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Influence of Structural Transformations on Electric and Magnetic Properties of $Fe_{81}B_{13}Si_4C_2$ Amorphous Alloy

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Abstract:

The structural transformations of the $Fe_{81}B_{13}Si_4C_2$ amorphous alloy under non-isothermal as well as under isothermal conditions were studied. The amorphous alloy was stable up to a temperature of about 450°C when the structural transformations began. The primary crystallization starts by forming Fe_3Si as main phase (more than 80 wt %), and two minor phases Fe_2B and Fe_3B. With the increase of the temperature the phase composition as well as ratio of present phases is changed and above 600°C it was confirmed the presence only two stable phases, Fe_3Si and Fe_2B. It was shown that all observed structural transformations have significant influence on the electric and magnetic properties of alloy. The electric resistivity of the crystallized alloy is lower than the amorphous one. The crystallized alloy possesses better magnetic susceptibility and retains the ferromagnetic properties in whole investigated temperature range.

Keywords*: Amorphous Materials, Metallic Glasses, Metals and Alloys, Phase Transition, Thermal Analysis, X-ray diffraction spectra.*

Introduction

Amorphous alloys, also known as "metallic glasses" are materials obtained by rapid quenching of melt at cooling rate of about 10^5-10^6 K s^{-1} in conditions where the crystallization is suppressed [1]. These materials possess a disordered distribution of atoms in the cooled melt and an excellent combination of physical properties which are very important technological applications [2]. The soft magnetic amorphous alloys are based on the ferromagnetic elements, Fe, Co and Ni and contain the glass forming elements such as Si, B, C and P [3-6]. The most stable amorphous alloys contain about 80 at. % of transition metal (ferromagnetic elements) and 20 at. % metalloid components (glass forming elements). From the practical point of view, these materials compared with the crystalline materials possess series of advantages such as the isotropy of magnetic properties, high magnetic softness combined with high mechanical hardness, high mechanical strength, low ribbon thickness and high electrical resistivity providing excellent soft magnetic materials properties for high frequency applications involved with very low loses [7,8]. The amorphous alloys are metastable materials and the elevated temperature as well as the prolonged performance could induce the process of change of their microstructure [9,10]. The formed microstructure involves the nanocrystals about 10 nm in size embedded in an amorphous matrix possessing soft magnetic properties superior to the amorphous and conventional crystalline magnetic

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alloys of same composition [11]. However, the crystallization of amorphous alloys can provoke the formation of a number metastable crystalline phases as well as the deterioration of their advanced properties making them useful only once. Therefore, the technological applications amorphous and nanostructured materials demand the knowledge of thermal stability, pressure effects, surface effects, microstructure, kinetic of crystallization as well as composition effects on the physical properties of these materials.

In this paper we have studied in detail the influence of temperature in the temperature range 25-700°C on structural transformations of amorphous $Fe_{81}B_{13}Si_4C_2$ alloy in order to find the influence of change microstructure on the magnetic and electric properties of alloy.

Experimental procedure

The ribbon-shaped samples of the $Fe_{81}B_{13}Si_4C_2$ amorphous alloy were obtained using the standard procedure of rapid quenching of the melt on a rotating disc (melt-spinning). The resulting ribbon was 2 cm wide and 35 μm thick.

the crystallization process was investigated by the DSC technique in a nitrogen atmosphere using a SHIMADZU DSC-50 analyzer. In this case, samples weighing several milligrams were heated in the DSC cell from room temperature to 600 °C in a stream of nitrogen at a flow rate of 20 mL min^{-1} at the heating rate of 20 K min^{-1}.

In order to investigate the structural transformations by the XRD technique, the samples of the amorphous alloy $Fe_{81}B_{13}Si_4C_2$ were annealed at the different temperatures (25-700°C) in a stream of nitrogen during 30 min. The X-ray powder diffraction patterns for the as-prepared alloy, as well as for the samples that were annealed at different temperatures, were recorded on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter. For the routine characterization, the diffraction data were collected in the range of 2θ Bragg angles (4-100° counting for 0.1 second). Silicon powder was used as an external standard for calibration of the diffractometer. All XRD measurements were done with solid ribbon-shaped samples at ambient temperature. For a quantitative analysis and determination of crystallite size we used HighScore plus with Rietweld structural models based on the ICSD database.

The electrical resistance of the ribbon was measured by the four-point method within a temperature range of 22–600°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.

