

Mechanical strain and temperature annealing effect on structural relaxation kinetics of the $\text{Fe}_{89.8}\text{Ni}_{1.5}\text{Si}_{5.2}\text{B}_3\text{C}_{0.5}$ amorphous alloy

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Structural changes of amorphous ribbon $\text{Fe}_{89.8}\text{Ni}_{1.5}\text{Si}_{5.2}\text{B}_3\text{C}_{0.5}$, causing its isothermal expansion, were investigated by sensitive dilatation method and X-ray analysis. The measurements were carried out concerning ribbon samples thermal expansion, having been exposed to constant strain degrees of $\sigma_1 = 130$ MPa, $\sigma_2 = 300$ MPa and $\sigma_3 = 475$ MPa at temperatures $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K. It has been determined that isothermal ribbon expansion is caused by the structural relaxation process. It has been shown that structural relaxation process occurs in two stages. In initial time interval linear logarithmic dependence of isothermal ribbon expansion upon time exists. This leads to a conclusion that activationally-controlled process is carried out in this time interval. The process time decreases with the increase in annealing temperature. The second time interval of structural relaxation process is characterized by linear dependence of isothermal expansion upon the square root of process time. Such time dependence of isothermal expansion shows that this time interval of structural relaxation process is a slow diffuse process. For both stages of structural relaxation process, for the ribbon sample exposed to strain degree of 475 MPa, rate constants were determined $k_1' = 6.25 \times 10^{-3} \text{ s}^{-1}$, $k_1'' = 9.56 \times 10^{-3} \text{ s}^{-1}$, $k_1''' = 14.59 \times 10^{-3} \text{ s}^{-1}$, $k_2' = 2.82 \times 10^{-4} \text{ s}^{-1}$, $k_2'' = 6.11 \times 10^{-4} \text{ s}^{-1}$, $k_2''' = 16.48 \times 10^{-4} \text{ s}^{-1}$ as well as activation energies $E_1 = 79.72$ kJ/mol, $E_2 = 165.80$ kJ/mol. The results of X-ray analysis show that during these processes the ribbon preserves its amorphous structure with reduced defects density and reduced internal strain. The paper shows that dilatation method may be successfully used in analysis of structural relaxation process kinetics, which, on the other hand, is not possible by means of DSC and X-ray analyses.

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1. Introduction

Annealed glassy alloy is far from the equilibrium state. By heating, glassy alloys crystallize upon a certain period. Structural relaxation occurs before the onset of crystallization. It is only then that slight changes in the atomic structure occur, which provides metastable state [1]. 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) [2, 3, 4]. Thermal expansion and viscosity of the glassy alloys are structural relaxation-sensitive [5]. When annealed isothermally, the entire glassy alloy shows practically a linear increase in viscosity with the rise of annealing temperature [6, 7]. Viscosity is expected to attain the constant value when the metal glass reaches the metastable state at determined temperature. Measuring of isothermal thermal expansion is suitable for the obtainment of quantitative data related to the key major parameters of the glassy state: activation energy of relaxation, diffusion activation energy, frequency factor, and the initial defect concentration.

2. Experimental

The amorphous ribbons of $\text{Fe}_{89.8}\text{Ni}_{1.5}\text{Si}_{5.2}\text{B}_3\text{C}_{0.5}$ alloy have been investigated. The ribbon samples were 20 cm long, 2 mm wide and 3 μm thick. Both nonisothermal and isothermal expansion of the ribbons was measured at the following strain degrees and temperatures respectively: $\sigma_1 = 130$ MPa, $\sigma_2 = 300$ MPa and $\sigma_3 = 475$ MPa, and $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K. These parameters were measured by a 10^{-5} m sensibility dilatometer. X-ray diffraction analysis of the as-cast and relaxed samples was performed by the $\text{Cu-K}\alpha$ radiation lines on a Phillips PW1710 device.

3. Results and discussion

In our previous papers [8, 9] we showed that the amorphous alloy $\text{Fe}_{89.8}\text{Ni}_{1.5}\text{Si}_{5.2}\text{B}_3\text{C}_{0.5}$ crystallize within the temperature range from 799 K to 890 K. Therefore, the process of the structural relaxation was studied at temperatures for 100 – 150 K lower than initial crystallization temperature. XRD patterns of samples of the investigated alloy exposed to the strain degrees $\sigma_1 = 130$ MPa and isothermally annealed for 30 minutes at

temperatures $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K are shown in the diagram below (Fig. 1).

