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Phase transformations and electrical and magnetic properties of $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ amorphous alloy

D. M. MINIĆ[a*], A. MARIČIĆ[b]
[a]*Military Technical Institute in Belgrade, Serbia*
[b]*Technical Faculty of Čačak, University in Kragujevac, Serbia*

The structural transformations of the $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ amorphous alloy under non-isothermal as well as under isothermal conditions were studied. The amorphous alloy was stable up to a temperature of about 480°C when the process of multy-step structural transformations began. The primary crystallization starts by forming Fe_3Si as main phase followed by crystallization of three new phases, iron-copper ($FeCu_4$) at 600 °C and iron-niobium-silicon ($Fe_{16}Nb_6Si$) and iron-boron (Fe_2B) at 650° C. At temperature above 700 °C, the crystallization two new minor phases occurs, niobium-silicon (Nb_5Si_3) and iron-silicon (Fe_5Si_3). With the increase of the temperature the weight, the composition of present phases as well as their weight ratio is slightly changed. It was shown that all observed structural transformations have significant influence on electric and magnetic properties of alloy. The electric resistivity crystallized alloy is higher that amorphous one but the crystallized alloy possesses better magnetic susceptibility and retains the ferromagnetic properties in whole investigated temperature range.

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1. Introduction

Amorphous alloy known also as ”metallic glasses” are materials which are kinetically metastable and thermodynamically unstable [1] Most of them are stable at temperatures close to room temperature and can be transformed to polycrystalline materials at higher temperatures [2]. In this case the formed polycrystalline magnetic materials with grain size less than 100 nm called “nanocrystalline materials” (Finmet and Nanoprem and their modifications) possess superior soft magnetic properties. [3-5]. These materials generally contain two structural components: one consisted of periodically positioned atom inside the crystallites and the other comprises all atoms located in the interfacial regions with strongly distorted structures [6]. Owing to the small grain size, the local magnetocrystalline anisotropy is randomly averaged out by exchange interaction leading to low or vanishing saturation magnetostriction [7].

The microstructure obtained by crystallization from the amorphous matrix can be controlled by the addition of elements such as Cu, Zr and Nb and by the heat treatment conditions such as heating rate, holding temperature and time [8, 9].

Copper and niobium, despite their small contents in alloy, affect the crystallization process and are responsible for nanocrystalline structure of Fe-based alloys. The copper, due to its very limited solubility in iron, forms small clusters, which can serve as sites for heterogeneous nucleation of Fe-based crystallites and increase their number by orders of magnitude. On the other hand, niobium, which is rejected from a crystallization front to the amorphous matrix, decreases crystal growth because of relatively smaller diffusivity of big atom in an amorphous phase [10]

Through crystallization process attained final microstructures of alloy enable them with specific physical properties which are very important for their application [11]. This microstructure is very sensitive to the annealing temperature and a study of microstructure evolution of nanomagnetic materials can provides guidance for tailoring the material of desired physical properties [12, 13]. In this paper we have studied in detail the influence of temperature in the temperature range 25-700°C on structural transformations of amorphous $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ alloy in order to find the influence the change of phase structure and microstrucuture on electric and soft magnetic properties.

2. Experimental procedure

By means of the standard procedure of rapid quenching of the melt on a rotating disc (melt-spinning method), amorphous ribbon samples with a chemical composition $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ (Vitroperm®) and with dimensions of 2.5 cm wide and 35 μm thick were prepared. The samples of as-quenched ribbon were sealed in a quartz tubes under technical vacuum and isothermally annealed for 1 h.

The samples were investigated by differential scanning calorimetry (DSC) using a DSC-50 analyzer (Shimadzu, Japan). For this purpose several milligrams of the alloy were heated from room temperature up to 700 ^{o}C in a stream of nitrogen flowed at X ml min^{-1} and with constant heating rates of 4 K min^{-1}.

