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Correlation Between Isothermal Expansion and Functional Properties Change of the $Fe_{81}B_{13}Si_4C_2$ Amorphous Alloy

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Abstract:

The structural changes effect on functional properties of ribbon shaped samples of the $Fe_{81}B_{13}Si_4C_2$ amorphous alloy during annealing process was investigated in this paper. Differential scanning calorimetry method has shown that this alloy crystallizes in one stage, in temperature range from room temperature up to 700 ^0C. Structural relaxation process was investigated by sensitive dilatation method in nonisothermal and isothermal conditions. It has been shown that structural relaxation process occurs in two stages by measuring thermal expansion at constant temperatures of $t_1 = 420^0C$, $t_2 = 440^0C$ and $t_3 = 460^0C$. The first stage is characterized by linear logarithmic dependence of thermal expansion upon time at constant temperature. The second stage of structural relaxation process is characterized by linear dependence of isothermal expansion upon the square root of process time. These results imply that the first stage of structural relaxation process is a rapid kinetic process, while the second stage of structural relaxation process is a slow diffusion process. The rate constants $k_{11} = 2{,}27 \cdot 10^{-3}\ s^{-1}$, $k_{12} = 2{,}79 \cdot 10^{-3}\ s^{-1}$, $k_{13} = 3{,}6 \cdot 10^{-3}\ s^{-1}$, $k_{21} = 0{,}67 \cdot 10^{-4}\ s^{-1}$, $k_{22} = 3{,}72 \cdot 10^{-4}\ s^{-1}$, $k_{23} = 21{,}53 \cdot 10^{-4}\ s^{-1}$ and activation energies $E_1 = 48{,}64$ kJ/mol and $E_2 = 366,\ 23$ kJ/mol were determined for both stages of structural relaxation process. The distinct correlation between structural relaxation process and magnetic susceptibility relative change was determined by thermomagnetic measurements. It has been shown that magnetic susceptibility can be increased by up to 80%, by convenient annealings after structural relaxation process, at magnetic field intensity of 8 kA/m.

Keywords: *Amorphous materials, Structural relaxation, Thermal expansion, Magnetic susceptibility.*

Introduction

The metallic glasses represent a novel class of metallic materials characterized by amorphous structure and metallic bond providing them with unique physical and mechanical properties that cannot be found either in pure metals or other amorphous materials [1]. These properties are attributed to their microstructure, characterised by the absence of the long-range order atoms [2]. The amorphous state of matter is, however, structurally and thermodynamically unstable and very susceptible to partial or complete crystallization during thermal treatment, which requires good understanding of alloy stability at various

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temperatures. Generally, the stability is a thermally activated process of transition from disordered amorphous structure to an ordered crystal structure. The requirements for the soft magnetic alloys with nonequilibrium structure produced by melt quenching technique involve the design of the proper chemical composition that provides improved levels of the properties, such as a high glass-forming ability, good casting properties of the alloy which in turn determine the surface quality and uniformity of the melt-spun ribbons, as well as an enhanced thermal stability of both magnetic properties and amorphous structure [3, 4, 5].

Annealed glassy alloy is far from the equlibrium state. When heated, glassy alloys cristalize upon a certain period. Structural relaxation occurrs before the onset of cristallization. It is only then that slight changes in the atomic structure occur, which provides metastable state. These changes are mainly related either to the disappearance (for $T < T_g$) or occurrence (for $T > T_g$) of free volume (T – annealing temperature, T_g – glass transition temperature) [6, 7, 8]. Thermal expansion and viscosity of the glassy alloys are structural relaxation-sensitive [9]. When annealed isothermally, the entire glassy alloy shows practically a linear increase in viscosity with the rise of annealing temperature [9]. Viscosity is expected to attain the constant value when the metal glass reaches the metastable state at the isothermal expansion temperature. Measurements of isothermal thermal expansion are suitable for the obtainment of quantitative data related to the following key parameters of the glassy state: activation energy of relaxation, activation energy of diffusion flow, frequency factor, and the initial defect concentration.