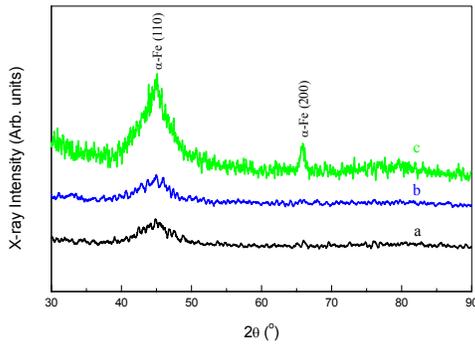


Fig. 1. XRD patterns of samples of the alloy $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ exposed to the strain degrees $\sigma_1 = 130$ MPa and isothermally annealed for 30 minutes at temperatures: a) $T_1 = 653$ K, b) $T_2 = 673$ K and c) $T_3 = 693$ K.

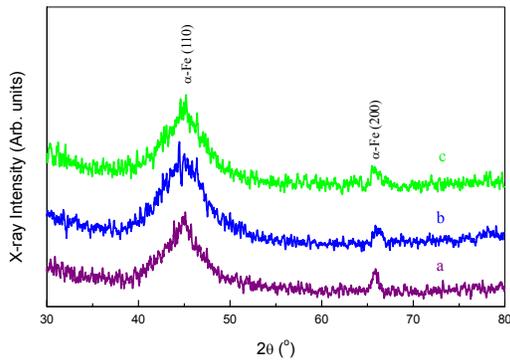


Fig. 2. XRD patterns of samples of the alloy $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ isothermally annealed for 30 minutes at temperature $T_3 = 693$ K, and exposed to the strain degrees: a) $\sigma_1 = 130$ MPa, b) $\sigma_2 = 300$ MPa and c) $\sigma_3 = 475$ MPa.

XRD patterns of annealed samples show the onset of the α -Fe phase crystal grain formation. The material is almost entirely amorphous, thus the peaks are of very low intensity. Bragg reflections for Fe ($2\theta > 80^\circ$) cannot be seen, probably due to the orientation of Bragg reflections which belong to minor groups, i.e. directions: (110) and (200). Therefore, Bragg reflection (211) cannot be seen due to the stated reasons. The diagram in Fig. 2 presents XRD patterns of samples isothermally annealed at $T_3 = 693$ K and exposed to strain degrees $\sigma_1 = 130$ MPa, $\sigma_2 = 300$ MPa and $\sigma_3 = 475$ MPa. Analysis of the XRD patterns given in Fig. 2 and Fig. 3 implies that annealing and mechanical strain had no significant impact on the crystal phases formation, but it only induce relaxation of the amorphous structure.

The diagram in Fig. 3 shows experimentally obtained temperature dependence of the thermal extension of the ribbon (Δl) at the constant heating rate of 20 K/min, and exposed to mechanical strain at degrees $\sigma_1 = 130$ MPa, σ_2

= 300 MPa and $\sigma_3 = 475$ MPa. The low temperature linear dependence of ribbon length $l_0(T)$ on the temperature is given by:

$$l_0(T) = l_0(T_p) \left[1 + \alpha_1^0 (T - T_p) \right], \quad (1)$$

T_p - being the starting temperature of heating, $l_0(T_p)$ - the initial length of the glassy alloy ribbon, α_1^0 - thermal expansion coefficient at low temperatures within the range from T_p to T_g (T_g - ideal glass transition temperature).

The deviation $\Delta l_f(T)$ of the real temperature dependence $l_f(T)$ of ribbon length from $l_0(T)$ may be represented as:

$$\Delta l_f(T) = l_f(T) - l_0(T). \quad (2)$$

The results presented in Fig. 3 show that the most intensive deviation $\Delta l_f(T)$ occurs within the area of glass transition temperature, whereas the deviation for sample exposed to the strain degree $\sigma_1 = 130$ MPa is also observed at temperatures $T < T_g$.

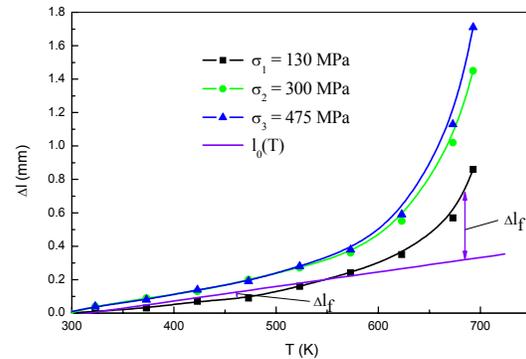


Fig. 3. Dependence of the thermal expansion of the ribbon obtained at the constant heating rate of 20 K/min at strain degrees $\sigma_1 = 130$ MPa, $\sigma_2 = 300$ MPa and $\sigma_3 = 475$ MPa.

