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IMPACT OF ANNEALING TIME ON THE FORMATION OF NANOCRYSTAL IN AMORPHOUS $FE_{75.5}SI_{13.5}CU_1NB_1B_9$ ALLOY AND THEIR ULTRA-SOFT MAGNETIC PROPERTIES

SAMIR KUMAR SAHA, KAZI HANIUM MARIA*, ENAYET HOSSAIN, MAHABUB ALAM BHUIYAN, D. K. SAHA[1] AND SHAMIMA CHOUDHURY

Department of Physics, University of Dhaka, Dhaka-1000, Bangladesh

ABSTRACT

To observe the impact of the annealing time on the alloy structure and ultra-soft magnetic properties of $Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$, the alloy was annealed in a controlled way in the temperature range 475 - 600°C for different annealing time from 5 to 30 min. Amorphosity of the ribbon and nanocrystalline state was evaluated by X-ray diffraction. Grain size and Si content increase with increasing annealing temperature and time; on the other hand lattice parameter decrease with increasing annealing temperature and time. The maximum permeability was observed at annealing temperature Ta = 525°C for 15 min, and thereafter it starts to decreases. Saturation magnetization increases with annealing temperature Ta for the samples and finally decreases during annealing at a temperature much higher than peak crystallization temperature. The results of the experimental observations are explained on the basis of existing theories of nanocrystalline amorphous metallic ribbons.

Key words: FINEMET, XRD, Grain size, Permeability, Saturation magnetization

INTRODUCTION

Since the first ever discovery by Yoshizawa *et al.* (1988), FINEMET have attracted much interest because of their excellent soft magnetic properties. The magnetic softness of FINEMET is based on the two-phase microstructure consisting of nanocrystalline ferromagnetic grains surrounded by a ferromagnetic amorphous matrix. FINEMET alloy is produced by crystallization of an amorphous *Fe–Si-B* alloy with small addition of Cu and Nb (Yoshizawa and Yamachi 1990, Noh *et al*. 1990). The existence and thermal stability of this microstructure are attributed to the presence of Cu and Nb in these alloys (Yoshizawa and Yamachi 1991). The perfect structure of the *Fe–Si–B–Cu–Nb* (FINEMET) alloys can be obtained by a controlled crystallization process, which involves annealing of the amorphous precursor at relatively low temperatures that are slightly below the crystallization temperature. This yields very fine nanocrystalline *αFe(Si)* precipitates dispersed in an amorphous magnetic matrix. FINEMET exhibits

*Corresponding author: < kazimaria@du.ac.bd>.
[1]Materials Science Division, Atomic Energy Centre, Dhaka-1000.

excellent permeability, a low saturation magnetostriction and a high saturation magnetization which finds use in electric power applications such as transformer cores and other inductive devices. These properties were reported to change upon annealing to pre-crystallization temperatures. The FeSiB alloy loses its soft magnetic properties when it is crystallized, but the soft magnetic properties of FINEMET alloys are significantly improved due to precipitation of the nanocrystalline phase. Therefore, the nucleation of nanocrystals in the amorphous matrix depends on the chemical composition and on the heat treatment conditions (Shiba *et al.* 2011)

The previous work (Shiba *et al.* 2012, Hossain *et al.* 2014, Hossain *et al.* 2016) mainly focused the magnetic softening observed in nanocrystalline phase but little attention was paid to the annealing time. Authors report the changes in magnetic properties with the microstructural evolution by studying several heat treatment conditions. The influences of annealing temperature and time on the microstructure of the nanocrystalline alloy $Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$ has been investigated in detail using the X-ray diffraction (XRD) method. Annealing temperature and annealing time dependence of initial permeability has been measured to observe extent of magnetic softness. The relationship between the initial permeability and the microstructure parameters of the nanocrystalline alloy was also discussed.

