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ELECTRICAL, MAGNETIC AND ELECTROCHEMICAL BEHAVIOUR OF NANOCRYSTALLINE $Fe_{70.5}Nb_{4.5}Cu_1Si_{16}B_8$ ALLOY

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The electrical, magnetic and electrochemical behaviour of $Fe_{70.5}Nb_{4.5}Cu_1Si_{16}B_8$ has been studied in the as-received and heat treated conditions. The as-received material was amorphous which crystallized in two different stages at 780K and 940K when heated continuously. At the primary crystallization stage, nanometre sized grain of ordered $Fe_{80}Si_{20}$ phase was formed. The superior soft magnetic properties were achieved after primary crystallization which were attributed to the averaging out of magnetocrystalline anisotropy due to the nanocrystalline structure and the reduction of magnetoelastic anisotropy energy due to the negative magnetostrictive nature of $Fe_{80}Si_{20}$ phase and positive magnetostrictive value of the rest amorphous phase. After primary crystallization spontaneous passivating nature of the alloy is also observed in electrochemical study.

INTRODUCTION

In search of materials having high saturation induction and excellent soft magnetic properties, a new generation of magnetic materials has been discovered by the addition of small amount of Nb and Cu in Fe-Si-B glassy system [1]. The glassy FeNbCuSiB alloy transforms to nanocrystalline grain of about 10 nm in course of annealing above the crystallization temperature. The nanostructured alloys have excellent soft magnetic properties combined with rather a high saturation flux density (B_s) about 1.2 to 1.3 T. In the present work crystallization, magnetic and electrochemical behaviour of $Fe_{70.5}Nb_{4.5}Cu_1Si_{16}B_8$ alloy have been studied.

EXPERIMENTAL

The $Fe_{70.5}Nb_{4.5}Cu_1Si_{16}B_8$ alloy prepared by melt spinning technique in the form of ribbon of 25 μm thin was used for the present study. Crystallization behaviour of the alloy was determined using Scanning Thermal Electrical Resistivity (STER) and Differential Scanning Calorimetry (DSC) techniques. STER measurement was carried out with 5 mA current and 5K/min scanning rate in a vacuum furnace. DSC was conducted at different scanning rate in argon atmosphere using Park-in Elmer DSC-7 apparatus.

Magnetic parameters such as coercivity and ac susceptibility were measured after annealing the samples in vacuum at different temperatures for 30 minutes. Coercivity was measured at a quasi-dc magnetic field and ac susceptibility was measured using Lock-in amplifier (PARC-5209) at a frequency of 5 kHz.

The electrochemical polarization test was carried out with EG & G PARC galvanostat/ potentiostat (Model 273A) using 0.1N Na_2SO_4 solution. In the electrochemical study, a platinum rod counter electrode and standard calomel reference electrode (SCE) have been used.

RESULTS

The temperature variation of resistivity normalized with room temperature as-received value is shown in Fig.1. The slope of the curve changes at different characteristic temperatures. The alloy is crystallized in two stages at 780K and 940K. X-ray diffractograms(Fig. 2) show that the ordered $Fe_{80}Si_{20}$ phase is formed at the primary crystallization temperature. At higher

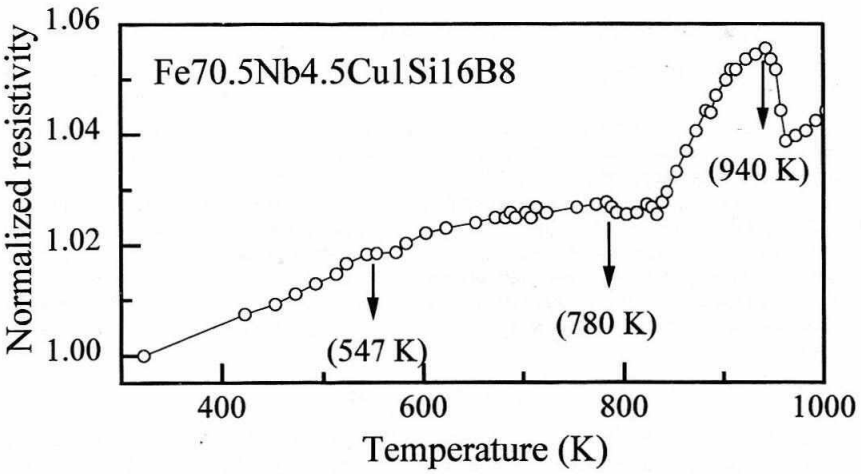

Fig.1:Temperature variation of resistivity showing different characteristic temperature

crystallization temperature. At higher temperature Nb and B rich phases are formed. Fig. 3 shows the occurrence of exothermic peak at the primary crystallization temperature which shifts toward the high temperature side with the increase of scanning rate. The activation energy (E_a) for the formation of ordered $Fe_{80}Si_{20}$ phase has been calculated from the values of peak temperature (T_p) of the transformation at different scanning rate (Φ) using Kissinger's relation[2]

$$\frac{d(\ln(\frac{\phi}{T_p^2}))}{d(\frac{1}{T_p})} = -\frac{E_a}{R} \qquad (1)$$

where R is a gas constant. The activation energy for the formation of ordered $Fe_{80}Si_{20}$ phase is found to be 58kCal/mole as calculated from eq. (1).

