

Structural Properties and Crystallization Behavior of FINEMET Fe₇₄Cu_{1.5}Nb_{2.5}Si₁₂B₁₀ Alloy Under Different Annealing Condition

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Abstract

The effect of annealing condition on nanocrystalline amorphous FINEMET type of alloy with nominal composition Fe₇₄Cu_{1.5}Nb_{2.5}Si₁₂B₁₀ prepared by rapid solidification method has been studied to observe the structural properties and crystallization behavior of the material. Nanocrystalline alloy with ferromagnetic bcc nanocrystals with size 15-29 nm embedded in a residual amorphous matrix was produced from amorphous precursor by appropriate annealing condition. The amorphosity of the material, primary crystallization temperature, the nanometric grain size, Si content and the lattice parameter of Fe(Si) nano-phase have been determined from XRD patterns of the samples annealed at different temperatures ranging from 475°C - 650°C with annealing time 5, 12, 20 and 30 minutes. The annealing temperature 475°C (with annealing time of 12 minutes) was determined as primary crystallization temperature with grain size 15 nm, Si content 16.25 at.% and lattice parameter 2.8431 Å. The grains were found to grow rapidly after 550°C attaining a maximum value of 29 nm at the annealing temperature of 650°C. The grain size and Si content increase whereas the lattice parameter decreases with the increase of annealing temperature and time.

Keywords: Amorphous matrix; nanocrystalline alloy; grain size; Si content; lattice parameter

I. Introduction

Fe-based nanostructured metallic alloys are already in deep attention of scientists and researchers due to its excellent soft magnetic properties. Materials like these types of alloys are generally developed through controlled crystallization from their amorphous state¹⁻³. FINEMET¹, for example, Fe₇₄Cu_{1.5}Nb_{2.5}Si₁₂B₁₀ alloy with a nanocrystalline grain structure is an attractive soft magnetic material⁴. The genre of this material, FINEMET, tells us about the nature of these kinds of materials featuring the terms FINE and METAL⁵, which had been derived for its excellent soft magnetic properties and fine crystal grains. The nanocrystalline alloy is produced by crystallization of an amorphous Fe-Si-B alloy with small additions of Cu and Nb. The additives Cu and Nb play an important role in formation of ultrafine microstructure of bcc Fe-Si nanograins with grain size 10-25 nm from which their soft magnetic properties are lastly derived and after which they were named nanocrystalline⁶. The basic principle for the crystallization method from amorphous solid is to control the crystallization kinetics by optimizing the heat treatment conditions such as annealing temperature, annealing time, heating rate etc. Before crystallization, the alloy is in the amorphous state and controlled crystallization of FINEMET type of Fe-Cu- Nb-Si-B alloys can be used to obtain partially crystallized materials with nm size Fe-Si nanograins embedded in residual amorphous matrix. The nanocrystalline and amorphous phase allow the material to exhibit extraordinary soft magnetic properties.

An appropriate heat treatment above the crystallization temperature 475°C - 650°C produces a homogeneous ultrafine grain structure composed of randomly oriented nanocrystallites. Cu and Nb, these two elements control the crystallization kinetics and cause nanometric size crystallites. Cu influences the nucleation process of α -Fe(Si) solid solution and has a tendency to segregate at the very beginning of nanocrystallization forming Cu rich clusters while Nb which is rejected at the crystal interfaces hinders

the grain growth because of its higher crystallization temperature and thus stabilizes the residual amorphous region⁷. Crystallization of amorphous material is a diffusion control phenomena where temperature and time are the relevant parameters. There are many reports about the magnetic softening under different annealing condition⁸⁻¹³. To our knowledge, a little work has been performed on the detail structural properties and crystallization behavior of FINEMET. Therefore, The aim of the present work was to develop the nanocrystalline state from amorphous precursor of the alloy with composition Fe₇₄Cu_{1.5}Nb_{2.5}Si₁₂B₁₀ and then a detail study of structural parameters such as grain size (D), Si content (at.%) and lattice parameter (a) of the nanometric grains of the alloy. Before going to measure the electric and magnetic properties, it is important to observe these structural parameters. The magnetic softening of the said nanocrystalline alloy under different annealing temperatures (475°C-650°C) and annealing time (15 minutes) has been reported¹⁴.