MATERIALS AND METHODS

Amorphous alloys in the form of ribbons have been prepared with the nominal composition $Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$ by rapid quenching method. The ribbons are on average 6 mm wide and 20 - 25 μm thick. The amorphosity of the ribbons has been confirmed by X-ray diffractometer (Phillips X' Pert Pro XRD) (PW 3040) with Cu-K_α radiation. Frequency dependence of complex initial permeability of the amorphous and annealed samples was measured in the frequency range of 1 kHz to 13 MHz using a HP4192A impedance analyzer. Temperature dependence of initial permeability of the as-cast and annealed ribbons is measured using a laboratory built furnace and Wayne Kerr 3255 B impedence analyzer. The magnetization measurements of the samples were done by a vibrating sample magnetometer (Model VSM-02, Hirstlab, UK) at room temperature as a function of field.

RESULTS AND DISCUSSION

Amorphosity and nanocrystalline states of the sample $Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$ have been studied by X-ray diffraction (XRD). In order to understand the impact of annealing, the samples were annealed at different temperatures from 475 to 650°C for different annealing time from 5 to 30 minutes. In Fig. 1a, the XRD spectra of as-cast and annealed at 475°C for 20 and 30 minutes have been presented. X-ray pattern of t_a = 30 minutes, clearly confirms the presence of crystalline phase identified as a bcc α-Fe(Si) solid solution developed in the amorphous matrix, whereas the amorphous state is retained having no crystalline peaks for t_a = 20 minutes. The samples annealed below 30 minutes showed the peak of a broader diffused pattern which were characteristics of amorphous material. These results are in good agreement with previous result (Shiba *et al.* 2012).