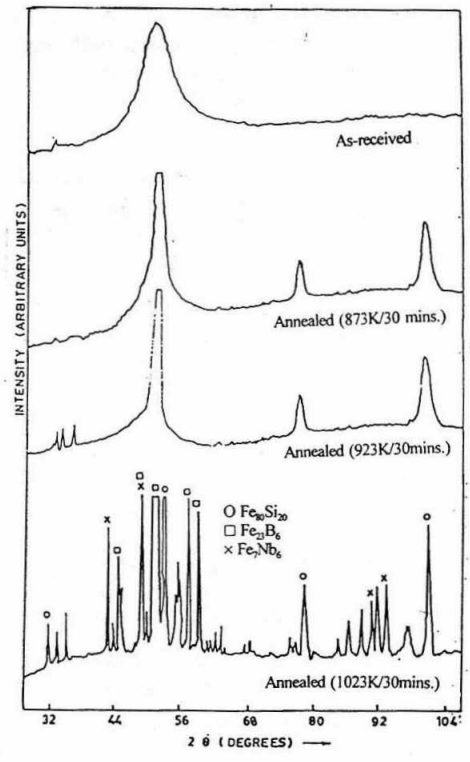

Fig. 2: X-ray diffractograms of as-received and different annealed samples showing the formation of different crystallized phases after annealing

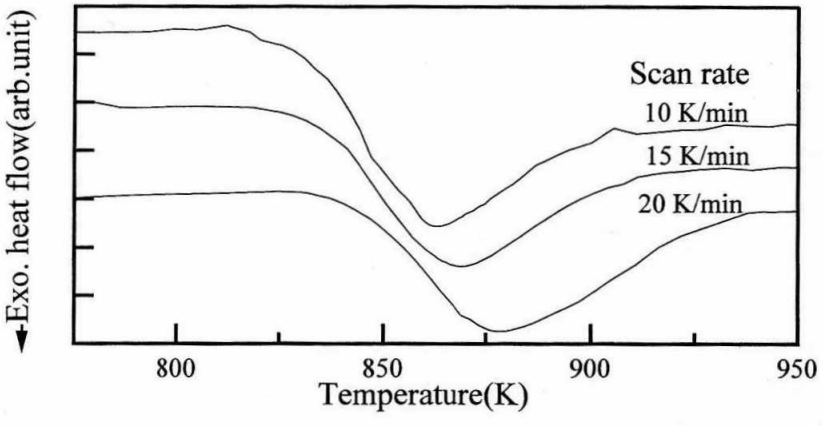

Fig. 3: DSC plot at different scanning rates

Fig. 4 shows the magnetic behaviour of different annealed samples. It is observed that coercivity (H_c) decreases and ac susceptibility increases with annealing temperature up to 850K above which a rapid increase in coercivity and decrease in susceptibility is found. The value of the coercivity and susceptibility for the alloy annealed at 850K become 2.5A/m and $60X10^3$ respectively.

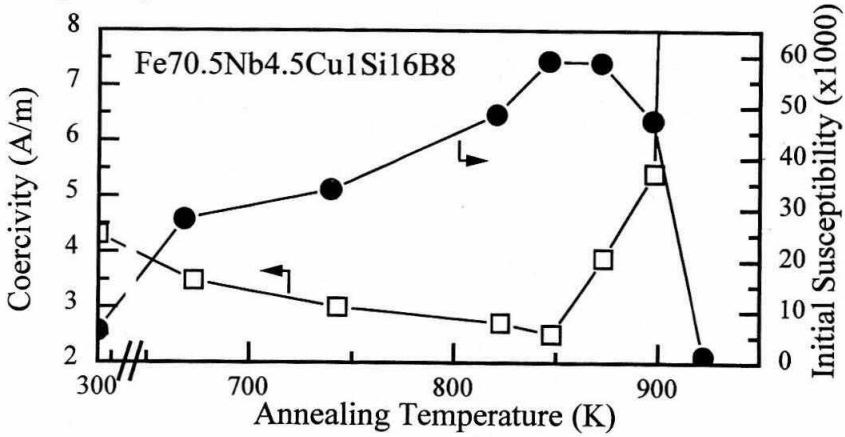

Fig. 4: Variation of coercivity and initial susceptibility with annealing temperatures

The result of the electrochemical polarization experiment for as-received and annealed samples is shown in Fig.5 In the as-received state the alloy is passive. It becomes spontaneously passive at the primary crystallization stage whereas it looses passivating tendency when annealed at 1023 K.

