Local Ordering Study of Nanostructure FeMnAl Alloys

by Kontan Tarigan

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$Fe_{55}Mn_{10}Al_{35}$ alloys were prepared by mechanical alloying. Local ordering around the central atom was examined with milling time using extended X-ray absorption fine structure. The structural and magnetic evolution was analyzed by EXAFS and Mössbauer study as a function of milling time. The first shell of the Fourier transformed spectra changed with milling time, indicating a change in the local ordering around the central Fe atom. X-ray diffraction patterns indicate a bcc phase after 24 h milling time. For 1 h milled sample, Mössbauer spectra analysed three sextets as bcc-Fe phase, broad sextet and Fe surrounded Al and Mn phase. The magnetization showed decrease with milling time corresponding to magnetic dilution.

***Index Terms*—Extended X-ray absorption fine structure (EXAFS), local structure, Mössbauer spectra and FeMnAl.**

I. Introduction

Fe based metallic alloys have been extensively studied for the applications of the magnetic devices [1]. The ferromagnetic behavior observed in Fe based alloys is due to the presence of Fe clusters on grain boundaries or due to the formation of Fe-rich magnetic phases even if the starting composition is non-magnetic element rich composition. However, the mechanism formation of these phases, the influence of structural properties that gives rise to ferromagnetism and the effect of nano sized structure on the magnetic properties of these systems are far from being understood, especially [2].

Mechanical Alloying (MA) has been used widely to prepare metastable phases such as supersaturated solid solution, amorphous phases and nanostructure powders, starting from a mixture of elemental components or inter-metallic compounds in many alloy systems [3], [4]. The fabrication of numerous binary alloys was achieved by MA technique such Fe-Al, Fe-Mn, Fe-C, and Fe-Si. The intermetallic Fe based alloys have been studied by a function of milling time as alloying process. The research with milling time is convenient to investigate mechanism of magnetic properties due to the influence of structural change.

Ternary Fe-Al-Mn system by MA technique has been studied in the literature, rarely. The former study achieved the effect of Mn or Al composition because the magnetic phase of Fe-Al-Mn system is dependent of structural changes with Mn or Al concentration. Especially, the microstructural change leads to a critical change of magnetic properties.

The microstructural properties are related to their atomic ordering in alloy composition. Atoms in solid have some regularity in the arrangement including the short range order and the long range order. The long range order can be examined by the X-ray diffraction (XRD) study, and the short range order is examined by the extended X-ray absorption fine structure (EXAFS) or scattering analysis with neutron or X-ray sources.

EXAFS technique has been used to examine the local structure and the ordering around concerned atoms in amorphous, nanocrystalline and crystalline materials. Our previous studies were devoted to reveal the local atomic structure on binary or ternary alloys such as Fe-Si, Fe-C, Fe-Co-Cu, and Ni-Ga-Mn alloy [5].

In this work, $Fe_{55}Al_{35}Mn_{10}$ alloys were prepared by the mechanical alloying techniques with process periods of 1, 4, 6, 12, and 24 h to investigate the relationship between the magnetic properties and the local structure. To understand the mechanism of solid state reaction by mechanical alloying on the atomic scale, the structural evolution of these alloys was examined by XRD, ^{57}Fe Mössbauer spectrometry, and EXAFS as a function of milling time. Special attention is paid to model the local structure and local ordering around Fe atoms in these nanostructured powders by means of both EXAFS technique and Mössbauer spectrometry and to the contribution of grain boundaries, the role of which is so important in the physical properties of such nanostructured materials.

II. Experiment

Fe-Al-Mn alloys were prepared by MA method using a SPEX 8000 mixer and mill with stainless steel ball and vial. Starting elements consist of appropriate amounts of Fe, Al and Mn (−80 mesh, 99.9%) powders. MA was performed under an Ar atmosphere to prevent oxidation during the alloying process. Chosen composition was $Fe_{55}Al_{35}Mn_{10}$ in order to study the influence of Mn and Al in Fe based system on the structural evolution properties. Structural change for prepared samples was examined by XRD and EXAFS spectroscopy. XRD traces were obtained with a monochromatic Cu K_α radiation. EXAFS experiments were carried out at the beam line 3C1 EXAFS of the Pohang light source(PLS). The PLS was operated with an electron energy of 2.5 GeV and the maximum current of 200 mA. The variation of magnetization was measured by vibrating sample magnetometer (VSM) with applied field of 1 T at room temperature. Mössbauer spectra were collected at