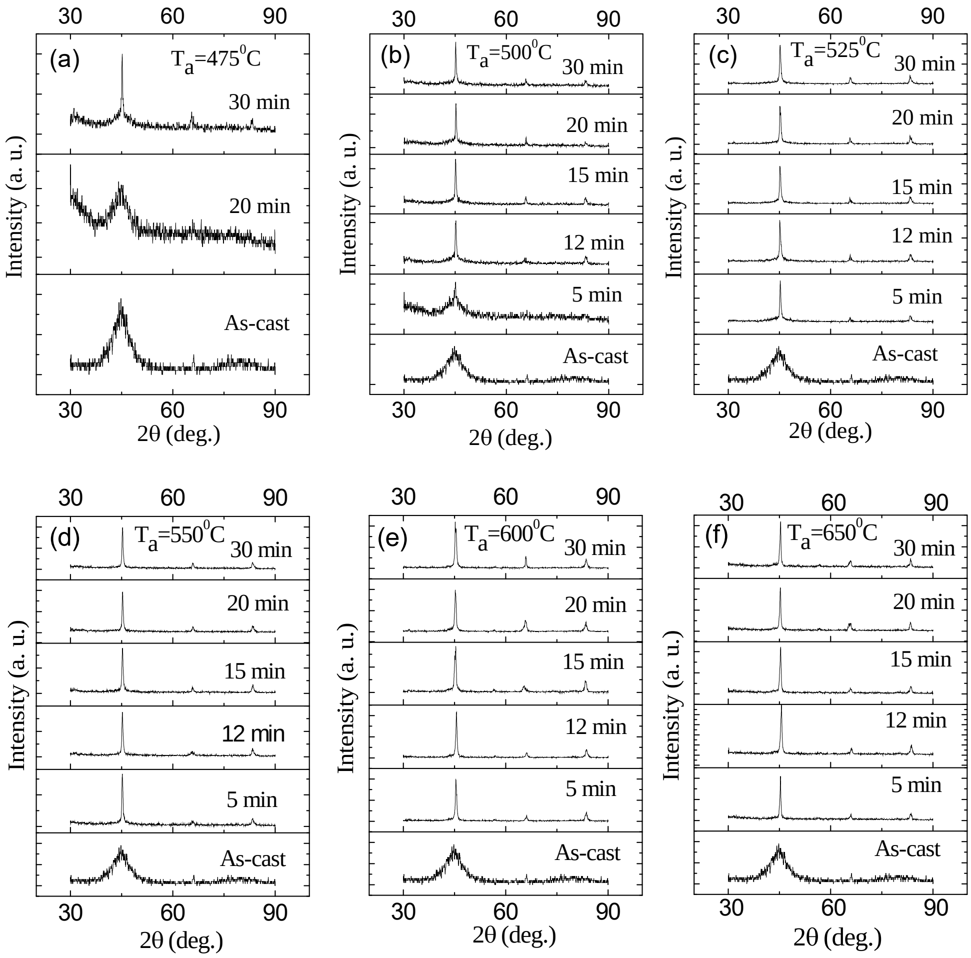

Fig. 1 (a-f). XRD patterns of $Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$ alloys for as-cast and heat- treated for 5, 12, 15, 20, 30 minutes at (a) 475°C, (b) 500°C, (c) 525°C, (d) 550°C, (e)600°C and (f) 650°C annealing temperature.

The XRD patterns for the sample annealed at 500 to 650°C for 5, 12, 15, 20, 30 minutes along with as- cast as shown in Fig. 1 (b-f). From Fig. 1(b), it was observed that no crystalline phase has been detected at T_a = 500°C for 5 minutes. On the other hand, crystalline phase appeared for t_a = 12 minutes or above. It was also observed that the maximum narrow peak intensity on (110) line at 2θ = 45.0934° for t_a = 30 minutes. The other two fundamental peaks corresponding to bcc α -Fe(Si) on (200) and (211) diffraction line at (2θ = 65.7649 and 83.2755), respectively have been identified but due to their low intensity they are not clearly visible in Fig. 1(b). In Fig. 1(c), it is noticed that there is a sharp crystalline peak at T_a = 525°C for t_a = 5 minutes. When the alloys are annealed at higher temperatures at 550, 600 and 650°C the peaks become sharper with higher intensity which have been shown in Fig. 1 (d), (e), (f), respectively. Therefore, it is apparent from the XRD pattern that the bcc Fe (Si) peaks become narrower and sharper with higher intensity with increasing annealing temperature and time. The crystallite sizes grow larger gradually with the increase of annealing conditions. It may be mentioned that no boride phase could be detected for the sample even annealed at T_a = 650°C. Generally boride phase are difficult to detect by X-ray as evidenced from numerous published research papers probably due to their small volume fraction.

Lattice parameter of an alloy composition was determined by the Debye- Scherrer method after extrapolation of the curve. Fig. 2(a) shows the variation of lattice parameter at different annealing temperature from 500 to 650°C for different annealing time 5, 12, 15, 20, 30 minutes. It was found that with the increase of annealing time and temperature, the lattice parameter decreased gradually. It means that the silicon content in α-Fe(Si) alloy increases with annealing time and temperature, since it is well known that the lattice parameter of bcc Fe(Si) alloys decreases with the increase of silicon content (Jing *et al*. 1996). Since the lattice parameters of these phases are significantly smaller than those of pure Fe (2.8664 Å), the values of lattice parameter, determined experimentally, were found to be in the ranges of 2.842 to 2.818.

Fig. 2(b-c) shows the variation of grain size and Si content of α-Fe(Si) nanograins for the corresponding sample. It was noticed that the grain size and Si content increased with annealing time which corresponded well with the reported results (Rubinstein *et al.* 2001, Herzer 1989). This can be explained that the element Si from the amorphous phase diffuses into α-Fe space lattice by diffusion during the crystallization process to form, $D_g = 79.5/\Delta\cos(\ldots)\theta$. Instrumental broadening of the system has determined from a θ - 2θ scan of standard Si. At 110 reflection’s position of the sample, the value of instrumental broadening was found to *α-Fe(Si)* nanograins which demonstrated that the crystallization behavior of FINEMET is a diffusion controlled process, where temperature and time are controlling parameters. Therefore, the longer annealing time results in more diffusion of Si enriching the Fe(Si) nanograins. It was also observed that the grain size and Si content at first increased gradually and then very slowly.