The X-ray diffraction (XRD) experiments were performed on an X-Pert powder diffractometer (PANalytical, Netherlands) using CuKα radiation in Bragg-Brentano geometry at 40 kV and 30 mA. The measurements were conducted in step scan mode in 0.05° (*2θ*) intervals with a measuring time of 30 s step^{-1}. The used diffractometer device is equipped with a secondary graphite monochromator, automatic divergence slits, and a scintillation counter.

The TOPAS V3 general profile and structure analysis software for powder diffraction data was used in the Rietveld refinement procedure [14].

For the microstructural examination by scanning electron microscopy (SEM) an XL 30 ESEM-FEG (environmental scanning microscope with field emission gun, manufactured by FEI, Netherlands) device equipped with an energy dispersive X-ray spectrometer from EDAX was used. The samples were inspected using 5 kV and 10 kV acceleration voltage at a magnification of 20000x and 10000x respectively.

The electrical resistance of the ribbon was measured by the four-point method within a temperature range of 20–600^{o}C in an argon atmosphere. Measurements of relative magnetic permeability were performed using a modified Maxwell method, based on the action of an inhomogeneous magnetic field on a magnetic sample. The magnetic force measurements were performed with a sensitivity of 10^{-6}N in an argon atmosphere.

3. Results

An EDAX analysis, Fig. 1 confirms that all expected elements were present in the as-prepared $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ amorphous alloy.

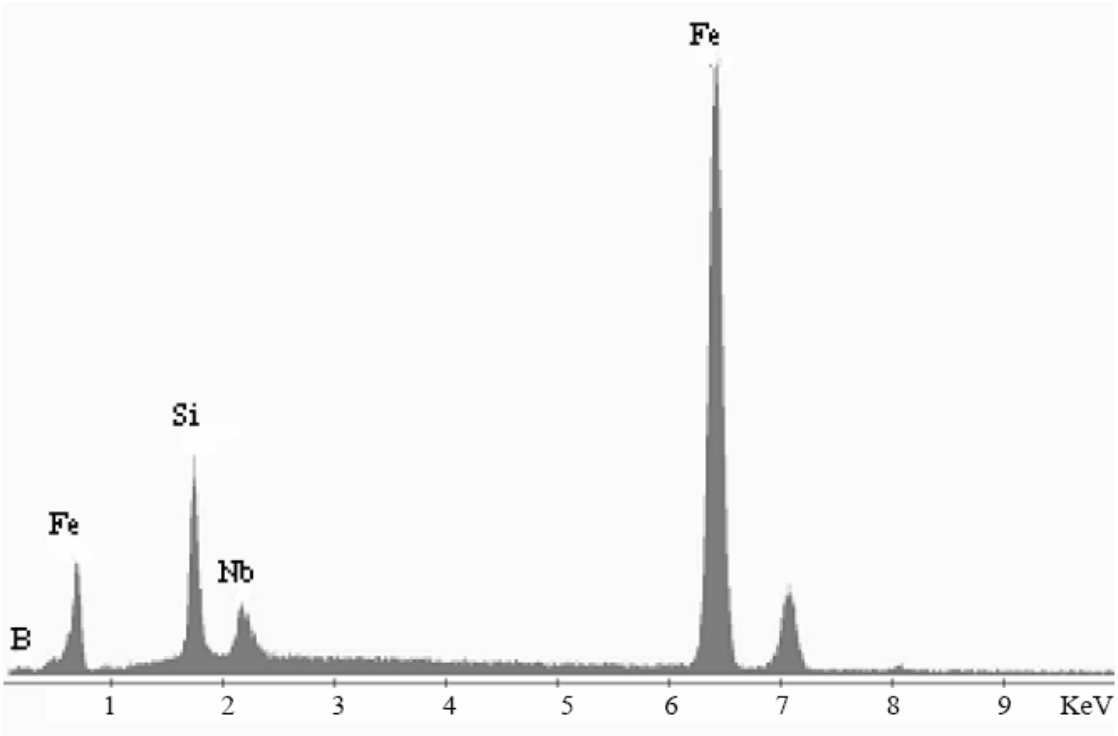

Fig. 1 EDAX spectrum of surface of as–prepared sample.