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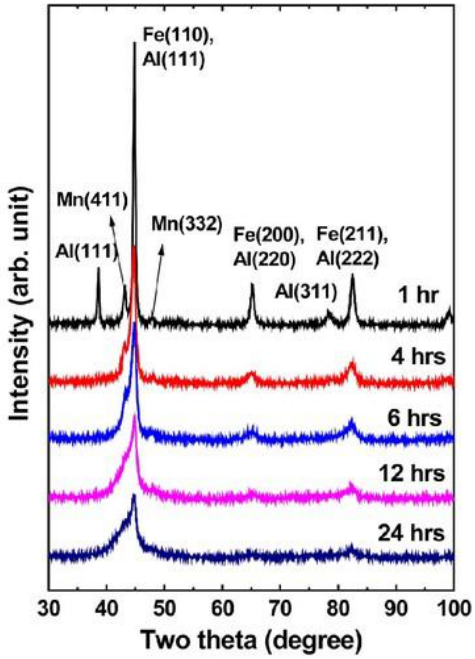

Fig. 1. XRD profiles of mechanically alloyed $Fe_{55}Al_{35}Mn_{10}$ powder with milling time.

300 K, with a conventional constant acceleration spectrometer in transmission geometry with a ^{57}Co source diffused into a Rh matrix. The hyperfine structure was refined using the MOSFIT program [6].

III. Results and Discussion

XRD patterns obtained from mechanically alloyed $Fe_{55}Al_{35}Mn_{10}$ powders are shown in Fig. 1. The 1 hr milled sample consists of mixed phase as bcc-Fe, bcc-Mn and fcc-Al. The Al and Mn diffraction peaks rapidly weak after 1 h alloying while the remaining Bragg peaks from the bcc-Fe phase became weaker and broader as the milling time increased. It could be assumed that the amorphization of Al and Mn occurs and deformation of Fe structure starts undergoing fracture and welding, repeatedly. With further milling time, the Mn(411) peak was buried into Fe(110) and Al(111) mixed peaks after 6 h milling time. It means that the Al and Mn atoms diffuse into the Fe structure and then bcc phase is formed after 24 h milling time as shown in Fig. 1. As a result, sample alloyed for 24 h shows a bcc phase and the estimated crystallite size is about 20 nm.

The local structure and the atomic ordering were examined by using EXAFS experiment. Variations of EXAFS spectra are related to information on the structural changes of alloys at atomic scale. Mostly the reduction of the amplitude of EXAFS spectrum is caused by the disorder in local structure. The phase shift of EXAFS spectrum is related to the change of chemical order [7].

Fig. 2 shows the EXAFS spectra of $Fe_{55}Al_{35}Mn_{10}$ alloy milled for 1, 4, 6, 12 and 24 h, respectively. As shown in Fig. 2, the amplitude decreased significantly as milling time

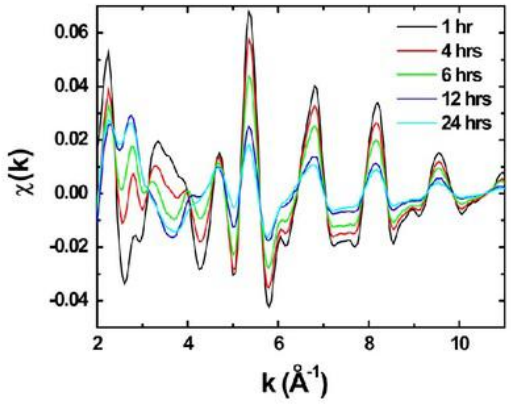

Fig. 2. EXAFS spectra of $Fe_{55}Al_{35}Mn_{10}$ alloys with milling time.

