sample chamber was filled with pure nitrogen gas. Then the EXAFS data were analyzed using IFEFFIT software, an interactive program for XAFS analysis.

3. Results and Discussion

Fig. 1 is the typical SEM images of the samples $Fe_{50}Mn_{50}$ showing that the particle shape and size are in nanocrystalline alloys with milling time of 1-, 6-, 12- and 24-hrs. In general, the average particles size estimated from the SEM images are found to decrease with increasing milling time. Similar particle shapes of SEM pictures were also obtained for all other samples, but the images were not shown here.

All the SEM images revealed that particles present in the $Fe_{50}Mn_{50}$ samples have quite similar shapes, where smaller particles are located on the surfaces of bigger particles. The particle size looks consistent with crystallite size which is revealed later in Fig. 3.

Fig. 2 shows XRD patterns of mechanically alloyed $Fe_{50}Mn_{50}$ powders. In the beginning of process, it shows the presence of Fe (Im-3m) and Mn (I-43m) phases. Their diffraction peaks become weaker and broader when the milling time is increased. This is due to the structure deformed. The alloying started from 6 hrs milling where the new peak was occurred at 35 degree and then become more completed afterward. For the 24 hrs milling sample, the Fe-(110) peak is buried into Mn-(411). It means that Fe and Mn atoms were diffused to each other, and thus a new alloy phase Fe-Mn was formed, but the Fe and Mn phases still remain. One can see, that the peaks position for 36- and 48 hrs milling are fixed even though there is 12 hrs difference of milling time, the peaks are tend to form a space group of fm3m.

Fig. 3 shows the crystallite sizes of $Fe_{50}Mn_{50}$ alloys processed by the mechanical alloying technique for 1-, 6-, 12-, 36- and 48 hrs milling, respectively. Based on the highest peaks of XRD data, the crystallite size of the samples were calculated using Scherrer method. In fact, the nano-structured powder is decreased from 28 to 10 nm by increasing the milling time from 1 hr to 48 hrs.

The local structure and the atomic ordering were also examined using EXAFS experiment. Variations of EXAFS spectra are related to the structural changes of alloys at the atomic scale. Mostly, the reduction of the amplitude of EXAFS spectrum is caused by the atomic disorder in local structure. The phase shift of EXAFS spectrum is related to the change of chemical order [8].

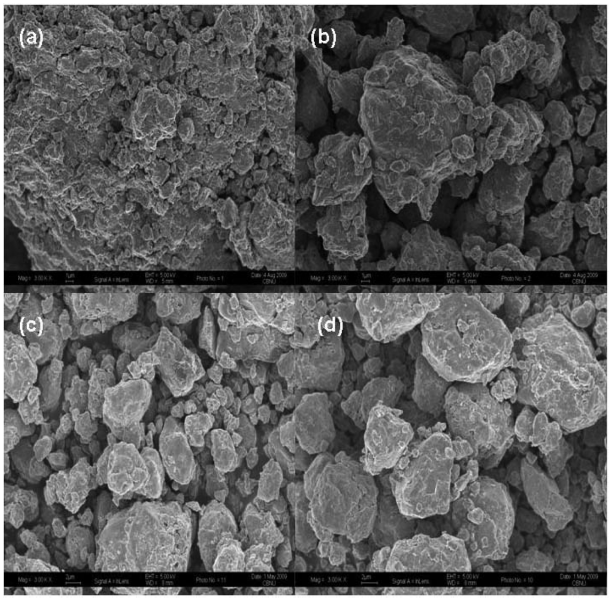

Fig. 1. Typical SEM images of $Fe_{50}Mn_{50}$ nanocrystalline alloys for milling of (a) 1 hr, (b) 6 hrs, (c) 12 hrs and (d) 24 hrs.

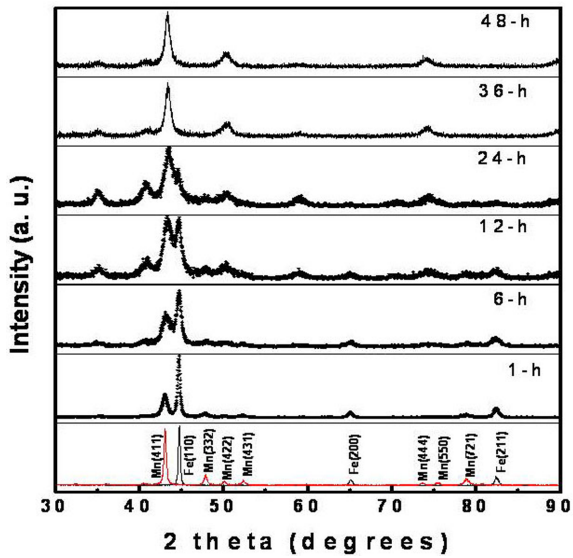

Fig. 2. (Color online) XRD patterns of $Fe_{50}Mn_{50}$ with different milling time.