The thermal behavior of the $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ amorphous alloy is depicted in the DSC curve, Fig. 2, at heating rate 4 Kmin^{-1}. The Curie temperature at 440 ^{o}C is followed by three well formed broad asymmetric exothermic peaks indicating a stepwise process of the structural transformation of the alloy in the broad temperature range from 480-700 ^{o}C. During structure transformation the system moves from the condition of the as-deposited amorphous alloy of higher excess free energy to the condition of the annealed sample exhibiting lower excess of free energy. The corresponding the enthalpies release of ΔH_1= 67.3 Jg^{-1} in temperature range 500-565 ^{o}C,

ΔH_2= 3.4 Jg^{-1} in temperature range 600-620 ^oC and ΔH_3= 31.7 Jg^{-1} in temperature range 660-700 ^oC give a measure of the thermal stability of the sample with respect to structure transformations involving nucleation and growth of crystals different phases in different temperature ranges.

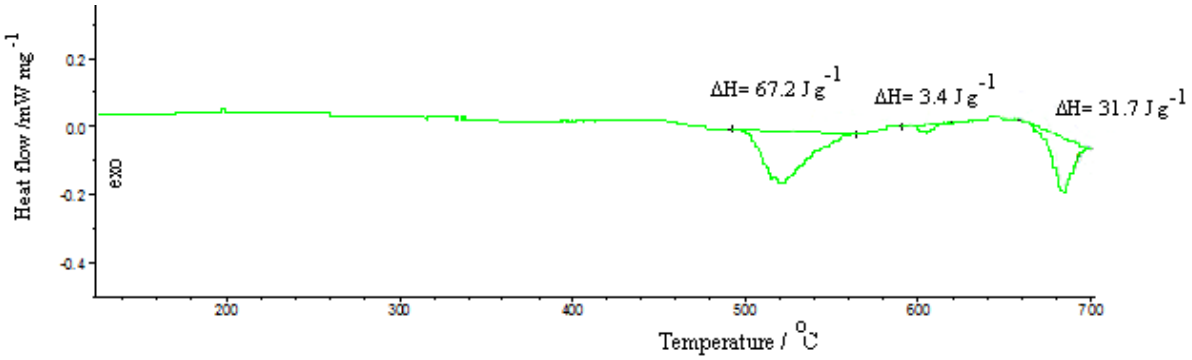

Fig. 2 DSC of as-prepared alloy at heating rate 4 $Kmin^{-1}$.

The XRD investigation of the as-prepared of $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ alloy confirmed the absence of a long range ordering. Fig. 3 shows the XRD patterns of an as-prepared alloy sample as well as samples of alloy which were subjected to 1 h annealing treatment at different temperatures (420, 480, 500, 540, 600, 650, 700, 750, 800 and 850 ^oC).

The amorphous state of the as-prepared alloy was confirmed by the X-ray diffraction method as shown at Fig.3. The diffraction pattern for the as-prepared alloy has only a spread halo in the 2θ range of 40-50^o and does not have any appreciable diffraction peaks indicating an absence of the long-range crystalline order.

The XRD analysis for the annealed samples (420 and 480^{o}C) displays beside the spread halo peak in the 2θ range from 40° to 50° which corresponds to the amorphous fraction of the material, also the presence of the crystalline Fe_3Si [ICDD-PDF 03-065-0146] phase (FCC or DO_3 crystal structure) as a major phase in crystallized alloy.