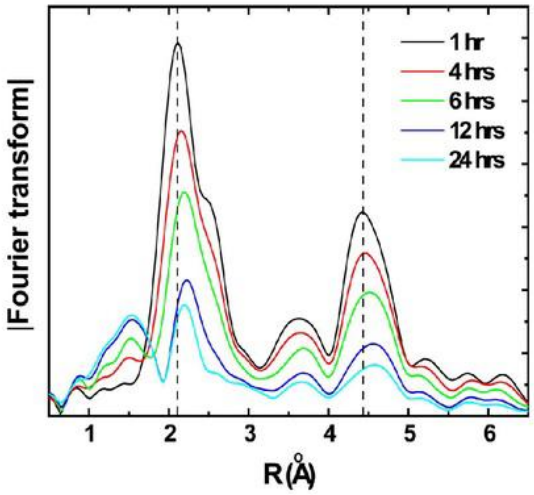

Fig. 3. EXAFS spectra of $Fe_{55}Al_{35}Mn_{10}$ alloys with indicated milling times.

increased. Also, the line shape was deformed with increasing of milling time. Before 6 h, the reduction of amplitude was dominant due to the structural deformation. However variations of the phase were dominant after 6 h. This indicates that the start of alloying in this period. It seems that the amount of the diffusion of Al and Mn atoms into Fe structure increased gradually as the milling time increased. Especially, the spectra near $k = 6.3$ Å^{-1} shows that there was no significant change before 6 h but changed gradually in structure. This means that no significant variation occurred in the local structure but the structure was changed gradually after 6 h.

The radial atomic density in real space can be seen in the Fourier transformed spectrum [8]. Fig. 3 shows the Fourier transform of EXAFS spectra measured at Fe K-edge with milling time. The vertical dot lines indicate the first shell and the third shell of pure Fe which is guide line to compare with alloyed samples. As shown in Fig. 3, the magnitude of the Fourier transformed spectra decreased gradually as the milling time increased. This suggests that the number of Fe-Fe bond decreased due to the diffusion of Al and Mn atoms into the bcc Fe shells. With increasing milling time, the first shell moves to

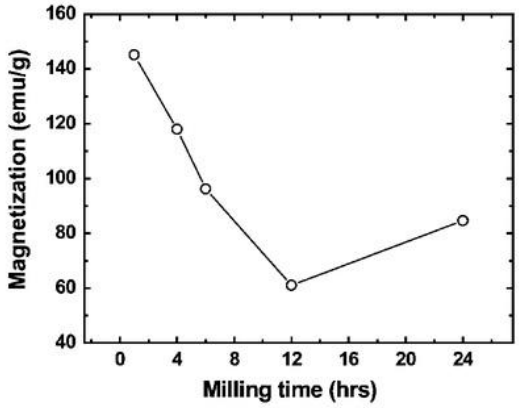

Fig. 4. Variation of magnetization of $Fe_{55}Al_{35}Mn_{10}$ alloys with milling times.

longer atomic distance corresponding to the increase of Fe-Mn and Fe-Al bonding. The shift of first shell peak represents the change of local structure around the Fe atoms due to formation of alloys with milling time. The higher shell peaks showing the long range ordering in Fe-Fe in the Fourier transform of EXAFS spectra also decreased and shifted to longer atomic distance. This indicates that the long range order also reduced with the increase of milling time. The 24 h milled sample exhibits the quite different position in the first shell with compare to the 1 h milled sample. It can be explained that the Fe-Fe ordering was changed to Fe-Mn and Fe-Al ordering indicating the alloy formation. These result are in good agreement with the XRD results.

The change of local structural ordering gives rise to the variation of magnetization. Fig. 4 shows the variation of the magnetization for $Fe_{55}Al_{35}Mn_{10}$ alloys with milling time. The magnetization decreased with the increase of milling time. This indicates that the mixed powder undergoes magnetic transform when the alloying of the mixed powder is progressed. With increasing milling time, welding and fracture of the powder particles occurs repeatedly. Thus, inter-diffusion of the Fe and Al and Mn increases, resulting in magnetic dilution, i.e., decrease of the magnetization. After 6 h milling time, the variation of magnetization showed slight fluctuation due to the alloying process to steady state. The variation of magnetization corresponds to the results of the XRD and EXAFS structural analysis.