II. Methods

Amorphous alloy in the form of ribbon has been prepared with nominal composition Fe₇₄Cu_{1.5}Nb_{2.5}Si₁₂B₁₀ by rapid solidification of the melt using single roller melt spinning technique. The ribbons were on an average 6 mm wide and 25 μ m thick. Using appropriate annealing condition, nanocrystalline states were obtained from amorphous ribbon. The ribbons were cut into several pieces each of length 25 mm. Heat treatment was performed on the amorphous ribbons using a carbolite furnace where, each piece of ribbon was wrapped by aluminium foil separately. Heat treatment was performed at six different temperature ranging from 475-650°C with of annealing time 5, 12, 20 and 30 minutes for each annealing temperature. After heat treatment, the samples were ready for XRD experiment. For XRD experiment, each sample was set on a glass slide and fixed the sample by putting adhesive tape at the two ends of the sample.

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A PHILIPS X'pert PRO X-ray diffractometer was used to get the X-ray data for the samples at the Materials Science Division, Atomic Energy Centre, Dhaka. The powder diffraction technique was used with a primary beam power of 40 kV and 30 mA for $\text{CuK}\alpha$ radiation. All the data of the samples were stored in the computer memory and later analyzed them using computer software "X'PERT HIGHSORE". The average grain size was determined from (110) line broadening of bcc Fe(Si) using Scherrer's formula¹⁵, Si content of the bcc Fe(Si) nanograins was estimated from the determined lattice parameter values in accordance with Bozorth¹⁶.

III. Results and Discussion

X-ray diffraction

The XRD spectra of as-cast and annealed samples have been presented in Fig.1. XRD pattern of as-cast sample clearly confirms the amorphous state with a diffused broad peak¹⁷. From Fig.1 (a), it is also clear that 5 minutes annealing at 475°C is not sufficient for crystallization, but 12 minutes annealing at 475°C clearly confirms the presence of crystalline phase identified as a bcc α -Fe(Si) solid solution developed in the amorphous matrix¹⁸.

So, at and above 475°C, a nano crystalline state embedded in the residual amorphous matrix has been obtained. The temperature below 475°C is not capable for the Fe-Si solid solution to start crystallization and hence annealing temperature 475°C can be called as primary crystallization temperature.

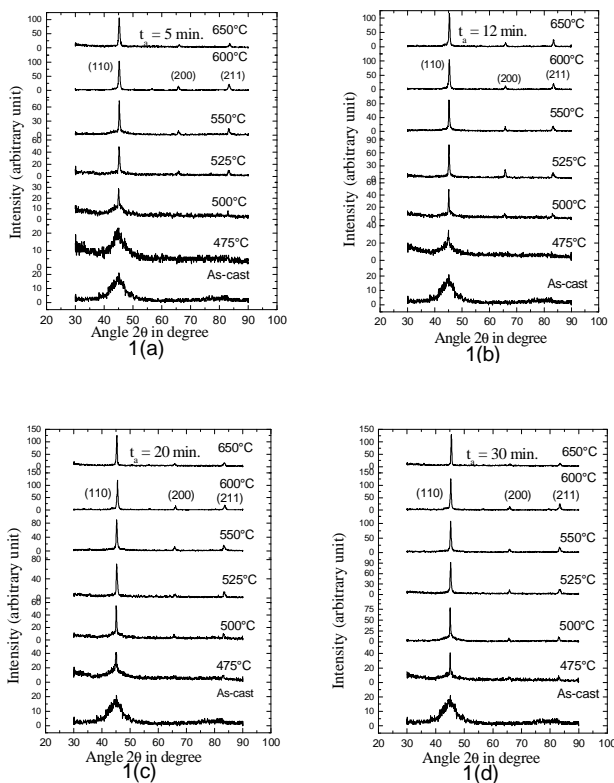


Fig. 1. X-Ray Diffraction patterns of $\text{Fe}_{74}\text{Cu}_{1.5}\text{Nb}_{2.5}\text{Si}_{12}\text{B}_{10}$ alloy for as-cast and annealed at 475°C -650°C for annealing time of (a) 5 minutes, (b) 12 minutes, (c) 20 minutes and (d) 30 minutes.

