Effect of structural parameters on variation of microstructural and magnetic properties of nanocrystalline alloy of Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{17.5}$B$_5$

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Amorphous ribbons of Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{17.5}$B$_5$ alloy have been annealed in the temperature range 475-700°C for X-ray diffraction (XRD) patterns. Crystallization induced by heat treatment resulted in the formation of a Fe-Si phase. The phase formed by primary crystallization has been found to be Fe-Si solid solution with a composition corresponding to disordered Fe-Si. Secondary crystallization of the Fe$_3$B and Fe$_2$B phases arises with the individual branches at the interfaces of the closely spaced crystals at the temperature 680°C, the spacing of such crystals was of the order of nanometer. Samples have been annealed in a controlled way in the temperature range 510-700°C with an interval of 10°C to 30°C for 1 h in order to study the effect of structural parameters of the nanocrystalline Fe(Si) grains on the variation of microstructural and soft magnetic properties. Temperature and frequency dependence of initial permeability of amorphous and devitrified toroid shaped samples have been measured. The permeability values showed little change as annealing time. Enrichment of Curie temperature has been observed for amorphous alloy due to the irreversible structural relaxation. The microstructures of the annealed samples are characterized as solid solutions of bcc Fe(Si) crystallites with grain sizes 5-19 nm and an abrupt increase 53 nm at 700°C. Silicon contents in the nanocrystalline phases determined from the lattice parameters are 12.67 to 15.48 at.%. The best magnetic properties have been observed when the annealing temperature is close to 575°C. Temperature dependence of real part of initial permeability of the annealed samples between the annealing temperature of 550°C and 575°C exhibits superparamagnetic/superferromagnetic behaviour at \( T > T_{c}^{am} \).

**Keywords:** Amorphous alloy, Finemet, Magnetic properties, Nanocrystalline alloy, Superferromagnetism

1 Introduction

A new class of ferromagnetic materials with nanocrystalline structure revealing excellent soft magnetic properties have been discovered by Yoshizawa et al. through controlled crystallization of Fe-Si-B amorphous alloys with the addition of copper and niobium. Fe-Si-B alloys with addition of Cu and Nb have been studied and used for many years since they exhibits good soft magnetic properties, several studies of the crystallization processes, thermal properties, microstructural and magnetic properties have been reported. Most reports focused on alloys with 5-10 at.% Si and 75-78 at.% Fe become this composition range used to have the greatest technological significance. The most frequently studied composition based on Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ known as Finemet more attention has been paid to the Fe-Si-B alloy with more than 10 at.% Si, with or without other alloying additions. The theoretical understanding of the nanometric grain with magnetic softness has been consolidated in the light of Random Anisotropy Model (RAM) proposed by Alben et al.

The vital role of exchange interaction is clearly evident when the measuring temperature exceeds the Curie temperature of the amorphous matrix \( (T > T_{c}^{am}) \) in the temperature dependence of permeability of these biphase alloys. For \( (T > T_{c}^{am}) \), the intergranular amorphous matrix becomes paramagnetic within which aFe(Si) ferromagnetic nanograins are embedded. The exchange coupling between the nanograins largely ceases to exist. Thus, for the measuring temperature \( (T > T_{c}^{am}) \), the initial permeability drops down by almost two order of magnitude and the coercivity increase correspondingly. For the measuring temperature \( (T > T_{c}^{am}) \), another interesting behaviour of
superparamagnetism/superferromagnetism can be studied. Gradual increase of annealing temperature increases the volume fractions of crystallites embedded in a still amorphous matrix. If the size of the nanocrystals is small enough and the intergranular matrix is sufficiently thick to minimize the magnetic interactions between them, then superparamagnetic behaviour of the nanocrystalline particles is expected.

In the present work, a Fe matrix is sufficiently thick to minimize the magnetic superparamagnetic behaviour of the nanocrystalline particles is expected.

In the present work, a Fe\textsubscript{73.5}Cu\textsubscript{7.5}Nb\textsubscript{7}Si\textsubscript{17.5}B\textsubscript{5} amorphous alloy was selected based on the composition of the Finemet alloy and the aim is to study the crystallization behaviour of the composition and its effect on the variation of microstructural and magnetic properties by increasing the glass-forming element Si and decreasing the amount of B.