A lot of papers have been dedicated to amorphous alloys ferromagnetism [10-15], comprising the results of investigation of magnetic properties for alloys of different content. Generally an amorphous structure is assumed to introduce fluctuations in exchange interactions, which influence magnetic behaviour. It has been shown that exchange interactions of 3d electrons of neighbour atoms are accountable for ferromagnetism of ferrous group metal based amorphous alloys, as well as of crystal alloys, while magnetic properties distinctiveness of amorphous metal alloys is generally determined by locally changeable surroundings of each transition metal (TM) atom [15]. Atomic disorder and defects of different levels play the main role in magnetic properties determination. The results of various elements impact on magnetic moment $\vec{M}$ and Curie temperature T_C of amorphous metal alloys are very inconsistent [7, 16, 17, 18]. Magnetization $\vec{J}$ and Curie temperature T_C decrease during the transition from crystal to amorphous state with all ferrous group metal based amorphous alloys. Magnetic moment in TM amorphous alloys is determined by the number of electrons introduced into TM 3d zone [7].

The aim of this paper is investigation of the structural changes effect on thermal and magnetic properties of the $Fe_{81}B_{13}Si_4C_2$ amorphous alloy during annealing process.

Experimental

The subject of the research is ribbon shaped amorphous metal alloy $Fe_{81}B_{13}Si_4C_2$. The investigated ribbon samples were 30 μm wide. The structural changes effect on functional properties of this alloy during annealing was investigated. Nonisothermal and isothermal ribbon expansion was measured at temperatures $t_1 = 420^0$C, $t_2 = 440^0$C and $t_3 = 460\ ^0$C by 10^{-5} m sensitivity dilatometer. X-ray diffraction analysis of the as-cast and annealed samples was performed by the Cu-K_α radiation lines. The crystallization process was investigated in a nitrogen atmosphere by the differential scanning calorimetry (DSC) method using SHIMADZU DSC-50 analyzer with nitrogen flow of 20 ml/min. The analyses were conducted in temperature range from room temperature to 700^0C at heating rate of $20\ ^0$C/min. Temperature dependence of the relative magnetic susceptibility was investigated by the modified Faraday method in the temperature range from room temperature up to 460^0C, in argon

atmosphere, whereby magnetic field gradient was 8 kA/m.

Results and discussion

Fig. 1 shows DSC thermogram of the alloy sample $Fe_{81}B_{13}Si_4C_2$, obtained at heating rate of 20^0C/min. The obtained thermogram shows one exothermic peak at around 500^0C, which implies that the crystallization process occurs in one stage.

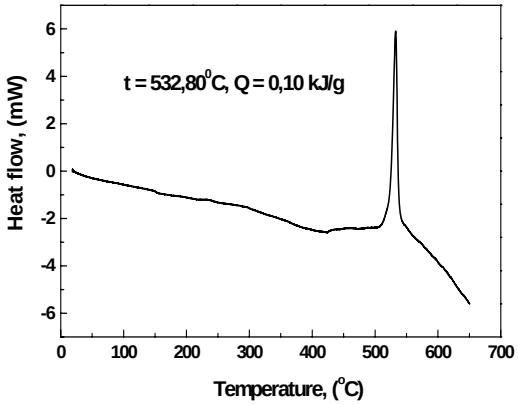

Fig 1. DSC thermogram of the alloy sample $Fe_{81}B_{13}Si_4C_2$ obtained at heating rate of 20^0C/min.

Fig. 2 shows XRD patterns of the as-quenched and annealed ribbon-shaped alloy samples $Fe_{81}B_{13}Si_4C_2$ [19].