The bcc Fe(Si) peaks become narrower and sharper at and above 475 °C, and henceforth with increasing annealing temperature and time, which is a clear indication that crystallite sizes are gradually growing larger¹⁹. At $2\theta=45.17^\circ\text{C}$, 65.71°C and 83.07°C , there are three fundamental peaks (110), (200), and (211) respectively corresponding to bcc Fe(Si) phase. On (110) diffraction line, the fundamental peak has a very high intensity, and the other two fundamental peaks corresponding to bcc α -Fe(Si) on (200) and (211) diffraction line have also been identified. For the taken sample, even annealed at 650°C, this is to be mentioned that no boride phase has been detected. This might have been happened due to their small volume fraction⁵.

Determination of grain size

A total of 24 samples, four samples(with annealing time 5, 12, 20 and 30 minutes) for each annealing temperature (475°C, 500°C, 525°C, 550°C, 600°C, 650°C) have been studied. The variation of grain size as a function of annealing temperature as well as annealing time are represented graphically (Fig.2).

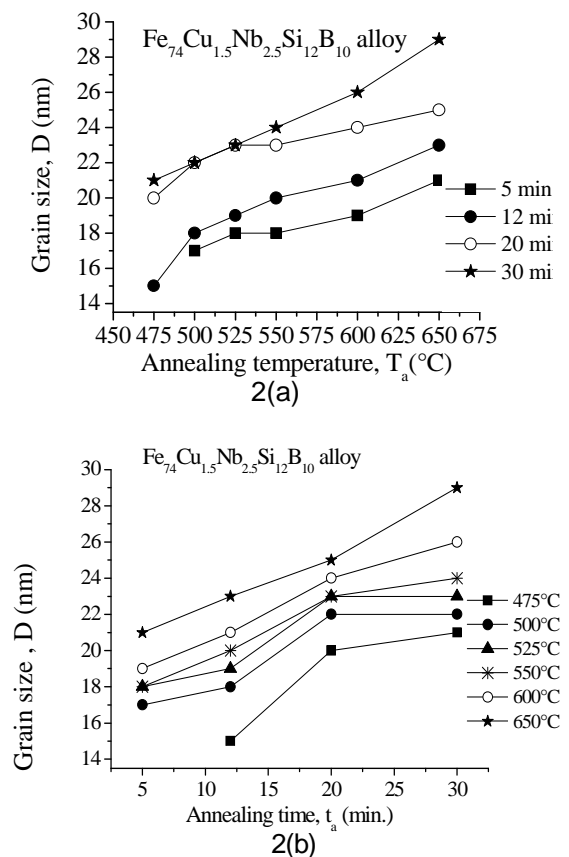


Fig. 2. Grain size as a function of (a) annealing temperature and (b) annealing time.

Grain size of all the studied samples was determined using the Scherrer's formula

$$D = \frac{0.9\lambda}{\Delta \cos \theta} \quad (1)$$

where, $\lambda = 1.54178 \text{ \AA}$ for Cu K α radiation and $\Delta = \text{FWHM}$ (Full Width at Half Maximum) of the peak in radian. Instrumental broadening of the system was determined from a θ - 2θ scan of standard Si. At 110 reflections position of the sample, the value of instrumental broadening was found to be 0.07° . This value of instrumental broadening was subtracted from the FWHM value of each peak (110).

It is seen from Fig.2 (a) that for any fixed annealing time, with increasing annealing temperature, the grain size increases gradually. This is a combined effect of Cu and Nb where, Cu acts as nucleation reagent and Nb hinders the grain growth. For 12 minutes of annealing at 475°C , formation of nanograins started with grain size 15 nm and then increases with increasing annealing temperature. The maximum grain size has been calculated to be 29 nm for 30 minutes of annealing time at temperature 650°C . Fig.2 (b) shows the variation of grain size as a function of annealing time. It is also seen from the figure that for any fixed annealing temperature, with increasing annealing time, the grain size increases gradually. The increase of grain size with increasing annealing temperature and time may be attributed due to the diffusion of Silicon into the nano grains¹⁴.