By means of XRD, the phase formation was identified and then microstructural evolution during crystallization was also calculated. The magnetic properties were measured by Vibrating Sample Magnetometer (VSM). Then, by combining these results, microstructural and magnetic properties of Fe\textsubscript{73.5}Cu\textsubscript{7.5}Nb\textsubscript{7}Si\textsubscript{17.5}B\textsubscript{5} alloy was elucidated.

2 Experimental Details

Amorphous ribbons (10 mm width and 20 µm thickness) of nominal composition Fe\textsubscript{73.5}Cu\textsubscript{7.5}Nb\textsubscript{7}Si\textsubscript{17.5}B\textsubscript{5} have been prepared by melt-spinning method in single roller equipment at the Laboratory of Amorphous Materials in Hanoi University of Technology. The purity of the material is Fe (99.98%), Cu (99+ %), Nb (99.8%), B (99.5%) and Si (99.9%) obtained from Johnson Matthey (Alfa Aesar Inc.). The amorphousity of the ribbons has been confirmed by XRD experiment carried out in a Philips X-pert Pro X-ray diffractometer with CuK\textalpha{} radiation.

The samples were annealed at 12 different temperatures for as cast and from 200°C to 650°C to study the annealing effect on permeability. Temperature dependence of initial permeability of the as cast and annealed ribbons is measured using a laboratory built furnace and Wayne Kerr 3255 B impedance analyzer with continuous heating rate of ~5°C / min with very low applied ac field of ~10\textsuperscript{-3} Oe from room temperature to above 650°C. From this measurement, Curie temperature (T\textsubscript{c}), of the as cast amorphous phase has been determined along with the study of superparamagnetic/superferromagnetic behaviour of nanocrystalline samples. The average grain size of the crystallites α-Fe(Si) were determined by Scherrer’s method after correction for instrumental boarding. Frequency dependence of complex initial permeability of the amorphous and the annealed samples was measured in the frequency range 1 Hz-1MHz. Saturation magnetization has been performed by VSM at room temperature.

3 Results

XRD patterns of as cast and annealing ribbons samples in the temperature range between 475°C-700°C have been presented in Figs 1-3. The as cast sample is in the amorphous state. The phase formed after the Fe\textsubscript{73.5}Cu\textsubscript{7.5}Nb\textsubscript{7}Si\textsubscript{17.5}B\textsubscript{5} alloy was heat treated at 580°C for 1 h and studied by XRD (Fig. 2) which indicated that Fe-Si phase was the dominant phase as the heat treatment temperature was increased. The {510} or Fe\textsubscript{2}B phase did not appear until heat treatment temperature 680°C. These results showed that Fe-Si phase formed during the first crystallization even at 580°C while secondary crystallization products of the {510} or Fe\textsubscript{2}B phase did not form until 680°C.

The lattice parameter of various annealed samples in the temperature range 520-700°C is shown in Fig. 4. The silicon content of α-Fe(Si) nanograins has been determined from the established quantitative relationship\textsuperscript{17} and is shown in Fig. 5. When the sample is annealed above the crystallization temperature, nanocrystalline grain of α-Fe(Si) is formed from amorphous precursor. In Fig. 6, the mean grain size of the nanograins determined from the X-ray fundamental line (110) using the Scherrer’s formula is presented. The grain size increases gradually up to 510°C and then attains a limiting value of 4 to 19 nm until 680°C. An abrupt increase of grain size above 680°C is noticed attaining a value of 53 nm at 700°C.

In Fig. 7, the real part of the complex initial permeability (µ′) up to f = 1 MHz has been presented for as cast and annealed samples. The curve shows that µ′ increase with the increase of annealing temperature and it drops at critical frequencies rapidly. In Fig. 8, µ′ has been presented as a function of annealing temperature (T\textsubscript{a}) at a fixed frequency of 1 kHz. The curve reveals initial permeability increase below the onset of crystallization (475°C in Fig. 1) and drops to a lower value at 525°C.

In Fig. 9, the temperature dependence of µ′ of the as cast amorphous ribbon and the samples annealed in the temperature range 450-525°C at the interval of 25°C has been presented. For the samples annealed in
the temperature range 450-500°C, the permeability passes through a maximum just before a sharp fall to near zero and the sample annealed at 525°C the sharpness of the fall is relatively smeared out.

In Fig. 10, the variation of $\mu'$ with temperature for the toroid samples annealed in the temperature range 550-600°C has been presented. In Fig. 11, the variation of $\mu'$ with temperature is shown for samples annealed at 625°C and 650°C.