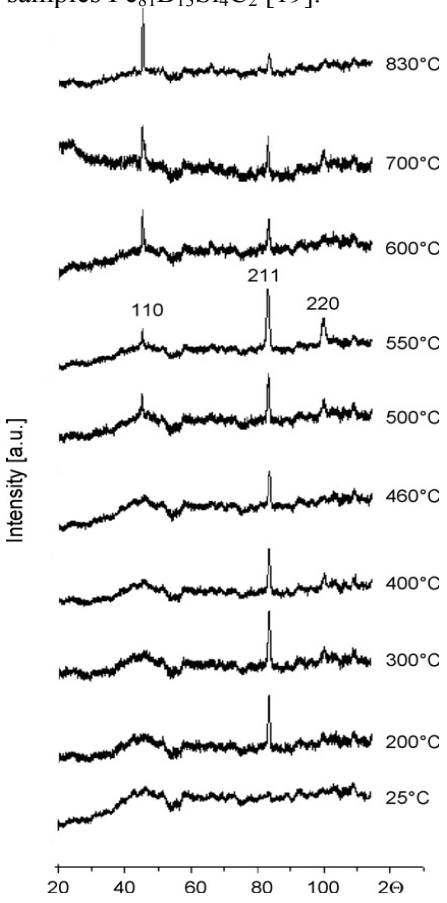

Fig. 2. XRD patterns of the as-quenched and annealed ribbon-shaped alloy samples $Fe_{81}B_{13}Si_4C_2$.

X-ray diffraction pattern of the as-quenched ribbon-shaped alloy sample shows only a broad halo at 2θ range of 40–55^0 suggesting an amorphous structure. Diffraction patterns of the ribbon-shaped alloy samples annealed at temperatures of t ≤ 460^{0}C contain the same halo as well as the original sample but also contain one sharp peak at 2θ = 83.2^0 indicating presence of structural deformed crystal phase as consequence of ordering Fe-clusters already present in as-cast alloy. The increase in annealed temperature results in a lower intensity of this peak and the appearance of the new sharp peak at 2θ = 45.6^0 whose height increases with an increase in annealing temperature. The greater intensity of that peak as well as a decrease in its half width indicates the increase in crystallinity of the alloy. This shows that at a higher temperature (above 500^{0}C) the process of crystallization occurs.

The structural relaxation process has been identified by dilatometric method in temperature range of around 100^{0}C lower than T_{CR}. Fig. 3 shows temperature dependence of thermal expansion (Δl) of the alloy sample $Fe_{81}B_{13}Si_4C_2$. Fig. 3 shows temperature dependence of the thermal expansion (Δl) of the same $Fe_{81}B_{13}Si_4C_2$ alloy sample, during first heating of up to 420^{0}C, during second heating of up to 440^{0}C and during third heating of up to 460^{0}C. The analysis of the obtained results shown in Fig.3 points out that the temperature range of linear dependence of thermal expansion increases upon each heating of the sample. During the first heating there is almost linear dependence of thermal expansion up to 150^{0}C. During the second heating the range of linear dependence expands up to 200^{0}C, and during the third heating up to 450^{0}C. It is obvious that such significant expansion of the temperature range of linear dependence is caused by structural relaxation process. Sudden thermal expansion is marked during first heating for the temperature higher than 350^{0}C, during second heating for the temperatures over 400^{0}C and during third heating for the temperatures over 440^{0}C. This sudden expansion is caused by more intensive structural relaxation process leading to gradual change of amorphous structure into crystal at higher temperatures.