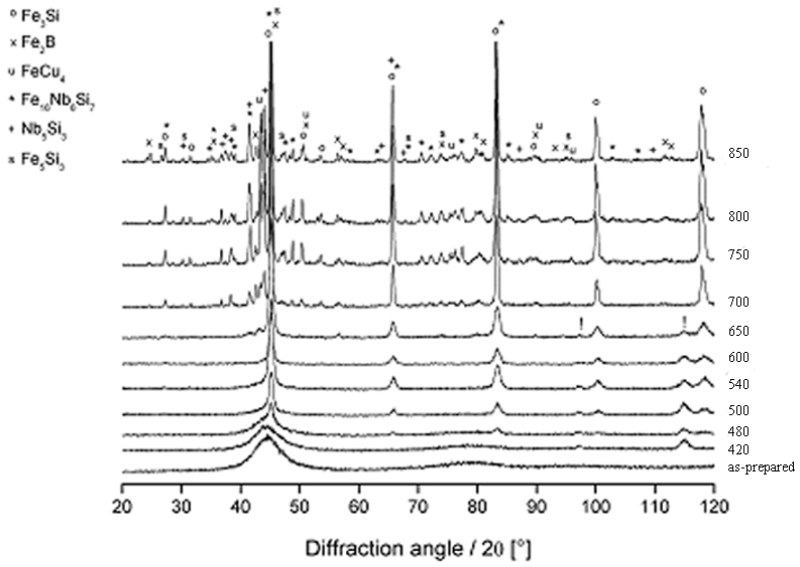

Fig. 3. XRD patterns of $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ as-prepared alloy and samples of alloy heated during 1 h at different temperatures as indicated in ^oC.

The attained structure remains unchanged until a temperature of 600 °C when a further transformation derives a crystalline phase $FeCu_4$ [ICDD-PDF 03-065-7002]. At this annealing temperature the copper-iron phase appears only in traces. Further structural change was observed at 650 °C annealing temperature. It is most likely that a rapid dissolution of B and Nb atoms into the Fe matrix led to the formation of two new phases; $Fe_{16}Nb_6Si_7$ [ICDD-PDF 00-053-0459] and Fe_2B [ICDD-PDF 00-036-1332]. The final structural transformation occurs at 700 °C giving two phases in traces, Fe_5Si_3 [ICDD-PDF 03-065-3593] and Nb_5Si_3 [ICDD-PDF 03-065-2785].

The quantitative XRD analysis was performed by the Rietveld refinement procedure [16]. Table 1 shows a relative phase contributions [wt %] as function of annealing temperature. The main found phase for all annealing temperature was Fe_3Si phase. With an increase of a temperature the relative contribution of the Fe_3Si phase observed primarily at 500 °C decreased very slowly and reached the minimum value of 85.0 wt % as the main phase for the highest annealing temperature.

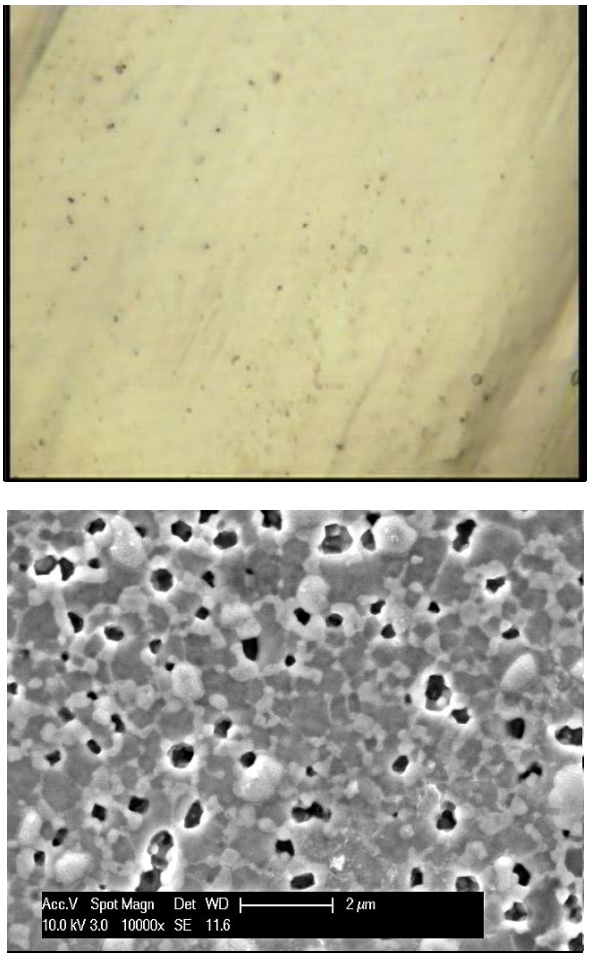

Fig. 4. SEM micrograph (surface), as prepared alloy and sample of alloy annealed at700 °C for 24 h.