4 Discussion
4.1 Crystallization process and the variation of microstructure of the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{17.5}$B$_5$ alloy

XRD spectra of Fig. 1 clearly confirm that the as cast sample is in the amorphous state of the quenched sample with a diffused broad peak. Upon annealing at 580°C for 1 h, a new crystalline phase identified as solid solution of bcc Fe (Si) forms for lower value of (20) with 100% peak intensity on (110) line at 45.19°.
The other two fundamental peaks correspond to \textit{bcc} \(\alpha\)-Fe (Si) on (200) and (211) diffraction line at \((2\theta = 65.65^\circ\) and \(83.43^\circ\)), respectively, have been identified but due to their low intensity they are not clearly visible in Fig. 2. An extra four peaks at \((2\theta = 43.33^\circ, 50.35^\circ, 41.47^\circ\) and \(48.63^\circ\)) of \{510\}, \{531\}, \{420\} and \{440\}, respectively have been observed for the sample annealed for 680°C and 700°C in Fig. 3. Combining the XRD results (Figs 1-3), the phases formed in the secondary crystallization products are not only Fe-Si compounds such as Fe\(_3\)B phase, but also the Fe-Si phase. The Fe-Si phase was indexed as belonging to B2 ordered structure, this crystal structure of the Fe-Si phase has not been previously reported in the Fe-Si-B amorphous system\(^7\). As crystallization proceeded, the volume
fraction of the products of secondary crystallization with the striped morphology increased at the expense of the amorphous matrix.

The lattice parameters of various annealed samples in the temperature range 520 and 700°C are shown in Fig. 4. With the increase of annealing temperature, lattice parameter decreases up to $T_a = 620°C$. For the annealing temperature of 650°C and above, increase of lattice parameter is observed. It is observed that the lattice parameter slightly decreases with annealing time. It means that the silicon content in $\alpha$-Fe(Si) alloy increases with annealing time since it is well known that the lattice parameter of $bcc \alpha$-Fe(Si) alloys decreases with the increases of silicon content $^{18,19}$. Since these lattice parameter of these phases are significantly smaller than those of pure $\alpha$-Fe (2.8664 Å), it can be speculated that the metalloid elements of alloy is dissolved in the $bcc$ Fe.

Fig. 3—XRD patterns of Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{17.5}$B$_5$ alloy heat treated at 680 and 700°C.
phase. But the metalloid element B is practically insoluble in $\alpha$-Fe ($< 0.01$ at. %) and the solubilities of Cu and Nb are low ($< 0.2$ at. % Cu, $< 0.1$ at. % Nb only above 550°C). Hence, the nanocrystalline phase consists essentially of Fe and Si.

Silicon content of $\alpha$-Fe (Si) nanograins have been determined and shown in Fig. 5. A gradual increase of Si content in nanocrystalline phase with increasing annealing time is observed. This can be explained by the fact that the element Si from the amorphous phase diffuses into $\alpha$-Fe space lattice by diffusion during the crystallization process to form $\alpha$-Fe(Si) nanograins. This means that the crystallization behaviour of this material is a diffusion controlled process with temperature and time as controlling parameter. So the longer annealing time results in more diffusion of Si enriching the Fe(Si) nanograins. The grain size increases gradually up to 650°C and then attains a limiting value of 4.5 to 13.5 nm until 650°C. An abrupt increase of grain size above 650°C is noticed, attaining a value of 19 and 53.85 nm at 680°C and 700°C, respectively. It is interesting to note that the

![Fig. 4—Variation of lattice parameter ($a$) with the annealing temperature ($T_a$)](image)

![Fig. 5—Variation of silicon content with annealing temperature ($T_a$)](image)
grain sizes remain almost unaffected with longer annealing time attaining the limiting value of 13 nm (Fig. 6). This value corresponds well with the results of Robinstein et al.\textsuperscript{21}, who observed that the grain sizes were nearly constant around 13 nm until 600°C beyond which they grow rapidly. This nanometric microstructure is achieved by the combined action of Cu and Nb. Cu which insoluble in $\alpha$-Fe, segregates prior to or at the very beginning of nanocrystallization, forming Cu-rich clusters and the nucleation of Fe(Si) grains in thought to be multiplied by clustering. On the other hand, the rejection of Nb at the crystal interface hinders the grain growth due to their higher crystallization temperature.

4.2 Magnetic properties

Magnetic initial permeability of the toroidal shaped samplesannealed at different temperatures has been measured with very low field, in order to correlate the microstructural features on the soft magnetic properties of the nominal alloy. The magnetic properties of the soft magnetic materials are mainly determined by the domain wall mobility especially in the range of reversible magnetization.