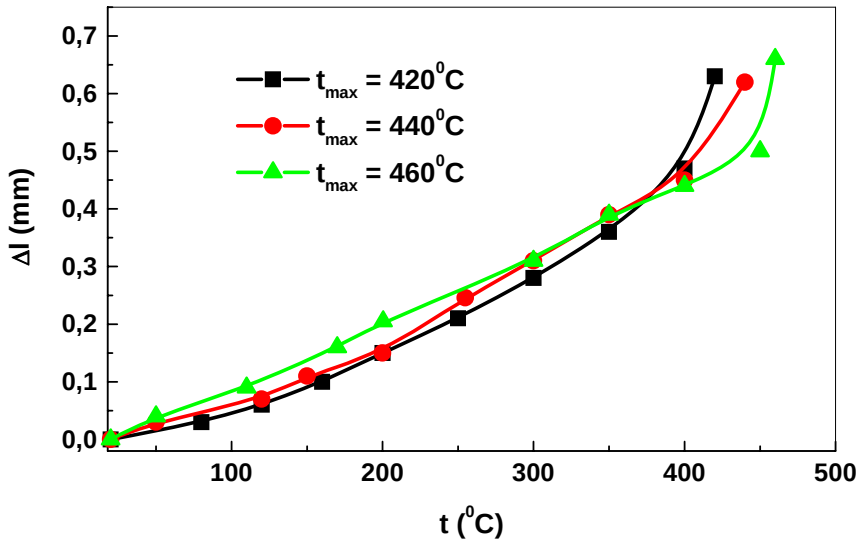

Fig. 3. Temperature dependence of thermal expansion (Δl) of the alloy sample $Fe_{81}B_{13}Si_4C_2$:(■ – first heating, ● – second heating, ▲- third heating).

Fig. 3 shows that the thermal expansion process occurs in analogue way with all three sample annealings. Temperature range of linear dependence of thermal expansion increases with every new annealing of the same sample.

Fig. 4 shows the isothermal expansion process of the alloy samples $Fe_{81}B_{13}Si_4C_2$ at different annealing temperatures.

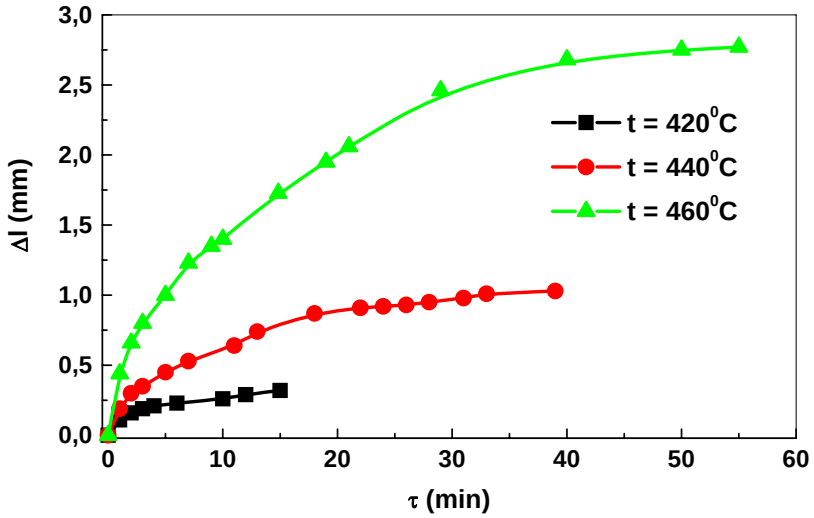

Fig. 4. Isothermal expansion of the alloy samples $Fe_{81}B_{13}Si_4C_2$ at different annealing temperatures.

Isothermal annealing of amorphous ribbons in the range of structural relaxation temperature causes their timely isothermal expansion. Isothermal expansion of the samples entails the transformation of the unstable amorphous structure into metastable equilibrium, i.e. structural relaxation which leads to a decrease in free volume.

In order to identify these processes, the Fig. 5 shows logarithmic dependence of isothermal expansion ln (Δl) = f (τ) upon time for the samples annealed at 420^{0}C, 440^{0}C and 460^{0}C. Linear dependence ln(Δl) upon time (τ) was obtained for the given time interval. This shows that the first stage of structural relaxation process is a fast kinetic process, characterized by transitions of atoms from higher towards lower energy state. The duration of the first stage of the structural relaxation process decreases with the rise in annealing temperature, i.e. τ_1 = 250 s at t_1 = 420^{0}C, τ_2 = 200 s at t_2 = 440^{0}C and τ_3 = 180 s at t_3 = 460^{0}C.