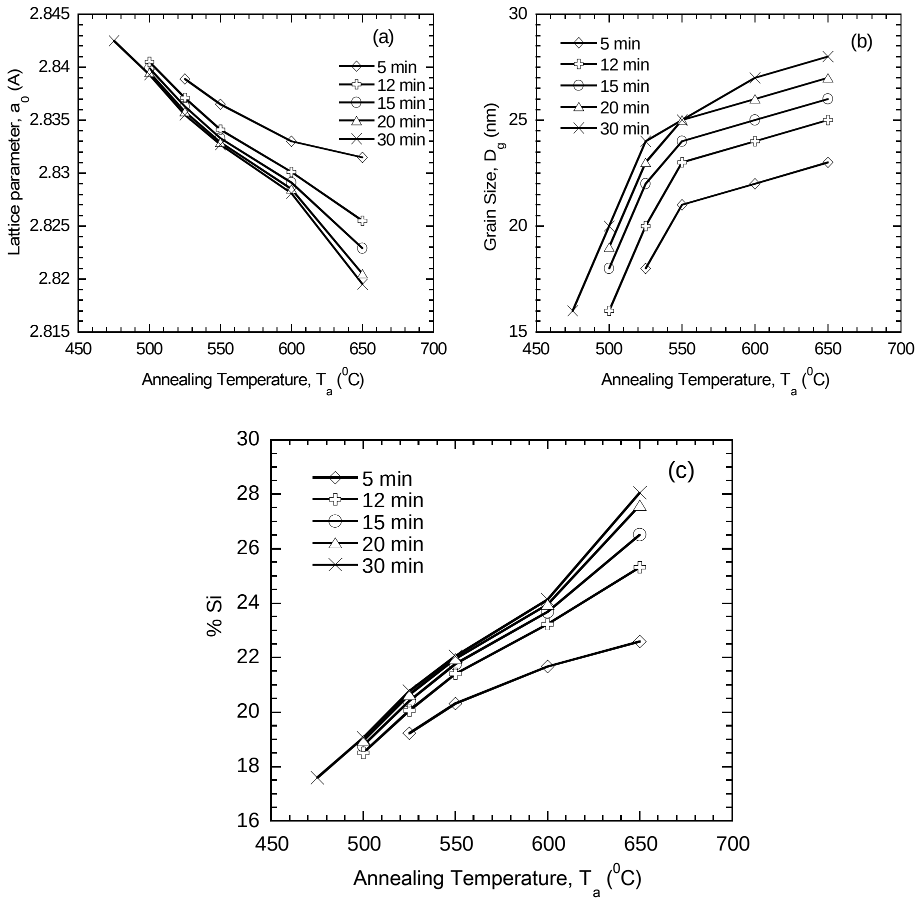

Fig. 2. Variation of (a) lattice parameter, (b) grain size and (c) Si content at different annealing temperature for different minutes for the nanocrystalline amorphous ribbon with composition $Fe_{75.5}Si_{13.}5Cu_1Nb_1B_9$.

In order to correlate the microstructural feature with soft magnetic properties of the alloys under study, initial magnetic permeability of the toroidal shaped samples annealed at different annealing conditions in very low field. The magnetic properties of the soft magnetic materials are mainly determined by the domain wall mobility especially in the range of reversible magnetization.

Fig. 3(a-f) shows the real part of the complex initial permeability as a function of frequency in the range of 1 to 500 KHz for the as-cast and annealed samples at different temperatures from 475 to 650°C for the various annealing temperatures from 5 to 30 minutes. It is found that the initial permeability of the as-cast sample is lower than the sample annealed above crystallization temperature. It may also be noted that at the crystallization temperature T_a = 475°C for the sample annealed at 5, 12, 15 and 20 minutes, the value of initial permeability is nearly equal to the as-cast sample.

