Nanocrystallization Process in Soft Magnetic Nanocrystalline Alloy $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ Studied by Mössbauer Spectroscopy

L.Sabetinejad, N.Sabetinejad ,G.Kheiry

***Abstract*—** In this work the structure evolutions of soft magnetic nanocrystalline alloy $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ have been studied. At first, amorphous ribbons were prepared by rapid solidification technique, then heat treatments were performed at temperatures 560°c for 1 h. X-ray diffraction (XRD), transmission electron microscopy (TEM) and Mössbauer spectroscopy measurements were conducted on the as-quenched and heat treated alloys to investigate their properties. The result of Mossbauer spectroscopy confirmed the formation of crystalline structures in amorphous matrix at 560°c. Increasing of temperature, over than 560°c, causes to formation of hard magnetic phases which is in agreement by XRD and TEM results.

***Keywords*—** nanocrystalline alloy, Finemet, Mössbauer spectroscopy

I. INTRODUCTION

In 1988, YOSHIZAWA first discovered a new type of soft magnetic materials which was derived from the conventional Fe-Si-B amorphous alloy system with a minor additions of Cu and M (M = Nb, Ta, Mo, W, etc.) [1−3]. After a suitable heat treatment, the alloy was obtained with α-Fe(Si) nanocrystallites embedded in anamorphous matrix consisting of Fe, Cu, Nb and B. The new alloy exhibits excellent soft magnetic properties and the typical composition is $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, known as Finemet. The Fine met alloy has attracted much attention due to its unique structure and excellent soft magnetic properties (high saturation magnetic flux density, high initial permeability, low coercively , and low loss)[4−5]However, the current study on Finemet alloy focused on the microstructure change and nanocrystallization under heat treatment. In this respect, phase evolutions taking place at various Heat-treatment temperatures were investigated using Mössbauer spectroscopy as a powerful tool to study structural variations, site occupancy, and magnetic structure and/or moment orientations, accomplishing other Characterization techniques used in this work, such as x-ray diffraction and TEM**.**

L.Sabetinejad, Department of Physics, Damavand Branch, Islamic Azad University. Department of physics, Iran University of Science and Technology Tehran,Iran Email: Leila.sabeti@gmail.com

N.Sabvetinejad, Department of Physics, Damavand Branch, Islamic Azad University, Tehran,Iran

G.kheiry, Department of physics, Iran University of Science and Technology Tehran,Iran

II. EXPERIMENTAL DETAILS

Amorphous Fe-based ribbons of nominal compositionFe73.5Si13.5B9Nb3Cu1 were prepared by the single roller Melt-spinning process at a wheel speed of 25 m/s using extra pure constituting elements. The as-spun samples were Heat treated at 560 1C for 1 h in a vacuum furnace. The crystalline structures of the as-spun and heat-treated samples were examined by X-ray diffraction (XRD) technique using Cu-Ka1 radiation.The micro structural study of the as-spun and heat treated samples was carried out using a 200 kV Philips transmission electron microscope (TEM). Finally, room-temperature Mossbauer spectra for the as-spun samples were also recorded on a conventional gamma-resonance spectrometer operating in constant-acceleration mode with ^{57}Co as source. The spectra were computer-analyzed using the recoil program.

III. RESULT AND DISCUSSION

A. Structural Analysis

Fig. 1 shows XRD patterns of the as-spun and heat treated sample. As can be realized from these patterns, for the as-spun samples only one broad peak around $2\theta = 45$ was noticed, indicating that these samples were amorphous. Single area diffraction patterns (SADP) obtained by TEM from different parts of these samples also revealed halo diffraction rings (Fig.2a) suggesting the formation of amorphous structure. XRD and TEM results were also supported by Mössbauer spectra of these samples by the appearance of a broadened Zeeman sextet which is typical for the fully amorphous FINEMET alloys**.** The XRD patterns of the samples heat treated at 560° C for 1 h are presented in Fig. 1 As is evident from this figure, the only phase formed after the heat treatment of these samples was α-Fe(Si) of bcc structure. The calculated mean grain sizes (d) of the α-Fe (Si) phase using Sherrer's formula [6] was 11.6 nm. (Fig.2b) also demonstrates the TEM bright field micrograph of sample. The presence of the crystalline (Fe (Si)) phase embedded in an amorphous phase could be also verified by

their corresponding SADP obtained (insets shown in (Fig.2b)).