Determination of Si content

Silicon content plays an important role for getting crystallization of the samples and the microstructure of the nano crystals largely depends on the diffusion of Si content into the nano grains. At and above the crystallization temperature (475°C), Fe and Si starts to form the bcc nanocrystals and with increasing annealing temperature, the Si content in the nanocrystal increases. The temperature and time dependence of Si content are shown in Fig.3.

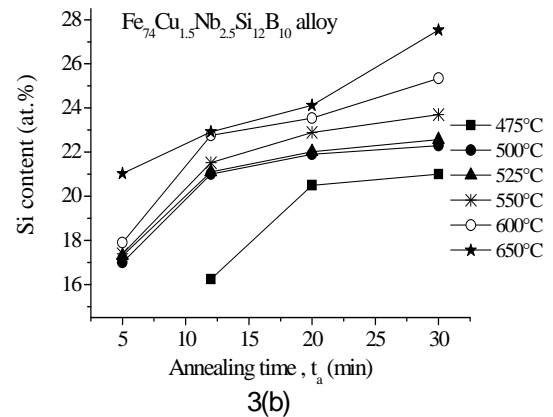
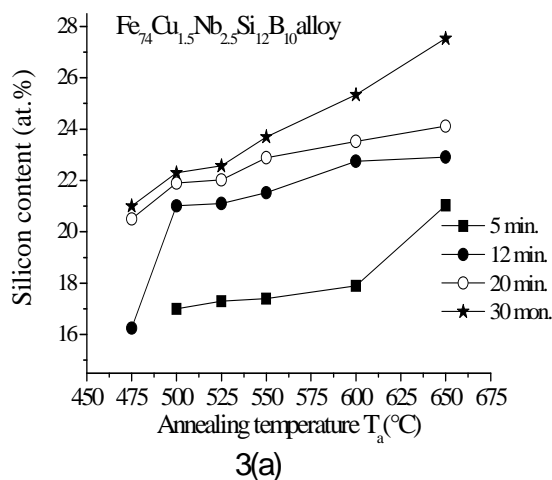


Fig. 3. Si content as a function of (a) annealing temperature and (b) annealing time.

The Si content in the nano grains were calculated from the quantitative relationship between the lattice parameter and Si content using the following equation (Pearsons handbook relationship).

$$x = \frac{a - 2.8812}{0.0022} \quad (2)$$

where, 'a' is the lattice parameter and 'x' is Si content (at.%) in the nanograins.

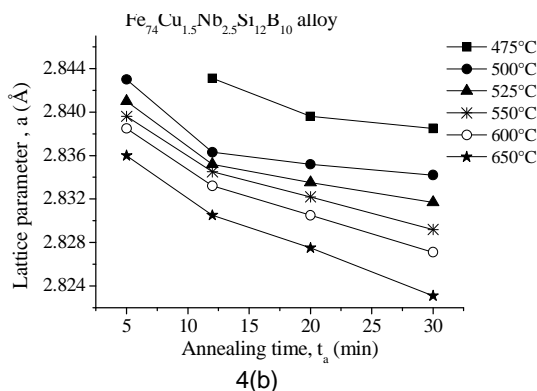
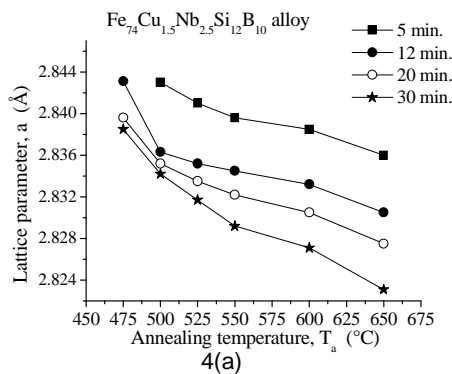
It is seen from the above two figures that with increasing annealing temperature and time, Si content increases gradually. Higher annealing temperature has a large diffusion rate which leads to large value of Si content into the nanocrystals. For 5 minutes annealing at 475°C , there is no Si content as search no grain growth.