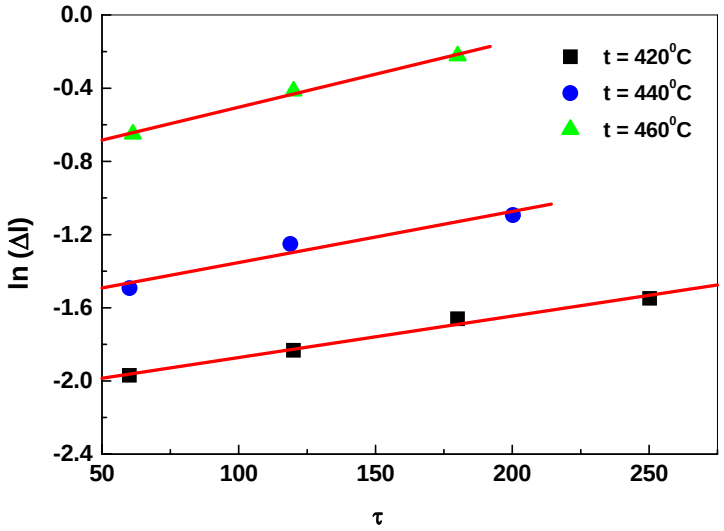

Fig. 5. Logarithmic dependence of isothermal expansion upon time ln (Δl) = f (τ) of the alloy samples $Fe_{81}B_{13}Si_4C_2$ annealed at 420^{0}C, 440^{0}C and 460^{0}C.

The second stage of the structural relaxation process is characterized by the linear

dependence $\Delta l = f\left(\sqrt{\tau}\right)$ (Fig. 6). Such dependence of isothermal expansion upon time suggests that the second stage of the structural relaxation process for all three annealing temperatures is a slow diffusion process, whereby the inter-cavity mass moves and the free volume decreases.

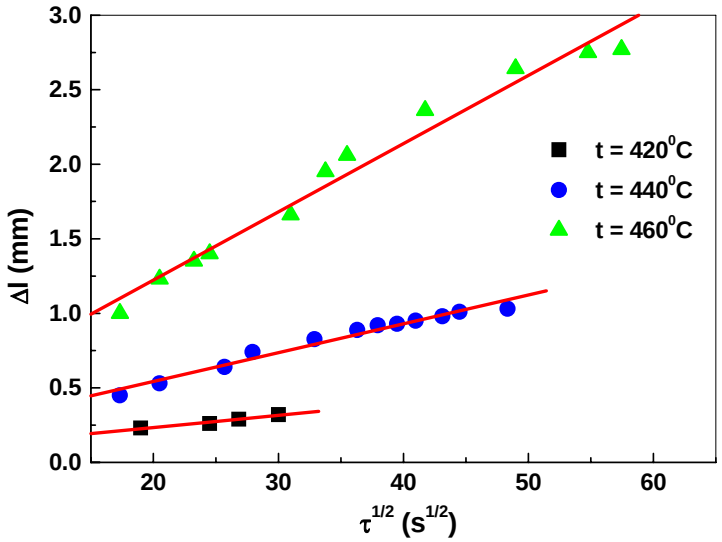

Fig. 6. The isothermal expansion dependence Δl upon $\sqrt{\tau}$ of the alloy samples $Fe_{81}B_{13}Si_4C_2$ annealed at temperatures 420^{0}C, 440^{0}C and 460^{0}C.

The rate constants for both stages of the structural relaxation process (k_1 and k_2) were determined from the slope $\Delta\ln(\Delta l) / \Delta\tau$ (Fig. 5) and $\Delta l / \Delta(\tau^{1/2})$ (Fig. 6).

Fig. 7 shows linear dependence ln k upon 1/T for both stages of structural relaxation process. According to equation $E = R\frac{\Delta \ln k}{\Delta(1/T)}$, the activation energies were obtained for both stages of structural relaxation process (E_1 and E_2).