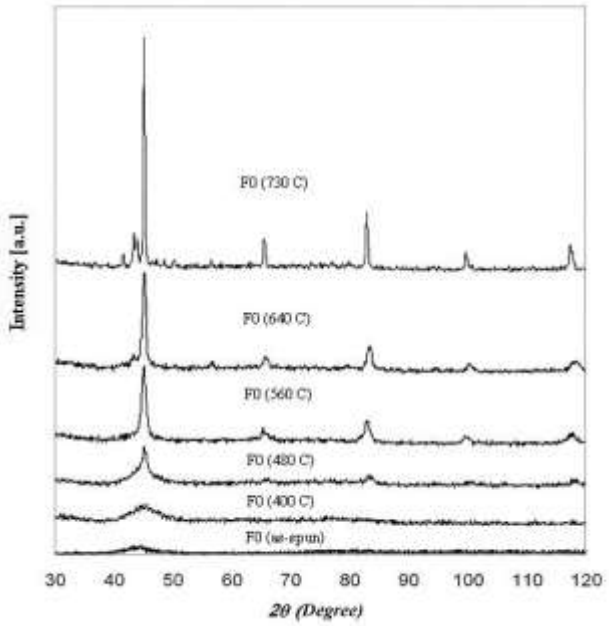

Fig 1. XRD of the as-spun and heat-treated sample

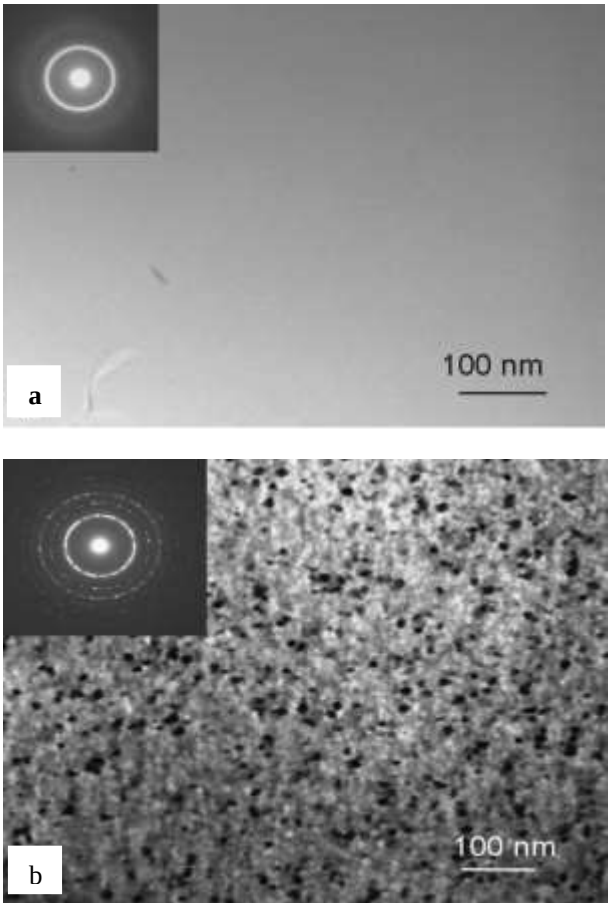

Fig. 2 (a)-TEM and SADP micrographs of the as-spun sample 2 (b) - TEM bright field image and SADP of nanocrystalline Fe (Si) phase of heat-treated sample

The average grain sizes of Fe(Si) phase obtained by TEM were 10nm. These are in close agreement with those obtained by Scherrer's formula [6] increase of The peak intensity due to increased number and size of the grains up to 640º c is observed. For Temperatures 640º and 730º in addition of producing larger ferromagnetic phases , some phases of hard magnetism of Fe_2B in the alloy can be seen that indicate by some extra peaks in pattern of diffraction.