Results and discussion

The thermal stability of alloy was investigated by thermal analysis. The DSC curve, Fig.1, involving series of endo- and exo-peaks in the temperature range of 200-560°C indicates a stepwise process of thermal stabilization of alloy. The broad endo- and exo-peaks in temperature range 200-400°C corresponding to relaxation of deformed amorphous structure are followed by endothermic hump at 400°C corresponding to Curie temperature and a short super-cooled liquid region before appearing a sharp exotermic crystallization peak at 532.8°C for heating rate 20°C min^{-1}. The enthalpy of crystallization was found to be 0.1 kJ g^{-1}.

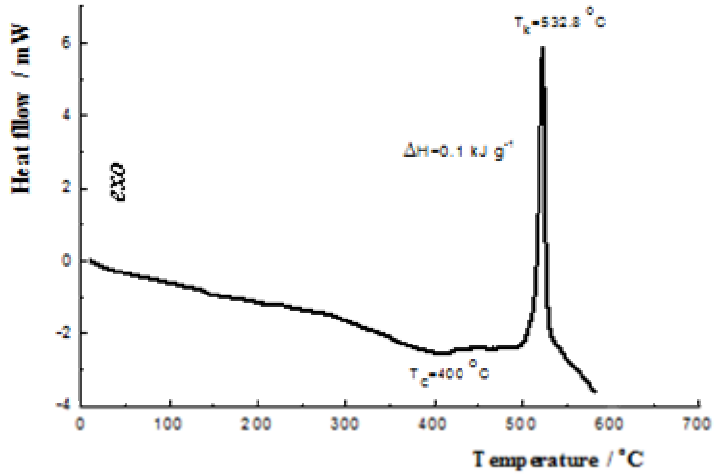

Fig.1 DSC curve for $Fe_{81}B_{12}Si_4C_2$; heating rate 20°C·min^{-1}.

The amorphous state of the as-prepared alloy was confirmed by the X-ray diffraction method as shown at Fig.2. The diffraction pattern of the as-prepared alloy shows a spread halo in the 2θ range of 40-50° characteristic for an amorphous structure indicating an absence of the long-range crystalline order and a small diffraction peak at 2θ=78.2°. This peak corresponds to the presence of small amounts of crystal Fe_3Si phase dispersed in amorphous matrix of as-prepared alloy [JCPDS-PDF 03-065-0146]. This structure remains unchanged after annealing at 400°C. The size of the coherently scattering regions, calculated from the half-width of the observed halo by Scherrer's formula, is about 0.71 nm, pointing out also the presence of highly disordered Fe clusters in an amorphous matrix.

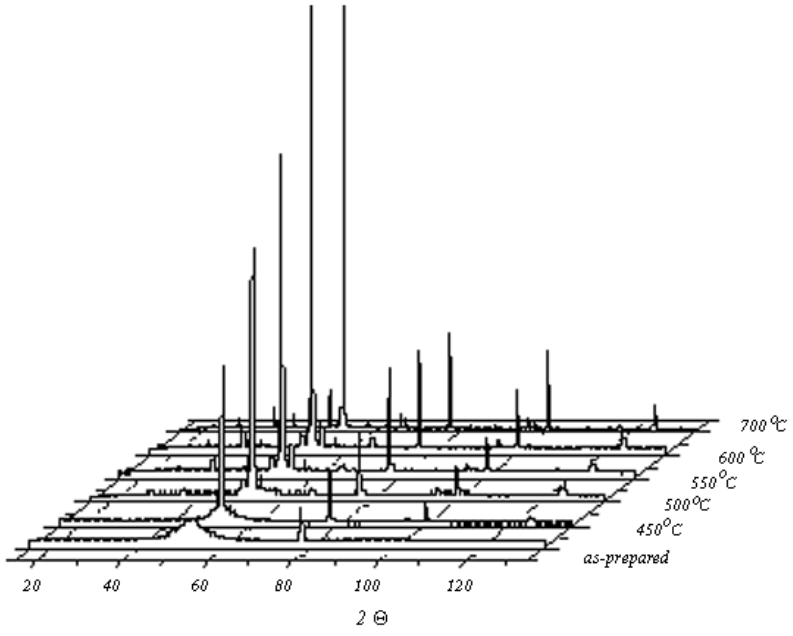

Fig. 2. XRD spectra of as-prepared alloy as well as samples of alloy annealed at different temperatures

The amorphous ribbon in the as-prepared state was repeatedly vacuum-annealed during 30 minutes at the indicated temperatures (450, 500, 550, 600, and 700°C) which are chosen according o DSC curve to catch up the main features of the thermal process. These results (Fig.2) show the begining of the crystallization already at 450°C. The diffraction patterns of the annealed alloy, in the temperature range 450-550°C contain the same halo as the original sample as well as a sharp peaks at $2\theta = 78.2^{o}$ and $2\theta = 46.8^{o}$ corresponding to the presence of Fe_3Si phase [JCPDS-PDF 03-065-0146]. An increase of the annealed temperature results in an increase of intensity of these peaks pointing out an increase of amount of crystalline phase Fe_3Si as a consequence of a partial crystallization of the Fe_3Si phase in an amorphous matrix.