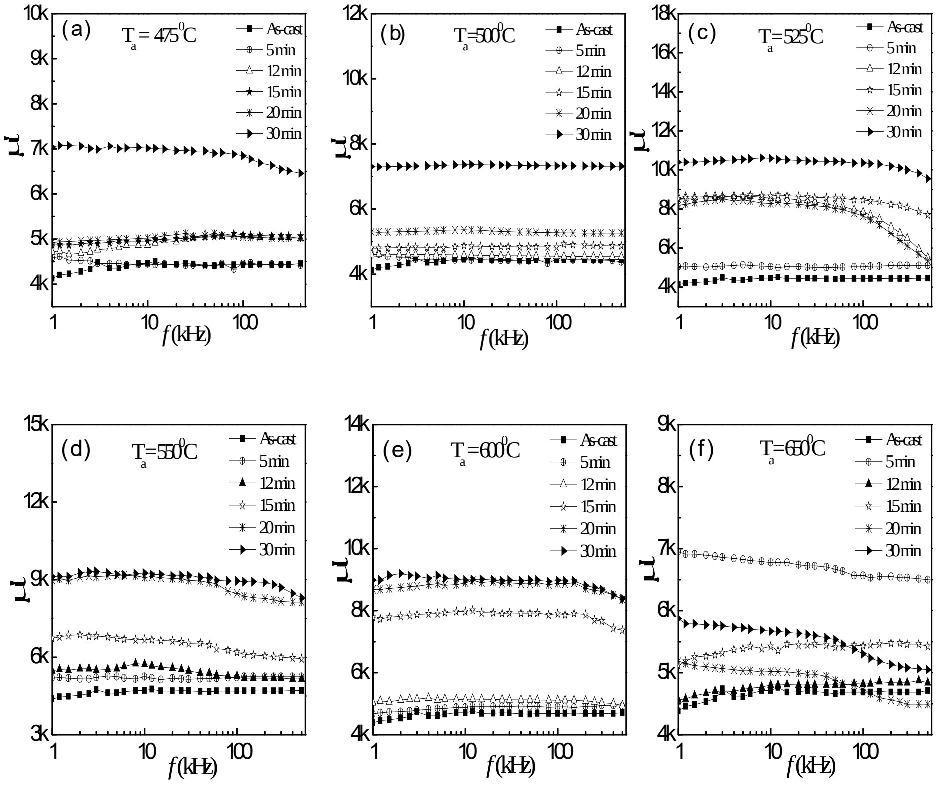

Fig. 3. Frequency dependence of real part of initial permeability, μ′ for different annealing time from 5 to 30 minutes at different annealing temperature (a) 475°C, (b) 500°C, (C) 525°C, (d) 550°C, (e) 600°C and (f) 650°C.

But when the sample annealed for the 30 minutes, a large value of initial permeability has been obtained. This is the time around which the initiation of crystallization takes place as found by the XRD results as shown in Fig. 1(a). In Fig. 3(b) the low frequency value of μ′ generally increases with the increase of annealing time at T_a = 500°C as the crystallization initiation at this annealing temperature. However, no critical frequency has been found within 500 KHz frequency range. By studying various paper about this sample, it is found that the critical frequency of this sample at T_a = 500°C above 500 KHz (Shiba *et al.* 2011).

The value of μ′ at the frequency of 1 KHz generally increases with the increase of annealing temperature and reaches maximum value at temperature T_a = 525°C as shown in Fig. 4. When the temperature is further increased beyond 525°C then the initial permeability starts to decrease rapidly. The decrease of real part of the complex initial permeability is due to the formation of Fe-B phase in the amorphous matrix due to its high magnetocrystalline anisotrophy (Hakim and Manjura 2004).

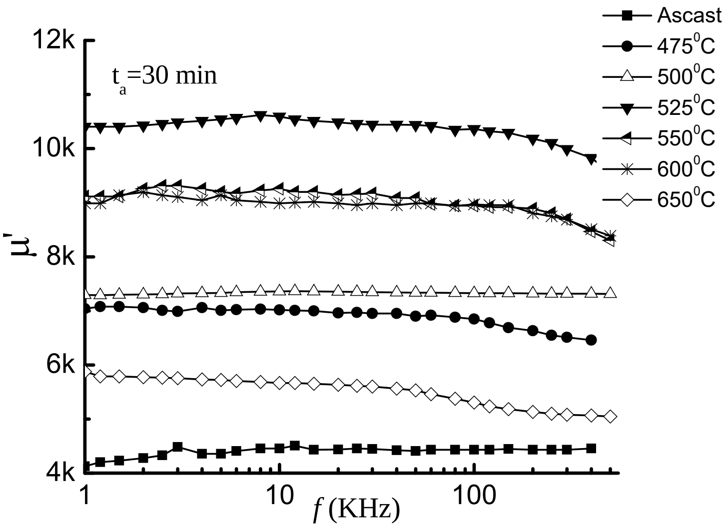

Fig. 4. Frequency dependence of real part of initial permeability, μ′ at different annealing temperature from 475 to 650°C for 30 minutes.