The crystallite size of the major Fe_3Si phase remains almost constant at about 9 nm when annealed for 1 h at temperatures between 500 and 600 °C, as shown in Table 2. In this temperature range Nb from the boundary area restricts significantly the growth of the Fe_3Si crystallites. On the other hand, the crystallite growth increases rapidly above 650 °C. This coincides well with the $Fe_{16}Nb_6Si_7$ phase occurrence. Generally, the increase of the heating temperature, as well as the extension of heating time, leads to the increase of intensities all present peaks pointing to the better crystallization of all present phases, as well as the growth of formed crystals, Table 2. It shows that the crystallization process starts with nanosized crystallites, and their growth is further temperature dependent.

SEM micrographs of surface at Fig. 4 show the amorphous structure as-prepared alloy and crystal structure of alloy after annealing at 700 °C.

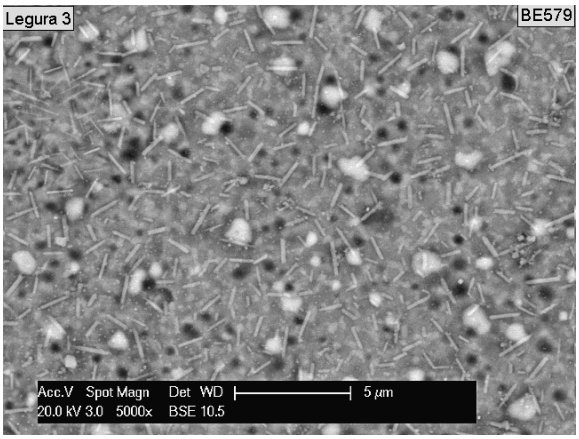

Fig. 5. SEM micrograph (surface), sample after heat treatment at 850 °C for 24 h.

The SEM micrograph of the surface sample after heat treatment during 24 h at 850 °C (cf. Figure 5) shows the presence more crystal grains of different shapes and colours corresponding to different phases found by X-ray analysis. The corresponding EDX analysis shows a significant alteration in composition. The areas which correspond to the black rifts in the sample surface are enriched with Si, Nb and Fe. The white, largest and almost spherical particles contain exclusively Cu. The EDX analysis of the dark-grey, basic area shows a major Si and Fe content while in the needle-like particles Nb is predominant.

Appearance of the thermomagnetic curve reflexes all kinds of changes in material magnetic moment induced by heating the alloy, Fig.6. It is sensitive on changes in atomic magnetic characteristics because of phase or structure transitions. Most pronouncing change on shown thermomagnetic curve represents the Curie point

(T_c=440°C), where the magnetization of appropriate phase falls almost to zero, because the magnetic interaction cannot resists to the thermal motion any more.

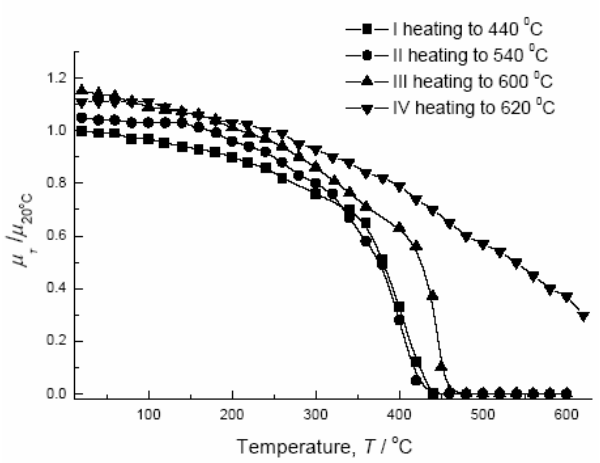

Fig. 6 Temperature dependence of relative magnetic susceptibility of alloy during four cycles of heating.