At the same time, besides the intense diffraction pattern of the Fe_3Si phase, weak peaks of two iron-boron phases became visible; the more stable (Fe_2B) phase according to [JCPDS-PDF 03-065-2693] as well as the less stable (Fe_3B) phase according to [JCPDS-PDF 00-039-1316]. With rise of annealing temperatures, the intensity of the iron-boron (Fe_2B) peaks slightly increased as well as the peaks of the iron-silicon (Fe_3Si). At temperature of annealing higher 600°C the peaks of Fe_3B phase completely disappeared and the presence only two phases (Fe_3Si and Fe_2B) was clearly noticed. The weight fractions of all observed crystalline phases are displayed as a function of the annealing temperature during the heating of alloy, Fig.3.

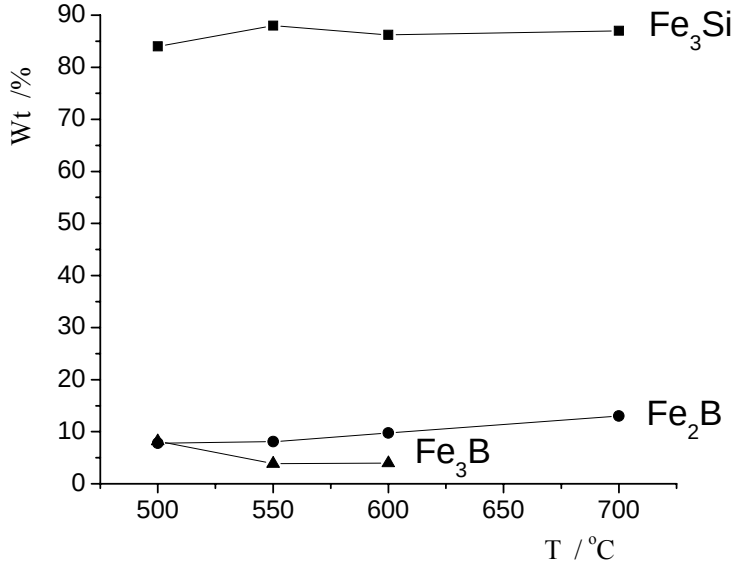

Fig. 3 Weight fractions of the observed crystalline phases as obtained by Rietveld refinement procedure, plotted as a function of the heating temperature (30 min).

For the qualitative determination of the phase composition of the crystallized alloy samples, Fig. 3, the JCPDS-PDF data base has been used. Besides the phase composition the quantitive determination of the content of each individual phase is essential and can be obtain from the Rietveld's refinement procedure [12]. This procedure is able to simulate the XRD pattern from given starting parameters. The purpose of this simulation is therefore to refine individual parameters e.g. phase content, crystallite size, and crystal lattice parameters, to obtain a good fit. For this purpose the Rietveld refinement program TOPAS V3.0 (Bruker AXS GmbH, Germany) was used [13]. This software enables the full handling of the instrument geometry and the instrument profile parameters. The quality of the refinement progress was controlled by monitoring the fit parameter R_{wp}, the goodness of fit (GOF), and

the Durbin-Watson factor. Besides, the values for the weight fraction for each phase in the penetrated sample volume, the values for the crystallite size, were determined by the Rietveld method as well.