B. Mössbauer study

Mössbauer spectroscopy is an isotope specific technique which can provide information about magnetic ordering via the hyperfine field, moment orientation, charge states and the local environment of the Mössbauer isotope. Atoms in sites which differ in their electronic or magnetic environment can be distinguished.

In this work, the magnetic behavior of the amorphous alloy and after heat treatment has been studied by Mössbauer spectroscopy in the temperature range 400ºC - 730°C.

For ^{57}Fe Mössbauer spectroscopic measurements, radioactive ^{57}Co in an Rh matrix was used at room temperature as source. The Mössbauer spectra were fitted using the Recoil program with the Voigt-based method, where the magnetic hyperfine parameter's distributions are represented by a sum of Gaussian.

i. Mössbauer spectra in amorphous state

The Mössbauer spectra obtained for the as-spun samples exhibited broadened Zeeman sextets which is typical for fully amorphous FINEMET alloys [7] in agreement with our XRD and TEM results. The as-quenched samples can be fitted by three components with wide magnetic field distributions. For alloys heat treated at 400 °C, a broad sextet (Fig 3)ascribed to a large distribution of hyperfine fields (Fig 4) could still be seen, suggesting that no major crystallization has taken place at this temperature for these alloys.

It is reported that heat treatment of as-spun FINEMET alloys at temperatures below the onset of crystallization could mainly give rise to atomic relaxation of the amorphous phase [8].

The initial magnetic softening is produced by the relaxation of internal stresses (magnetoelastic anisotropy) within the amorphous state. The latter magnetic hardening (after annealing between 440 and 480 ◦C) seems to be a consequence of the appearance of Cu-enriched clusters of diameter around 5 nm which form even before the onset of crystallization. Simultaneously with this Cu-atom segregation, α-FeSi grains start to nucleate. [9]

Mössbauer studies have shown a bimodal character for average magnetic hyperfine distribution of amorphous phase with two different magnetic fields (~12T, ~22T) Due to the Presence of two magnetically distinct types of iron sites: a lower one ascribed to Fe atoms preferentially surrounded by Cu, Nb and B atoms (Cu-clusters) and another higher one attributed to those surrounded by Si and B atoms [10]. The Mössbauer spectra obtained for the alloys heat treated above 400 °C indicated the onset of crystallization. After heat treatment, these three components are merged together and the amorphous parts of the samples are represented just by one component. This component in the sample with high

fraction of crystallinity has a very low magnetic hyperfine field (B_{hf}) with very broad distribution. This indicates that during the annealing a segregation of Fe and Si atoms occurs. The tiny amount of Fe atoms left in the residual amorphous part is mostly surrounded by the other atoms than Fe and Si.