The Mössbauer measurements allowed us to observe the alloy formation at every stage of the alloying process [9]. The room temperature Mössbauer spectra taken at different milling times are shown in Fig. 5. For the 1 h alloyed sample, the Mössbauer spectrum shows the presence of a magnetic sextet corresponding to bcc-Fe phase. As the alloying process progresses, the Mössbauer spectra are characterized by broadened lines due to the variation of Fe environment with Al and Mn diffusion.

The Mössbauer spectra were first fitted using a hyperfine field distribution which reveals a priori the presence of three main components. From Mössbauer spectrometry, for 1 hr milling time, one observes a magnetic sextet with different broadened lines. They can be decomposed into 3 magnetic components: one with an Hyperfine field of 33.1 T, a second one at 30.6 T,

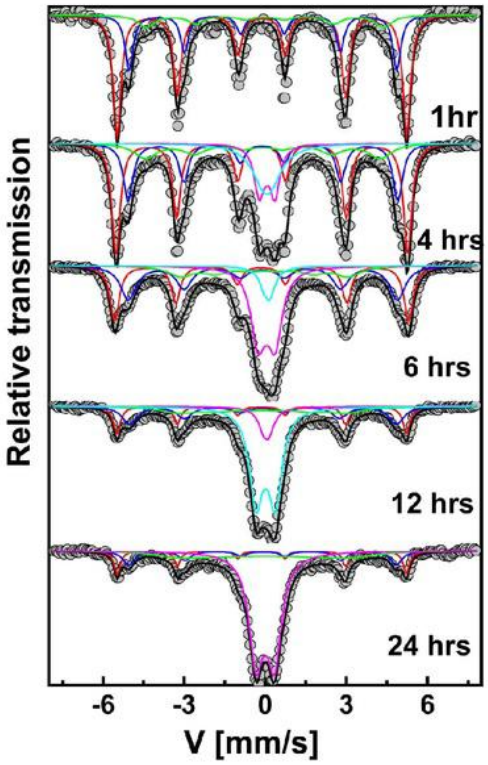

Fig. 5. Mössbauer spectra of $Fe_{55}Al_{35}Mn_{10}$ mechanically alloyed powders for various milling times.

and a third one at 27.5 T. The first sextet is clearly attributed to Fe in bcc environment which is consist of 8 nearest neighbors of Fe and 6 next nearest neighbors of Fe. The second one can be assigned to Fe with 7 nearest neighbors of Fe, 1 nearest neighbors of Al and 6 next nearest neighbors of Fe resulting from the milling. The third sextet can be assigned to 6 nearest neighbors of Fe, 2 nearest neighbors of Al and 6 next nearest neighbors of Fe. The role of Mn is being less important because of its low content. One can also observe a small quadrupolar component already for 2 h, which can be attributed to Fe surrounded preferentially by Al. This means that Al diffuses into Fe bcc grains. For milling times over 2 h, the central part increases at the expense of the magnetic contribution. One quadrupolar doublet (QD) has to be introduced as well as a single line (SL), both increasing with milling time. The paramagnetic fraction (PF) is the sum of these two late components. The single line could be attributed to Fe into fcc-Al grains.

One observes that both components with 33 and 30.5 T decrease but remain present. The component at 27.5T *a priori* disappears but in fact a broad line component was used to describe the low field part which is attributed to Fe with surrounding including Al as nearest neighbors and next nearest neighbors, and Mn atom also is contributed.

The evolution of Mössbauer spectra show that there is some alloying but Al does not completely diffuse into bcc-Fe grains: one can consider a core shell model with no Al in the core and Al enriched shell. This fact gives so far different results with

compare to structural analysis but the progress of alloying is well agree to XRD and EXAFS results and Mössbauer analysis gives more detailed explanation.

IV. Conclusion

The local structural and magnetic properties of mechanically alloyed $Fe_{55}Al_{35}Mn_{10}$ powders were studied by using XRD, EXAFS, VSM measurement, and Mössbauer spectrometry as a function of milling time. The structural evolution with XRD and EXAFS indicated the formation of bcc phase after 24 h milling time. Fourier transformed EXAFS spectra exhibited the atomic distribution surround Fe central atom with milling time. The Al and Mn atoms diffused into the bcc phase with the increase of milling time. For Mössbauer study represented the three kinds of component and the increase of bcc phase while the bcc-Al still was slightly remained after 24 h milling time. The role of Mn was being less important due to its low content.

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