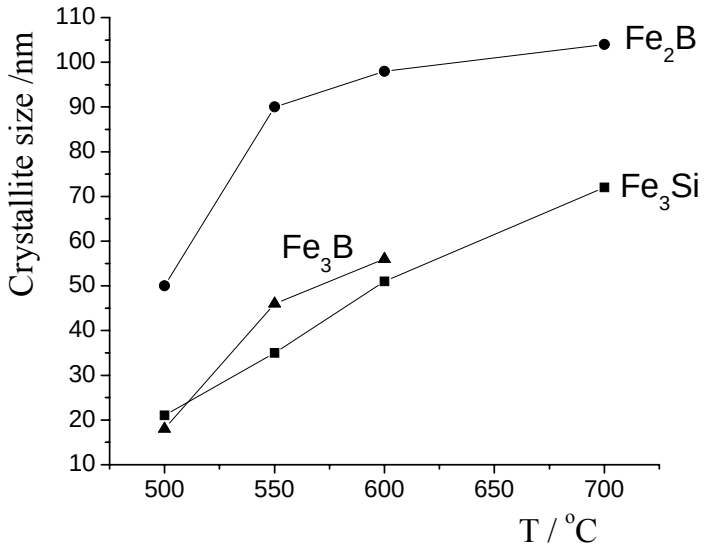

Fig. 4 Crystallite size as deduced from Rietveld refinement data for all observed phases.

An increase of the heating temperature, a decrease of the half width of the peak as well as the extension of heating time, lead to the increase of intensities of all present peaks pointing to the better crystallization of all present phases, as well as the growth of formed crystals. The change of the crystallite dimensions of formed phases with increasing temperature of heating are shown in Fig.4. It shows that the crystallization process starts with nanosized crystallites, and their growth is further temperature dependent.

The temperature dependence of the relative magnetic susceptibility of the as-prepared $Fe_{81}B_{13}Si_4C_2$ amorphous alloy during two cycles of heating to different temperatures is presented in Fig. 5. The appearance of this thermomagnetic curve reflexes all kinds of changes in magnetic moment induced by heating of the alloy. Magnetic moment is sensitive on changes in atomic magnetic characteristics because of phase or structure transformations. Most pronouncing change on shown thermomagnetic curve represents the Curie point (T_c = 390°C), where the magnetization of appropriate phase falls almost to zero, because the magnetic interaction cannot resist to the thermal motion any more. The annealing at the temperature near 200°C is sometimes called as "stress-relieving process" 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, the 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 320-390°C as result of getting closer to the Curie temperature of the amorphous alloy.

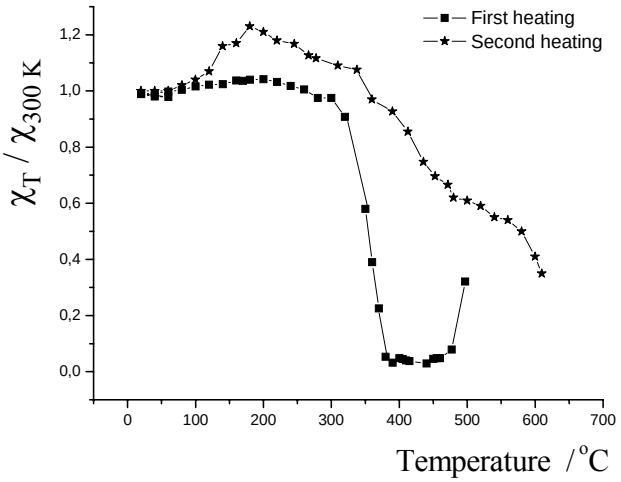

Fig. 5 Change of relative magnetic susceptibility with temperature during two heating cycles of alloy.

During further heating in the temperature region from 390-480°C, the alloy loses its ferromagnetic properties. With further heating, the magnetic susceptibility starts to rise, and the alloy regains its ferromagnetic properties since the crystallization process starts at about 490°C. After the first heating, the magnetic susceptibility increases 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 second heating above the crystallization temperature, the alloy maintains its ferromagnetic features in the whole temperature region, whereas the maximum change in the magnetic susceptibility occurs at about 200°C as a consequence of further phase transformation of the crystallized alloy.

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.

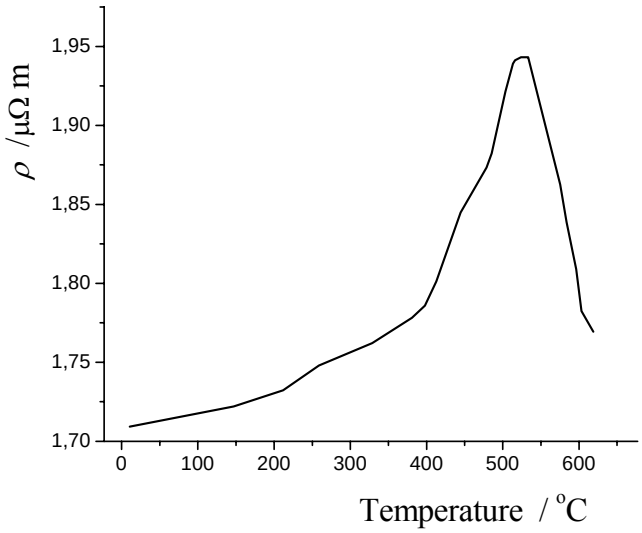

Fig. 6 Change of the electrical resistivity of as-prepared alloy with the temperature.