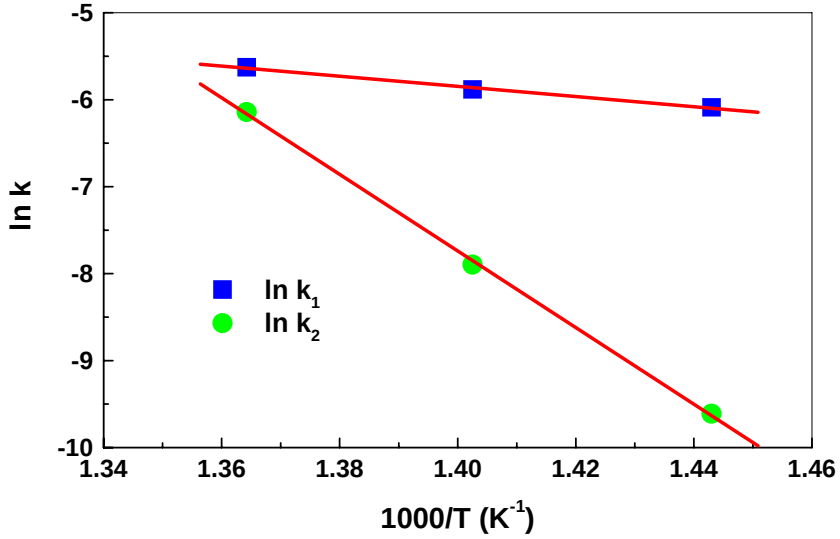

Fig. 7. Dependence ln k on 1/T of the alloy samples $Fe_{81}B_{13}Si_4C_2$ annealed at temperatures 420^{0}C, 440^{0}C and 460^{0}C (ln k_1 – first stage, ln k_2 – second stage of the structural relaxation process).

The obtained kinetic parameters for both stages of the structural relaxation process of the alloy samples $Fe_{81}B_{13}Si_4C_2$ annealed at temperatures 420^{0}C, 440^{0}C and 460^{0}C are shown in Tab. I.

Tab. I. Kinetic parameters of the structural relaxation process of the alloy samples $Fe_{81}B_{13}Si_4C_2$ annealed at temperatures 420^{0}C, 440^{0}C and 460^{0}C

t (^{0}C)	$k_1 \cdot 10^{-3}$ (s^{-1})	$k_2 \cdot 10^{-4}$ (s^{-1})	E_1 (kJ/mol)	E_2 (kJ/mol)
420	2.27	0.67		
440	2.79	3.72	48.64	366.23
460	3.6	21.53		

With the increase in annealing temperature, rate constants of both stages of structural relaxation process increase.

Thermomagnetic measurements were used to investigate temperature dependence of the relative change in magnetic susceptibility within three heating cycles in temperature range from room temperature up to 460^{0}C. Fig. 8 shows dependence of the relative change in magnetic susceptibility upon temperature of amorphous alloy $Fe_{81}B_{13}Si_4C_2$.

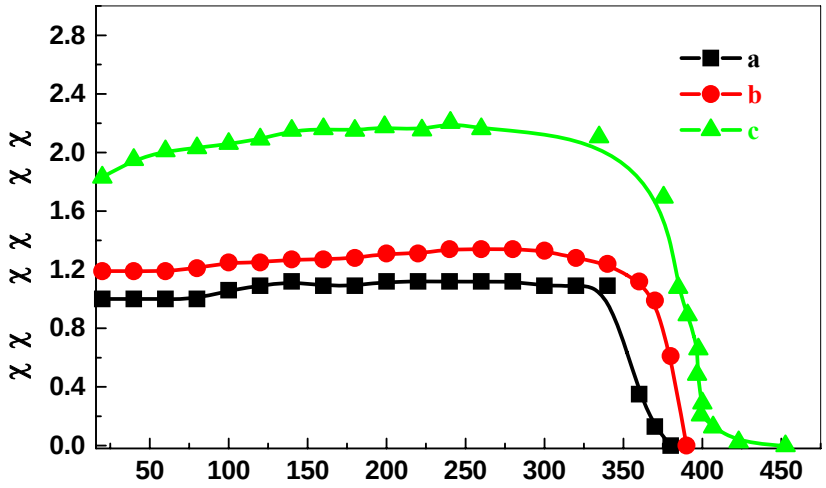

Fig. 8. Temperature dependence of relative change in magnetic susceptibility of amorphous alloy $Fe_{81}B_{13}Si_4C_2$: a) first heating up to 420^{0}C, b) second heating up to 440^{0}C, c) third heating up to 460^{0}C in argon atmosphere.