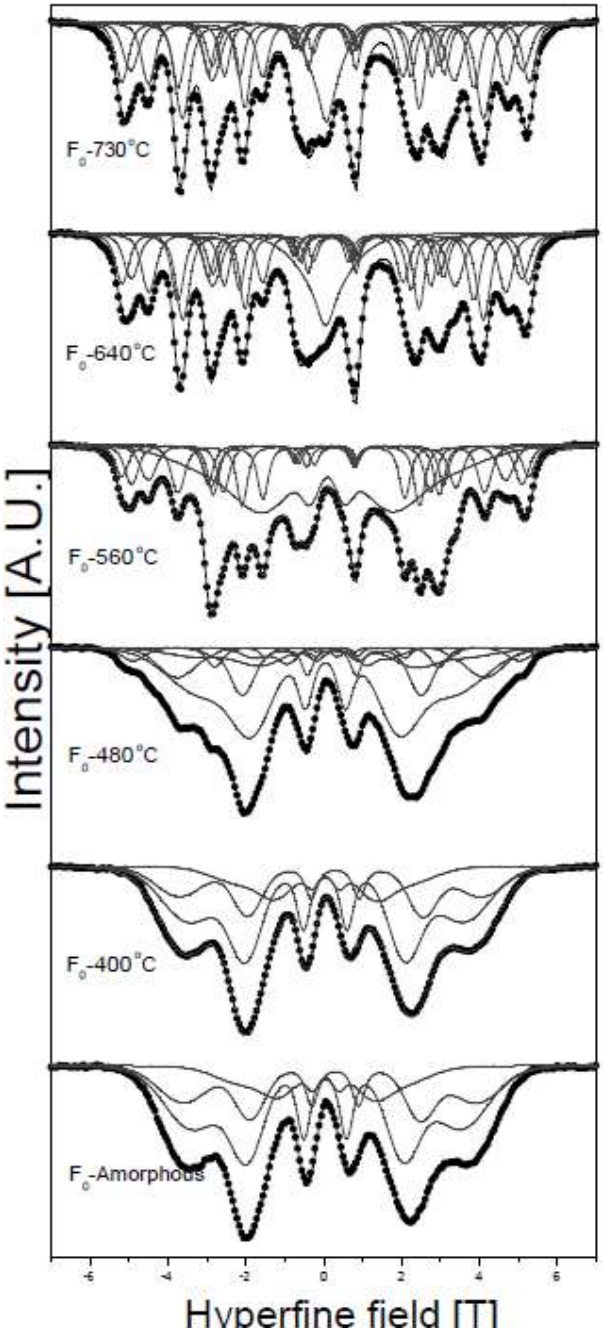

Fig. 3 Mössbauer Spectra of as- spun and heat- treated sample

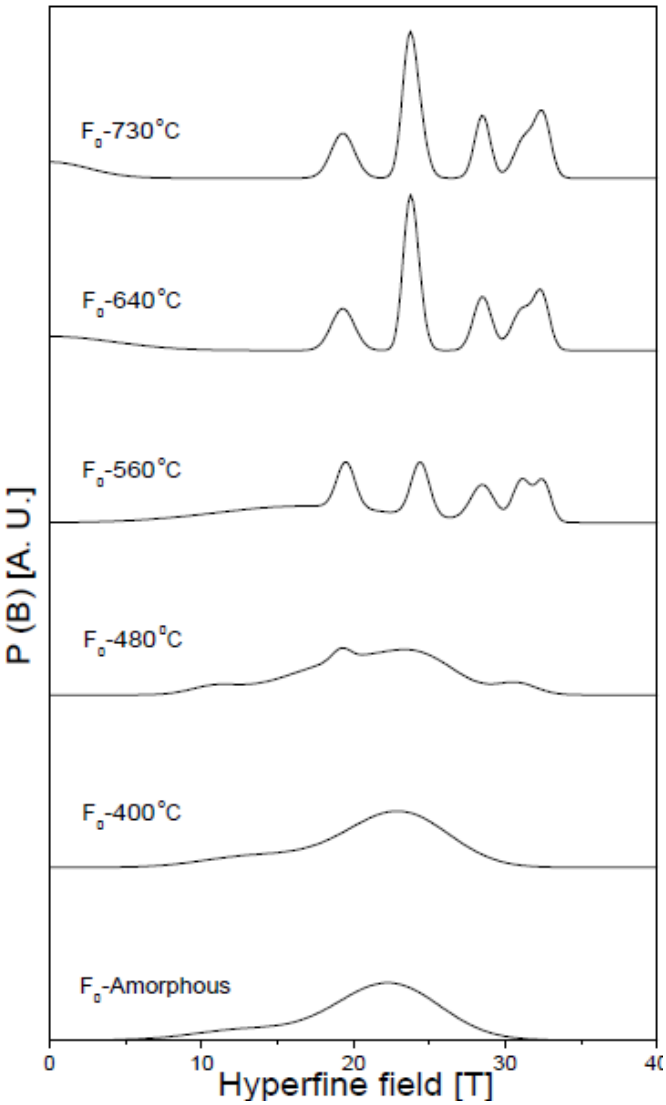

Fig. 4 Distribution of Magnetic Hyperfine Field for as-spun and heat- treated sample