In Fig. 7, $\mu'$ up to $f = 1000$ kHz has been presented for as cast and annealed samples. The general characteristic of the curves is that $\mu'$ remains fairly constant up to some critical frequency and then $\mu'$ drops rapidly due to the increase of the loss component of complex permeability. The low frequency value of $\mu'$ generally increases with the increase of annealing temperature while the critical frequency decreases. This trend of increase of low frequency permeability is observed up to the annealing temperature of 575°C. For the annealing temperature of 500°C, the low frequency permeability decreases and for 625°C, it drops to a very low value.

In Fig. 8, $\mu'$ has been presented as a function of annealing temperature $T_a$ at a fixed frequency of 1 kHz. The curve reveals itself strong dependence of initial permeability on annealing temperature. When annealed at temperatures below the onset of

Fig. 6—Variation of grain size ($D$) with annealing temperature ($T_a$)

Fig. 7—Frequency dependence of permeability ($\mu'$) at different annealing temperatures
crystallization, an increase of initial permeability with annealing temperature was observed due to irreversible structural relaxation of the amorphous matrix, i.e., stress relief, increase of packing density by annealing out micro-voids and changing the degree of chemical disorder. At the annealing temperature of 525°C, the permeability drops to a lower value. This is the temperature around which initiation of crystallization takes place. The decrease of permeability may be attributed due to the new stresses develop in the amorphous matrix by the growing crystallites, which act as pinning centers for the domain walls constraining the domain wall mobility as well as weak intergrain magnetic coupling since the growing crystallites are far apart from each other representing small volume fraction that cannot be exchange coupled and the anisotropy cannot be averaged. Further, the increase of annealing temperature leads to the increase of permeability due to the increased volume fraction of $\mu$-Fe(Si) nanograins coupled via exchange interaction resulting in a reduction of anisotropy energy. An enhancement of initial permeability by two orders of magnitude was observed for the annealing temperature of 575°C.

For the annealing temperature above 575°C, $\mu'$ drops to lower value radically. The probable reason might be the evolution of boride phase (Fig. 2) and non-magnetic $fcc$ Cu. This leads to the increase of magnetocrystalline anisotropy to a high value, which essentially reduces the local exchange correlation length weakening the intergranular magnetic coupling as a result of which magnetic hardening takes place.

In Fig. 9, the samples annealed in the temperature range 450-525°C permeability pass through a maximum just before a sharp fall to near zero with the manifestation of Hopkinson effect characterizing the ferro-paramagnetic transition of the amorphous phase. However, for the sample annealed at 525°C, the sharpness of the fall is relatively smeared out which might be an indication of the initiation of nucleation since no crystalline phase could be detected for this annealing temperature by XRD (Fig. 1). The accurate determination of $T_c$ of the amorphous materials is really difficult due to irreversible components of the structural relaxation like long-range internal stress, topological and chemical short-range order. This structural relaxation without destroying the amorphous state may influence $T_c$. Therefore, during
the measurement of \( T_c \) the heating rate should be adjusted in such a way that no substantial relaxation takes place. However, the Curie temperature estimated from the curves presented in Fig. 9 for the as cast and annealed samples in the amorphous state has been given in Table 1.

It can be observed from Fig. 10, as the annealing temperature is increased above the crystallization temperature, the sharpness of the fall to lower values of permeability is progressively smeared out with the appearance of a tail in the high temperature region. These results are in good agreement with those previously reported for the Finemet composition \(^{17}\). Curie temperature of residual amorphous matrix determined from the derivative of \( \mu' \) versus \( T \) curves has been presented in Table 1.

From Table 1, it can be observed that the Curie temperature of the as cast amorphous ribbons is 335°C. The Curie temperature improves when the sample is annealed in the temperature range 450-500°C. From XRD, no crystalline phase was observed up to the annealing temperature of 500°C. Enrichment of Curie temperature occurs because of irreversible structural relaxation. Further, from the analysis of the Mössbauer spectra for the quenched and annealed samples below the crystallization temperature it has been observed that this treatment leads to the increase in packing density of atoms\(^{22}\). Increase in packing density of atoms might have significant contribution in the enrichment of Curie temperature in the amorphous state. Above the crystallization temperature, Curie temperature of the amorphous matrix decreases significantly. The probable reason of decreasing the Curie temperature of the amorphous phase when annealed at and above the crystallization temperature is that the amorphous matrix is depleted with iron and the relative amount of