The annealing at the temperature near 200°C is sometimes called as stress-relieving and usually enhances properties of the amorphous material. In this process, internal strains and the free volume are reduced in the starting material. These changes are accompanied by subtle inter-atomic movements, causing the changes in the electron structure. This leads to an increase in the number of electrons with unpaired spin in the direction of the outer magnetic field; this also leads to a decrease in the number of electrons spinning in the reverse direction and causes an increase in the magnetic susceptibility upon cooling. At the same time, strains and a decrease in the free volume during structural relaxation enable greater mobility of the walls of the magnetic domains and this behavior further contributes to the increase in the magnetic susceptibility.

During further heating, it is noticed the decrease in the magnetic susceptibility in the temperature region from 380-440°C as result of getting closer to the Curie temperature of the amorphous alloy.

During further heating in the temperature region from 450-660°C, the alloy loses its ferromagnetic properties. After the first heating, the magnetic susceptibility increases by 8 % as compared to the value in its amorphous state and as compared to the value in its relaxed state after the first heating. During the repeated heating above the crystallization temperature, the crystallized alloy maintains its ferromagnetic features in the whole temperature region, as a consequence of phase transformation of the alloy. The magnetic susceptibility alloy after crystallization is higher by 16% as compared to the value in amorphous state.

Generally speaking the electrical resistivity of the ordered (crystalline) alloy is lower than the disordered (amorphous) alloy of the same composition; therefore, the temperature dependence of electrical resistivity clearly shows each structural stabilization step which causes the change in the ordering of the investigated material.

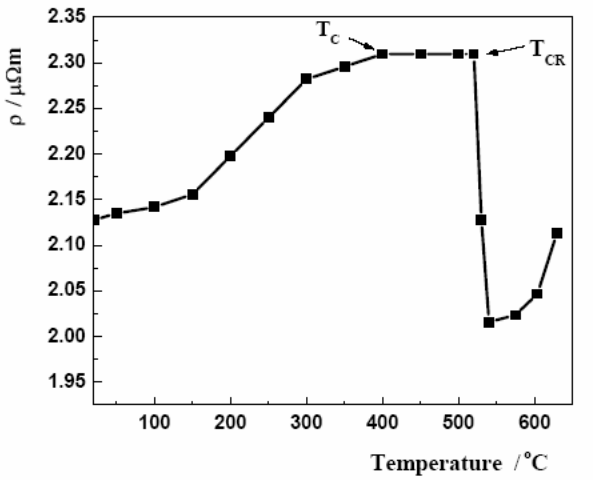

Fig. 7 Temperature dependence of the electrical resistivity of as-prepared alloy.

Fig. 7 shows the temperature dependence of the electrical resistivity of as-prepared alloy in the temperature range of 20-630 °C. The relaxation processes occurring in the alloy during thermal treatment in temperature range from room temperature up to Curie temperature (440 °C) cause the increase of electrical resistivity. The beginning the crystallization at temperature about 510 °C causes the abrupt decrease electrical resistivity which starts to increase after second step of crystallization of alloy in temperature range 510-630 °C. In this case, the presence of new formed new crystal phases in amorphous matrix causes the abrupt rise of electrical resistivity at 520°C.

4. Conclusion

Thermal treatment of the $Fe_{73.5}Cu_1Si_{15.5}B_7$ amorphous alloy under non-isothermal as well as under isothermal conditions provoked the structural transformations occuring in temperature range 460-700°C. The primary crystallization starts by forming Fe_3Si phase. This process is followed by crystallization of three new phases, iron-copper (FeCu4) at 600 °C, iron-niobium-silicon ($Fe_{16}Nb_6Si$) and iron-boron (Fe_2B) at 650° C. At temperature above 700 °C, the crystallization two new minor phases occurs, niobium-silicon (Nb_5Si_3) and iron-

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*Corresponding author: dminic2003@yahoo.com