The temperature dependence of the electrical resistivity of the amorphous alloy in the temperature range of 20-630°C is shown in Fig.6. The slow increase of electrical resistivity was caused by the structural relaxation processes in the temperature range of 200-380°C. This process is followed by sadden increase of electrical resistivity in the vicinity of Curie temperature T_c at 390°C at which point the effect that the scattering of conductive electrons had on the magnons disappeared. At that temperature, the amorphous alloy loses its ferromagnetic features. The beginning of crystallization at about 520°C causes the sharp drop of electrical resistivity.

During heating up to 600°C, the alloy crystallizes getting lower electrical conductivity. The linear change of electrical resistivity with a rising temperature during the second heating shows that the process of structural transformations of alloy was completed during the first heating to 600 °C, Fig.7.

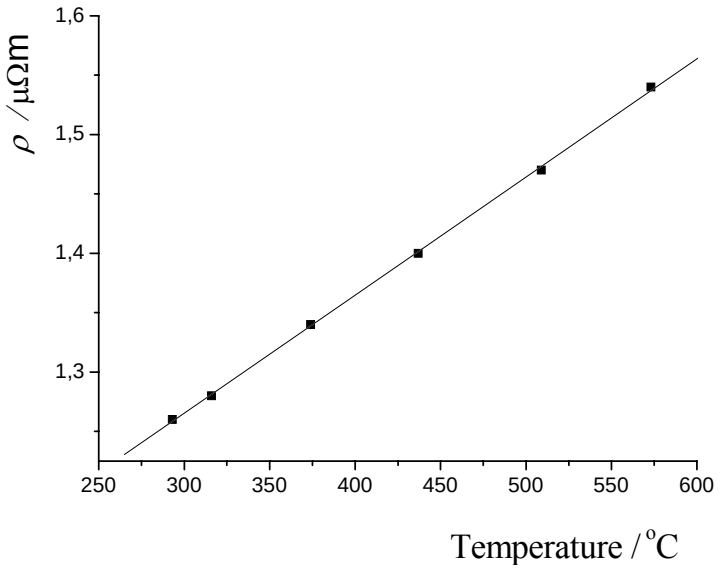

Fig. 7 Change the electric resistivity of alloy during second heating.

Conclusion

Thermal treatment of the $Fe_{81}B_{13}Si_4C_2$ amorphous alloy under non-isothermal as well as under isothermal conditions provoked the structural transformations occuring in temperature range 450-540°C. The primary crystallization starts by forming iron-silicon (Fe_3Si) as main phase (more than 80 wt %), and two less present iron-boron phases, Fe_2B (7.8 wt. %) and Fe_3B (8.2 wt. %). With the increase of the temperature the weight ratio of all present phases as well as the size of crystallites are changed. Above 600°C it was confirmed the presence only two stable phases, Fe_3Si (87 wt %) with the crystallite size 72 nm and Fe_2B (13 wt. %) with the crystallite size 104 nm. It was shown that all observed structural transformations have significant influence on electric and magnetic properties of alloy. The electric resistivity of the crystallized alloy is lower than the amorphous one. The crystallized alloy possesses better magnetic susceptibility and retains the ferromagnetic properties in whole investigated temperature range.

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Садржај: *Проучаване су структурне трансформације $Fe_{81}B_{13}Si_4C_2$ аморфне легуре у неизотермалним као и у изотермалним условима. Показано је да је испитивана аморфна легура стабилна до око 450°C када подлеже низу структурних трансформација. Примарна кристализација почиње формирањем Fe_3Si као најзаступљеније кристалне фазе (more than 80 mas%) и две мање заступљене кристалне фазе Fe_2B і Fe_3B. Са порастом температуре мења се фазни састав и масени однос присутних фаза. Изнад 600°C потврђено је само присуство две стабилне фазе Fe_3Si и Fe_2B. Показано је да опажене структурне трансформације имају значајан утицај на електрична и магнетна својства. Електрична проводљивост кристалне легуре је знатно нижа. Међутим кристализацијом магнетна пропустљивост расте и кристална легура задржава феромагнетна својства у целом температурском интервалу.*

Кључне речи*: Аморфни материјали, метална стакла, метали и легуре, фазна трансформација, термичка анализа, рендгенски спектри.*