Lattice parameter determination

The lattice parameter of the nano grains depends on the Si content. The annealing temperature dependence of lattice parameter for the samples is shown in Fig.4 (a). At the primary crystallization temperature, the lattice parameter of bcc nanophase was found to be 2.8431 \AA and then with increasing annealing temperature, the lattice parameter decreases. The lattice parameters of α -Fe(Si) phases are always smaller than that of pure Fe, the value of which is 2.8664 \AA ²⁰. Fig.4 (b) shows the annealing time dependence of lattice parameter and it is clear from figure that for any fixed annealing temperature, lattice parameter also decreases with the increase of annealing time. The decrease of lattice parameter is due to the contraction of α -Fe lattice as a result of diffusion of silicon²¹ with smaller atomic size into the iron lattice with larger atomic size forming a substitutional solid solution during the crystallization process to form α -Fe(Si).

Table 1. Variation of Grain size (D), Si content (%) and Lattice parameter (a) with annealing temperature (Ta) and annealing time (ta)

T _a (°C)	t _a (min)	D(nm)	(%)Si	a (Å)	T _a (°C)	t _a (min)	D(nm)	(%)Si	a (Å)
475	5	-	-	-	550	5	18	17.4	2.8396
	12	15	16.25	2.8431		12	20	21.52	2.8345
	20	20	20.5	2.8396		20	23	22.89	2.8322
	30	21	21	2.8385		30	24	23.7	2.8292
500	5	17	17	2.843	600	5	19	17.9	2.8385
	12	18	21.01	2.8363		12	21	22.75	2.8332
	20	22	21.9	2.8352		20	24	23.53	2.8305
	30	22	22.3	2.8342		30	26	25.34	2.8271
525	5	18	17.3	2.841	650	5	21	21.03	2.8360
	12	19	21.1	2.8352		12	23	22.92	2.8305
	20	23	22.02	2.8335		20	25	24.12	2.8275
	30	23	22.57	2.8317		30	29	27.53	2.8231

**Fig. 4.** Lattice parameter as a function of (a) annealing temperature and (b) annealing time

IV. Conclusion

The effect of annealing conditions on the structural properties and crystallization behavior of nanocrystalline FINEMET alloy ($\text{Fe}_{74}\text{Cu}_{1.5}\text{Nb}_{2.5}\text{Si}_{12}\text{B}_{10}$) were studied. The amorphous and nanocrystalline phases were confirmed by X-Ray Diffractometer (XRD). The annealing temperature 475°C (with 12 minutes of annealing time) can be considered as primary crystallization temperature because

nanometric grains start to form from amorphous precursor at this temperature. The grain size and Si content of the bcc Fe(Si) nano crystals increases whereas the lattice parameter decreases with the increase of annealing temperature and time. This is due to the diffusion of Si atom into the nanograins which results in an increase of grain size and Si content as well as decrease of lattice parameter.

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References

1. Yoshizawa, Y., S. Oguma, K. Yamauchi, 1988. New fe-based soft magnetic alloys composed of ultrafine nanograin structure. *J. Appl. Phys.*, **64**(10), 6044-6046.
2. Yoshizawa, Y. and K. Yamauchi, 1990. Materials transaction, fe-based soft magnetic alloys composed of ultrafine nanograin structure. *Japan Institute of Metals*, **31** (4), 307-314.
3. Yoshizawa, Y. and K. Yamauchi, 1991. *Materials Science and Engineering*, **A 133**, 176-179.
4. Okumura, H. D. E. Laughlin, M.E.Mchenry, 2003. Magnetic and structural properties and crystallization behavior of Si-rich FINEMET materials. *Journal of magnetism and magnetic materials*, **267**, 347-356.
5. Mondal, S. P. Kazi Hanium Maria, S S Sikder, Shamima Choudhury, D K Saha and M A Hakim, 2012. Influence of Annealing Conditions on Nanocrystalline and Ultra-Soft Magnetic Properties of $\text{Fe}_{75.5}\text{Cu}_1\text{Nb}_1\text{Si}_{13.5}\text{B}_9$ Alloy. *Science Direct, J. Mater. Sci. Technol.*, **28**(1), 21-26.
6. Herzer Giselher, *Nanocrystalline Soft Magnetic Alloy. Handbook of Magnetic Materials*, **10**, (chapter 3).
7. Fravco, V. C. F. Conde, A. Conde, 1998. Changes in magnetic anisotropy distribution during structural evolution of $\text{Fe}_{76}\text{Si}_{10.5}\text{B}_{9.5}\text{Cu}_1\text{Nb}_3$. *Journal of magnetism and magnetic materials*, **185**, 353-359.
8. Hakim, M. A. S. Manjura Hoque, 2004. Effect of Structural parameters on soft magnetic properties of two phase nanocrystalline alloy of $\text{Fe}_{73.5}\text{Cu}_1\text{Ta}_3\text{Si}_{13.5}\text{B}_9$. *Journal of magnetism and magnetic materials*, **284**, 395-402.