<table>
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<tr>
<th>Annealing temperature, ( T_a ) (°C)</th>
<th>Curie temperature, ( T_{c^{am}} ) (°C)</th>
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<tbody>
<tr>
<td>as cast</td>
<td>335</td>
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<tr>
<td>450</td>
<td>345</td>
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Table 1—Relation of annealing temperature (\( T_a \)) and Curie temperature (\( T_{c^{am}} \))
$T_a$ in the amorphous matrix increases, which weakens the exchange interaction resulting in a decrease of Curie temperature of the amorphous matrix.

At higher measuring temperatures above $T_{c}^{am}$, the superparamagnetic and superferromagnetic behaviour is observed depending on the size and volumetric fraction of crystalline phases and the separation between the crystallites, which demonstrated by Franco et al\textsuperscript{17}. The practical requisite for observing superparamagnetic relaxation in the nanocrystalline alloys is the absence of interactions between nanograins in the residual amorphous matrix. Superparamagnetic behaviour is evident from the temperature dependence of the initial permeability for the sample annealed at 550°C and is shown in Fig. 10. For this sample, the exchange interaction between the nanograins mainly occurs via sufficiently thick interfacial amorphous matrix in which the nanocrystallites are discrete. When the measuring temperature approaches the Curie temperature of the intergranular amorphous phase, which is much lower than that of nanograins (~600°C), the exchange coupling between the crystallites is largely reduced. As a consequence, the initial permeability drops down to a very low value.

From the results of the temperature dependence of permeability for samples annealed above 550°C, the grain coupling is largely but not completely interrupted above $T_{c}^{am}$ and still persists to higher value of permeability compared to the sample annealed at 550°C. A system in which the magnetic coupling between particles is significant and prevents superparamagnetic relaxations, has been termed superferromagnetism by Morup\textsuperscript{23}. The precise coupling mechanism for this type of behavior at $T > T_{c}^{am}$ may be explained in terms of exchange penetration through the thin, paramagnetic intergranular layer and/or dipolar interactions\textsuperscript{24}.

From Fig. 8, it can be observed that the value of $\mu'$ has dropped to a very low value for the annealing temperature of 625°C. It has been reported earlier that this fall of $\mu'$ to a very low value might occur due to the evolution of boride phase at higher $T_a$ of 600°C. In our experiment, the boride phase has been detected by XRD (Fig. 3). Since the anisotropy constant $K_1$ of Fe$_3$B (430 kJ/m$^3$) is five order of magnitude higher than the average anisotropy $<K>$ of $\alpha$-Fe(Si) nanograins (4 J/m$^3$), minor evolution of Fe$_3$B phase can cause significant damage to exchange interaction\textsuperscript{25}.

5 Conclusions

Based on the results obtained by means of XRD and VSM, the following conclusion for the crystallization behaviour and magnetic properties of the Fe$_{73.5}$Cu$_3$Nb$_3$Si$_{17.5}$B$_3$ alloy can be drawn:

1 From XRD measurements, the crystallization induced by heat treatment resulted in the formation of a Fe-Si phase. The phase formed by primary crystallization has been found to be Fe-Si solid solution with a composition corresponding to disordered Fe-Si. Secondary crystallization of the Fe$_3$B and Fe$_2$B phases arises with the individual branches at the interfaces of the closely spaced crystals at the temperature 680°C, the spacing of such crystals was of the order of nanometer.

2 Isothermal annealing of Fe$_{73.5}$Cu$_3$Nb$_3$Si$_{17.5}$B$_3$ amorphous alloy leads to improvement of soft magnetic properties. The permeability values showed little change as annealing time. At lower annealing temperature, the enhancement of permeability takes place due to the structural relaxation. The best magnetic properties have been observed when the annealing temperature is close to 575°C. Curie temperature of the as cast amorphous ribbon is 335°C. The enrichment of Curie temperature was observed for samples annealed below the crystallization temperature due to structural relaxation. Curie temperature of the interfacial amorphous phase has decreased for samples annealed above the crystallization temperature due to the depletion of Fe and increase of relative amount of $T_a$ in the residual amorphous phase. Temperature dependence of real part of initial permeability of the annealed samples between the annealing temperature of 550°C and 575°C exhibits superparamagnetic/superferromagnetic behaviour at $T > T_{c}^{am}$.

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References