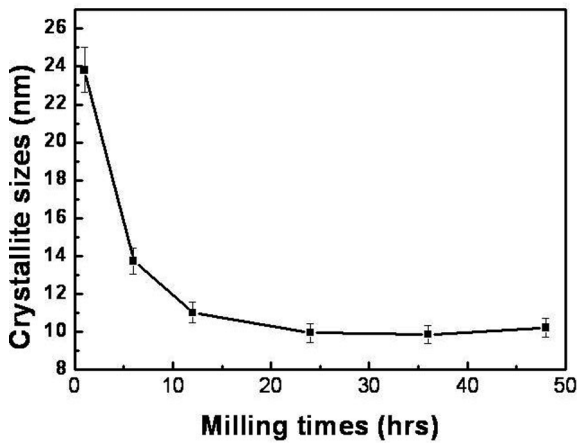

Fig. 3. The variation of the crystallite size of nanocrystalline alloys respect to the milling time.

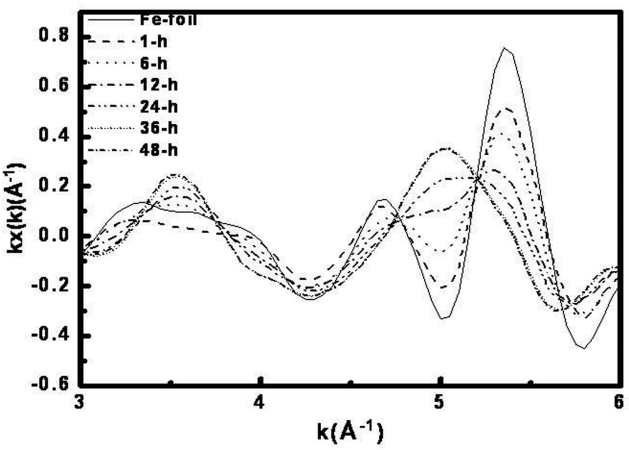

Fig. 4. The *k*-weighted EXAFS spectra.

Fig. 4 shows *k* weighted EXAFS spectra for mechanically-alloyed $Fe_{50}Mn_{50}$ for different milling time of 1-, 6-, 12-, 24-, 36-and 48 hrs, respectively. The decreasing of the amplitude until 6 hrs milling time indicates that the fracture and the cold welding of Fe and Mn were dominant and there was a minor change in the local structure. However, the significant changes in the amplitude and the phase took place after 12 hrs milling time. This indicates that the alloying was dominant and new phases were formed after 12 hrs milling time. The amount of the new phases increased as the processing time increased. It seems that the amount of the inter diffusion of Fe and Mn atoms increased gradually as the milling time increased. One can see also, the spectra of 36- and 48 hrs milled almost same. It means that after 36 hrs milling time the new phase of nanocrystalline alloy was occurred and fixed until 48 hrs milling time. These results are in a good agreement with the of XRD results.

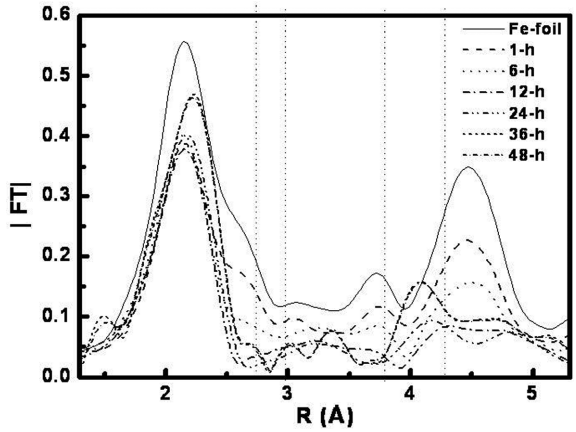

Fig. 5. Fourier transformation of EXAFS spectra which was measured at the Fe K-edge.

Fig. 5 shows that the Fourier transform (FT) of the EXAFS spectra measured at the Fe K-edge. The radial atomic density in real space can be seen in the spectrum Fourier transformation. The peaks of the Fourier transformation spectra have the local structural information, such as the coordination number, the bonding distance, and the information on the vibration of neighboring atoms [9]. The magnitude of the Fourier transformation spectra decreased when the milling time is increased. This suggests that the number of Fe-Fe bond decreased, due to the inter diffusion of Fe and Mn atoms.