9. Miguel, C. S. Kaloshkin, J. Gonzalez, A. Zhukov, 2003. Curie Temperature behavior on annealing of Finemet type amorphous alloys. *Journal of Non-Crystalline Solids*, **329**, 63-66.
10. Tejedor, M. B. Hernando, M. L. Sanchez, V. M. Prida, P. Gorria, 2001. magnetic domains and magnetoimpedance effect during the nanocrystallization of Fe_{73.5}Cu₁Nb₃Si_{16.5}B₆ ribbons. *Journal of Non-Crystalline Solids*, **287**, 396-400.
11. Ohnuma, M. D.H.Ping, T. Abe, H. Onodera, K. Hono, 2003. Optimization of the microstructure and properties of Co-substituted Fe-Si-B-Nb-Cu nanocrystalline soft magnetic alloys. *Journal of Applied Physics*, **93**, 9186-9194.
12. Shindo, D. Y.G.Park, Y. Yoshizawa, 2002. Magnetic domain structure of Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ films studied by electron holography. *Journal of magnetism and magnetic materials*, **238**, 101-108.
13. Mondal Siba, P. kazi Haniun maria, S. S. Sikder, Shireen Akhter, Shamima Choudhury, 2011. Correlation between structure and magnetic properties of amorphous and nanocrystalline Fe₇₄Cu_{0.5}Nb₃Si_{13.5}B₉ alloys. *Journal of Bangladesh Academy of Sciences*, **35**, 187-195.
14. Hossain Enayet, Shamima Choudhury, M. A. Bhuiyan, K. H. Maria, M. H. Mesbah Ahmed, D. K. Saha, and M. A. Hakim, 2014. Magnetic Softening of Nanocrystalline Fe₇₄Cu_{1.5}Nb_{2.5}Si₁₂B₁₀ Alloy by the Process of Annealing. *Adv. Sci. Focus*, **2**, 12-16.
15. Cullity, B. D., 1959. Elements of X-ray diffraction, Addison-Wesley publishing company, Inc. London, England, 262.
16. Bozorth, R.M., 1968. Ferromagnetism, D. Van Nostrand-company, Inc. Princeton, New jersey, 74.
17. Manjura Hoque. S, M.A. Hakim, F. A. Khan, N. H. Nghi, 2007. Thermal behavior and magnetic properties of Co- and Cr-substituted Nd_{5.5}Fe₆₆Cr₅Co₅B_{18.5}. *Physica B*, **396**, 70-74.
18. Mariano, N.A., C.A.C.Souza, J.E.May. S.E.Kuri, 2003. Influence of Nb content on the corrosion resistance and saturation magnetic density of FeCuNbSiB alloys, *Materials Science and Engineering*, **354**, 1-5.
19. Saha, D. K. and M. A. Hakim, 2006. Crystallization Behavior of Fe_{73.5}Au₁Nb₃Si_{13.5}B₉ Amorphous- Nanocrystalline Soft Magnetic Alloy, *Journal of Bangladesh Academy of Sciences*, **30(2)**, 177-187.
20. Hakim, M. A., S. Manjura Haque, Bazlur Rashid, and Manjurul Haque, 2005. Effect of annealing time on structure and magnetic properties of amorphous nanocrystalline-FeCuNbSiB alloys. *Journal of Bangladesh Academy and Sciences*, **29(1)**, 117-126.
21. Manjura Hoque, S. F. A. Khan, M. A. Hakim, N. Chau, 2007. Ultra-soft magnetic properties of devitrified Fe_{75.5}Cu_{0.6}Nb_{2.4}Si₁₃B_{8.5} alloy. *Materials Chemistry and Physics*, **101**, 112-117.