ii. Mössbauer Spectrum in nanocrystalline state

Mössbauer Spectrum in Nanocrystalline state has very complicated hyperfine structure. The Mössbauer spectra show multiple narrow lines, which represent structurally different Crystallographic sites assigned to the iron-silicate grains, Superimposed on a broadened Zeeman sextets ascribed to the residual Amorphous. In process of analysis the Mössbauer spectra it was found that there are five non-identical configurations for the iron in the crystalline phase, which show that the number of close neighboring silicon or next near neighbors is various. These components with magnetic hyperfine fields (B_{hf}) around 19.5, 24.5, 28.5, 31.0 and 32.0 T are from irons with 4, 5, 6, 7 and 8 irons as nearest neighbors. In $560^{\circ}c$, spectrum is influenced by two Magnetic Components. One component located within the low-speed broadband lines, is amorphous phase effect, which decreases with increasing temperature. At this area, the peaks corresponding to the crystalline phase are overlapped with the peak of the amorphous component. The distribution lines of

the second magnetic component, which are the farthest lines visible comparative to the center of spectrum, and in the range of top speed, are sharp and related to the crystalline phase [11]. Increasing the percentage of crystalline silicon phase leads to crystalline phase transformation from bcc to the DO3, which is formed with about 10% to 30% silicon [12]. In $560^{\circ}c$ structure changes from bcc to DO3 has occurred because of the high penetration of silicon into crystal grains. Above $560^{\circ}c$, Component of the remaining amorphous phase becomes an asymmetric doublet, while the Second Component of the crystalline deposits show the structure of the magnetic hyperfine yet. Generally there are two important temperature ranges which the magnetic behavior of nanocrystalline alloys is different there. The first range is related to low temperatures that both phases (crystalline and amorphous) are ferromagnetic. In this range, strong exchange interaction between nano grains and amorphous phase is responsible for the overall magnetic behavior in sample. The second region is related to higher temperatures that the ferromagnetic grains are distributed in paramagnetic networks. In this range, the property of the crystalline phase strongly depends on two parameters: the volume fraction of crystalline phase and the distance between grains. These parameters influence the type of interactions between grains. In materials with low crystalline volume fraction, direct exchange interaction between grains can be neglected. It can be considered in the range of temperatures near the Curie temperature of amorphous network.

A rapid decline in the exchange interaction between phases occurs and leads to disruption coupling between $Fe(Si)$ nano crystals. Reduction of exchange interaction is due to reduction of the magnetic properties of amorphous phase which is responsible for transferring exchange between nano grains. Thus, the nanocrystalline grains have been decoupled. For a community of single particles that are not interacted, with a further increasing in temperature, thermal energy will disappear the magnetic state, and superparamagnetic chaos will be overcome magnetic behavior of material [11]. Obviously for the alloys with high crystalline volume (70% - 80%) with a distance between $1-2\ nm$ in higher temperatures, interaction between grains occurs within the paramagnetic amorphous network. In this case, the Interactions between grains cause magnetic ordering and prevent superparamganetice even in higher temperatures. Here the paramagnetic amorphous network plays an important role as transmitter of exchange coupling and the most likely interaction is RKKY interaction [11]. As can be observed in samples at temperatures 730°C, high crystalline volume fraction, about 90%, prevent superparamagnetic behavior in the system.

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