The vertical dot lines indicate the first, second, third, and fourth shells of pure Fe which served as the guide lines (for alloyed samples to be compared). As also shown in Fig. 5, the intensity of the shell's peak in the Fourier transformation spectra gradually decreased with increasing the milling time. Before 36 hrs milling, the first shell did not move, which is corresponding to the Fe-Fe bonding. The third shell showing the long-range ordering in Fe-Fe in the Fourier transformation of EXAFS spectra decreased and shifted to a longer atomic distance. This indicates that the long range order reduced with the

increase of the milling time. The peaks of 36- and 48 hrs milling exhibit different position at the first, second, third and fourth shell compared to the 1-, 6-, 12-, and 24 hrs milled ones. It can be explained that the Fe-Fe ordering is changed, due to the alloy formation of Fe-Mn ordering. This result is in agree with the XRD data. The changes in the local structural ordering caused the variation of magnetic properties for the samples.

After analyzing SEM, XRD and EXAFS data, we measured hysteresis loops (*M-H* curves) of the samples. From these results, the coercivity H_c and magnetic saturation

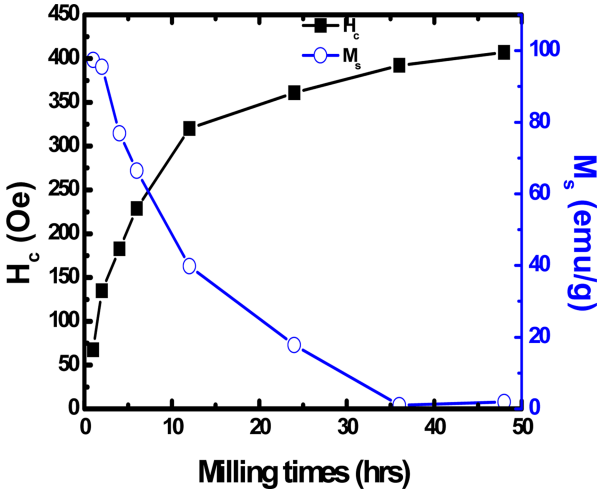

Fig. 6. (Color online) Magnetic saturation (M_s) and coercivity (H_c) alloys as functions of milling times.

M_s were obtained, as shown in Fig. 6. From Fig. 6 one can see, that M_s slowly decreases during the alloying process.

However, after 36 hrs milling time *Ms* almost constant, which is also consistent with XRD result. This indicates that there is no substantial change in the structure of the mixed powder.

This process could be related to the dilution of Fe by Mn, and also the decrease of the crystallite size with increasing the milling time. Also in Fig. 6, one can see that the coercivity (H_c) is found to be increased with milling time in the initial stage, then it seems that reaching a maximum value of approximately at 400 Oe after 48 hrs milling time. The increase of H_c could be attributed to the crystallite size reduction for Fe, but the domain never arrived at single domain size regime and a condition highly disordered, lost part of their high magnetic anisotropy are never occurred [10, 11].

The increase of H_c continuously and reaches to a maximum value of ~400 Oe as the milling time with 10 nm crystallite size, is probably due to non single-domain size for $Fe_{50}Mn_{50}$ nanocrystalline alloys. Usually the single domain size is around 3 nm.

4. Conclusion

The relatively single phase of $Fe_{50}Mn_{50}$ metastable alloys is explicitly shown in the EXAFS spectra by the variation of amplitude and phase between 36 hrs and 48 hrs milling time which is almost the same anywhere. The significant change of the structural phase revealed that new atom neighbors of the central Fe by Mn atoms were increased during the MA process. Based on the analyzed of magnetic property (*Hc*), it revealed that Fe-Mn nanocrystalline has not arrived yet in single domain regime.

Acknowledgments

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References

[1] C. Suryanarayana, Progress in Materials Science **46**, 1-184 (2001).
[2] C. Suryanarayana and C. C. Koch, Hyperfine Interactions **130**, 5 (2000).
[3] I. Chicina, Journal of Optoelectronics and Advanced Materials **8**, 439 (2006).
[4] M. M. Rico *et al.*, Phys. Stat. Sol. (a) **189**, 811 (2002).
[5] Yong-Goo Yoo, Bingzhi Jiang, J. M. Greneche, Dong-Seok Yang, and Seong-Cho Yu, J. Magn. Magn. Mater. **304**, e715 (2006).
[6] Hongwei Shi, Debo Guo, and Yifang Ouyang, J. Alloys Compd. **455**, 207 (2008).
[7] F. Offi, W. Kuch, and J. Kirschner, Phys. Rev. B **66**, 064419 (2002).
[8] D. S. Yang, I. Kim, Y. G. Yoo, B. Jiang, S. G. Min, and S. C. Yu, J. Kor. Phys. Soc. **50**, 1062 (2007).
[9] D. S. Yang, I. Kim, Y. G. Yoo, and S. C. Yu, J. Phys. Soc. Japan **71**, 487 (2002).
[10] J. Sort, S. Surinach, J. S. Munoz, and M. D. Baro, Phys. Rev. B **65**, 174420 (2002).
[11] Nam, J. H. J. Kor. Ceram. Soc. **39**, 1119 (2002).