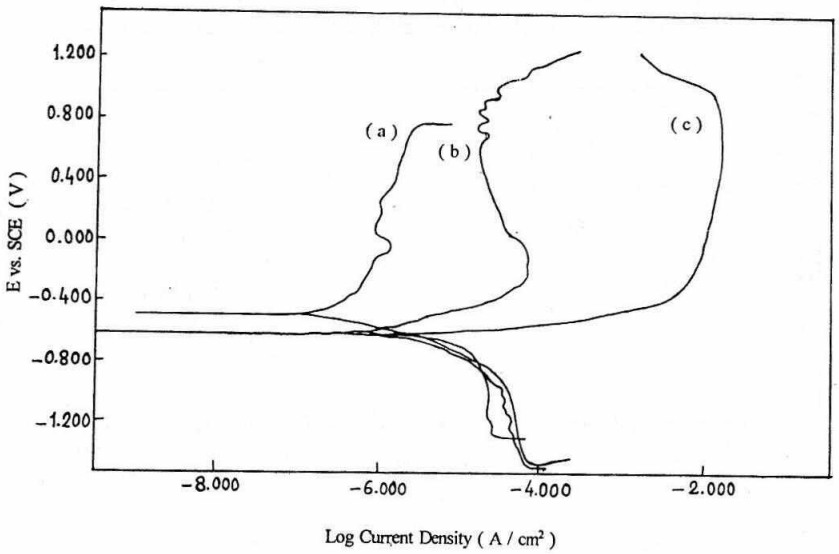

Fig. 5: Electrochemical potentiodynamic polarization study of as-received sample (a), and samples annealed at 873K (b) and 1023K (c)

DISCUSSION

During crystallization of $Fe_{70.5}Nb_{4.5}Cu_1Si_{16}B_8$ alloy, Cu atoms segregate and act as nucleation centres. The slowly diffusing component Nb restricts growth of crystal and effectively reduces grain size. Grain size drops with increase of Nb content. The broadening of XRD peaks for sample annealed at the primary crystallization temperature and also the literature value[3] suggest that the grain size of ordered $Fe_{80}Si_{20}$ phase is less than 13 nm. Usually a drop in resistivity is observed when a alloy crystallizes from amorphous phase. However, in the present case the reverse is observed since here electrons scattering from grain boundaries dominate over the intragrain scattering due to the nanocrystalline structure.

The magnetic softening at the initial stage of annealing (below primary crystallization temperature) is associated with decrease in magnetoelastic anisotropy in amorphous state due to relaxation of internal stress. Enhancement of soft magnetic properties after primary crystallization is due to the formation of nanocrystalline $Fe_{80}Si_{20}$ phase whose grain size (<13nm) is smaller than the exchange correlation length. Hence magnetocrystalline anisotropy will average out resulting low coercivity and high susceptibility. The soft magnetic properties are enhanced further due to the competing nature of saturation magnetostriction constant of $Fe_{80}Si_{20}$ phase (negative) and rest amorphous phase (positive) which reduces the magnetoelastic anisotropy[4]. The rapid magnetic hardening at higher annealing temperature is associated with the formation of borides having strong magnetocrystalline anisotropy.

It is observed from the Fig.5 that the passivating tendency of the alloy is enhanced after stress relaxation and formation of ordered $Fe_{80}Si_{20}$ phase. It is interesting to note that the appearance of grain boundary after primary crystallization does not cause an increase in anodic dissolution which is contrary to the expectation. The Nb which concentrates near the grain boundary imparts more resistance to the anodic dissolution causing improvement in the passivating nature of the alloy in their nanocrystalline state. The formation of secondary crystallization products when annealed at 1023 K cause losing of passivating tendency.

CONCLUSIONS

Scanning thermal electrical resistivity measurement shows that as-received $Fe_{70.5}Nb_{4.5}Cu_1Si_{16}B_8$ alloy crystallizes in two different stages. In primary crystallization process which takes place at 780K , ordered $Fe_{80}Si_{20}$ phase is formed with the grain size less than 13nm. Boron rich phases are formed at the secondary crystallization temperature. The activation energy for the formation of ordered $Fe_{80}Si_{20}$ phase is 58kCal/mole.

The coercivity becomes minimum (2.5 A/m) and initial susceptibility is maximum ($60x10^3$) after primary crystallization. Due to the formation of small grains (less than 13nm) at the primary crystallization state the magnetocrystalline anisotropy averaged out to zero which enhances the soft magnetic properties of the material. The magnetic property enhances further due to the formation of negative magnetostrictive $F_{80}Si_{20}$ phase in a positive magnetostrictive amorphous matrix which reduces the effective magnetoelastic anisotropy of the materials.

Passivating tendency enhances after primary crystallization which is attributed to the presence of Nb near the grain boundary which creates increased resistance to the anodic dissolution.

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