The analysis of the measurement results shown in Fig. 8 shows that upon first heating in the temperature range of amorphous state and upon cooling to room temperature, magnetic susceptibility increases by 20%. After the second heating of up to 440^{0}C in the temperature range of amorphous state and upon cooling to room temperature, magnetic susceptibility increases by 80%. The increase in magnetic susceptibility upon each heating is caused by structural relaxation process. This process leads to decrease in the number of defects, mechanical strains and free volume in alloy sample, which enables greater mobility of magnetic domain walls. With simultaneous thermal influence and the influence of external magnetic field, atoms of reversed direction in-between domain walls move towards energetically more favourable domain. All this leads to the increase in magnetic susceptibility upon cooling. Upon each annealing Curie temperature T_C slightly increases. This is caused by greater thermal stability of the structure due to structural relaxation process.

Conclusion

Thermal expansion process occurs in analogue way in case of all 3 samples. Temperature range of linear dependence of thermal expansion depends on annealing temperature. It increases with every subsequent sample annealing. Structural relaxation process of amorphous alloy $Fe_{81}B_{13}Si_4C_2$ occurs in 2 stages at all annealing temperatures. The first stage of structural relaxation process is a fast kinetic process, which has a reduced duration with the increase in annealing temperature. The second stage of structural relaxation process is a slow diffusion process. We monitored the temperature dependence of relative change in magnetic susceptibility in 3 heating cycles in temperature range from room temperature up to 460^0C. The increase in magnetic susceptibility upon each heating is caused by structural relaxation process. With every subsequent annealing T_C moves towards higher values as a result of greater thermal stability of the structure due to structural relaxation process. Thus, dilatometric and thermomagnetic measurements have proved that there is a strong correlation between the structural relaxation process and certain thermal and magnetic properties of the investigated alloy.

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Садржај: *У овом раду испитиван је утицај структурних промена аморфне легуре* $Fe_{81}B_{13}Si_4C_2$ *у облику траке у току процеса одгревања на њена функционална својства. Методом DSC у температурском интервалу од собне температуре до 700* ^{0}*C показано је да ова легура кристалише у једном ступњу. Процес структурне релаксације испитиван је осетљивом дилатометријском методом у неизотермским и изотермским условима. Мерењем топлотног ширења при константним темпаратурама* $m_1 = 420^0C$, $m_2 = 440^0C$ *и* $m_3 = 460^0C$ *показано је да се процес структурне релаксације одиграва у два ступња. У првом ступњу егзистира линеарна зависност логаритамске зависности топлотног ширења од времена при константној температури. Други ступањ структурне релаксације карактерише линеарна зависност изотермског топлотног ширења од квадратног корена времена. Ови резултати указују на закључак да је први процес брзи кинетички, а други спори дифузиони процес. За оба процеса одређене су константе брзине* $\kappa_{11} = 2{,}27\cdot10^{-3}\ s^{-1}$, $\kappa_{12} = 2{,}79\cdot10^{-3}\ s^{-1}$, $\kappa_{13} = 3{,}6\cdot10^{-3}\ s^{-1}$, $\kappa_{21} = 0{,}67\cdot10^{-4}\ s^{-1}$, $\kappa_{22} = 3{,}72\cdot10^{-4}\ s^{-1}$, $\kappa_{23} = 21{,}53\cdot10^{-4}\ s^{-1}$ *и енергије активације* $E_1 = 48{,}64$ *кJ/mol и* $E_2 = 366,\ 23$ *кJ/mol. Термомагнетним мерењима утврђена је изразита корелација између процеса структурне релаксације и релативне промене магнетне сусцептибилности. Показано је да се након структурне релаксације, погодним одгревањима, магнетна сусцептибилност може повећати до 80% при јачини магнетног поља од 8 кA/m.*

Кључне речи: *Аморфни материјали, структурна релаксација, термална експанзија, магнетна сусцептабилност.*