The field dependence of magnetization for amorphous as-cast and annealed samples at different annealing time for different annealing temperature has been measured by using a vibrating sample magnetometer. Previous studies (Shiba *et al.* 2012) have shown that the magnetization of the samples is saturated at the amorphous and annealed states

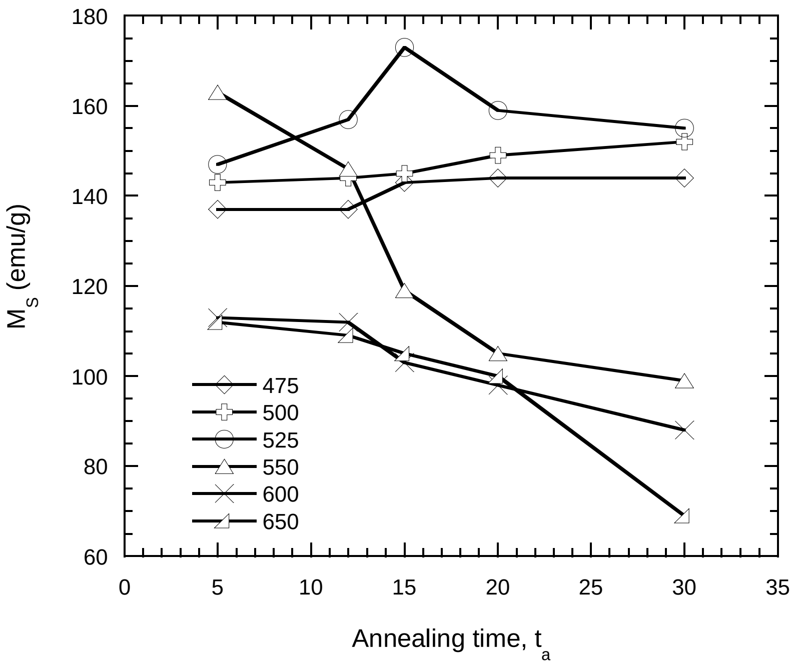

Fig. 5. Saturation magnetization vs annealing time at different annealing temperature.

within an applied field of 2000 Oe. In this report, the effect of annealing time on the magnetization of the annealed samples has been shown in Fig. 5. It is found that at lower annealing temperature 475 and 500°C, saturation magnetization increase with increasing annealing time. This increase may be attributed to irreversible structural relaxation, increase of the packing density of atoms by annealing out micro-voids and changing the degree of chemical disorder (Lovas *et al.* 2000). In case of T_a = 525°C, the maximum saturation magnetization has found for the annealing time 15 mins and then saturation magnetization starts to decrease with time. It may be attributed to the enrichment of the residual amorphous phase with Nb weakens the coupling between ferro-magnetic nanograins which in turn reduces saturation magnetization (Berkowitz *et al.* 1981). Also the role of Si diffusion into Fe (Si) nanograins and these local environments also may have effect in decreasing M_S. The decrease of M_S for the sample higher annealing time on ordering of Fe_3Si nanograin cannot be ruled out.

A linear decrease of saturation magnetization with increasing annealing time has been observed at higher annealing temperature 550 to 650°C. XRD results confirmed that grain size of the nanograins increased with the increase of annealing time. It can be conjectured that this increased grain size causes weak magnetic coupling between the nanograins. As a result, M_S decreases with the increased annealing time.

CONCLUSION

On the basis of the above results and discussion, conclusions can be drawn that the annealing time has great impact on the formation of nanocrystals and evolution of soft magnetic properties of $Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$. Lattice parameter decreases with increasing annealing time whereas grain size and Si content increase both with annealing time and annealing temperature. Above the crystallization temperature, frequency dependent permeability and saturation magnetization are found to be decreased with the increase of annealing time.

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