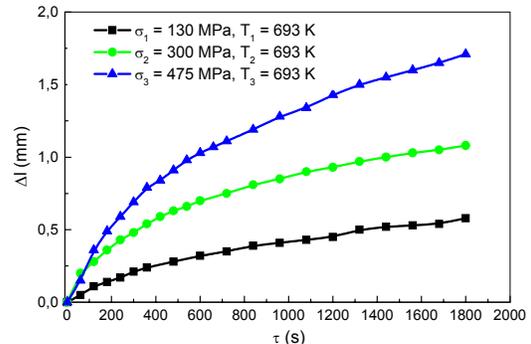


Fig. 4. Dependence of isothermal thermal expansion of the ribbon on strain degrees for 30 minutes, at temperature $T_3 = 693$ K.

The diagram in Fig. 4 presents isothermal dependence of the thermal expansion of the amorphous ribbon samples on strain degrees for 30 minutes, at temperature $T_3 = 693$ K. The analysis of the results presented in Fig. 4 reveal that structural relaxation process of the amorphous alloy $\text{Fe}_{89.8}\text{Ni}_{1.5}\text{Si}_{5.2}\text{B}_3\text{C}_{0.5}$ during the isothermal process occurs in two stages.

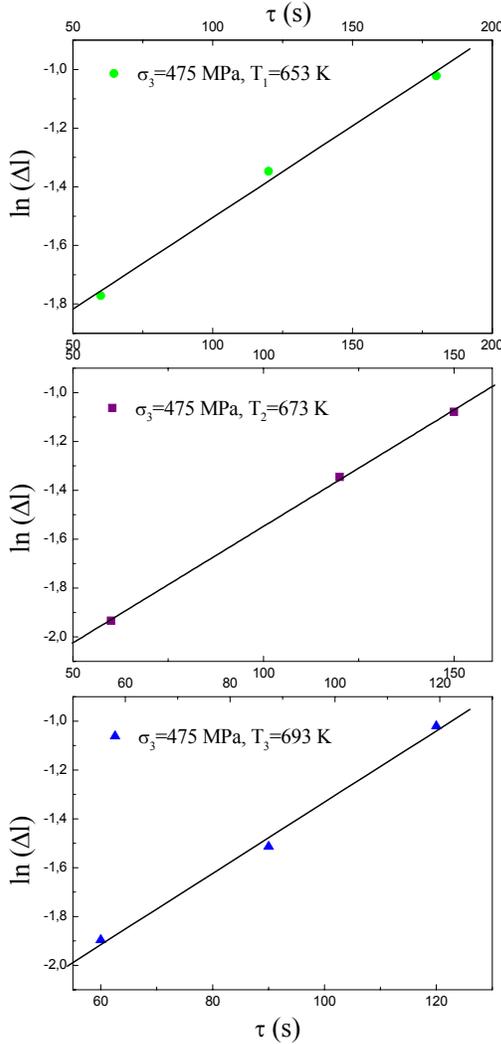


Fig. 5. Logarithmic dependence of isothermal expansion $\ln(\Delta l) = f(\tau)$ on time for the samples exposed to strain degree $\sigma_3 = 475$ MPa at temperatures $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K.

The diagram in Fig. 5 shows logarithmic dependence of isothermal ribbon expansion on time $\ln(\Delta l) = f(\tau)$ for the sample exposed to strain degrees $\sigma_3 = 475$ MPa at temperatures $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K. In initial time interval the obtained linear dependence $\ln(\Delta l) = f(\tau)$ shows that at the beginning the structural relaxation process is activationally controlled 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. at $T_1 = 653$ K is $\tau_1 = 180$ s, at $T_2 = 673$ K is $\tau_2 = 150$ s, and at $T_3 = 693$ K is $\tau_3 = 120$ s. The second stage of the structural relaxation process is characterized by the linear dependence $\Delta l = f(\tau^{1/2})$ (Fig. 6). Such dependence suggests that the second stage of the structural relaxation process is a diffusion process, whereby the inter-cavity atoms move and the free volume decreases. Fig. 6 shows incomplete diffusion process during annealing to 1800 s at the stated temperatures. The rate constants for both stages of the structural relaxation process were determined from the slope $\Delta \ln(\Delta l) / \Delta \tau$ (Fig. 5) and $\Delta l / \Delta(\tau^{1/2})$ (Fig. 6).

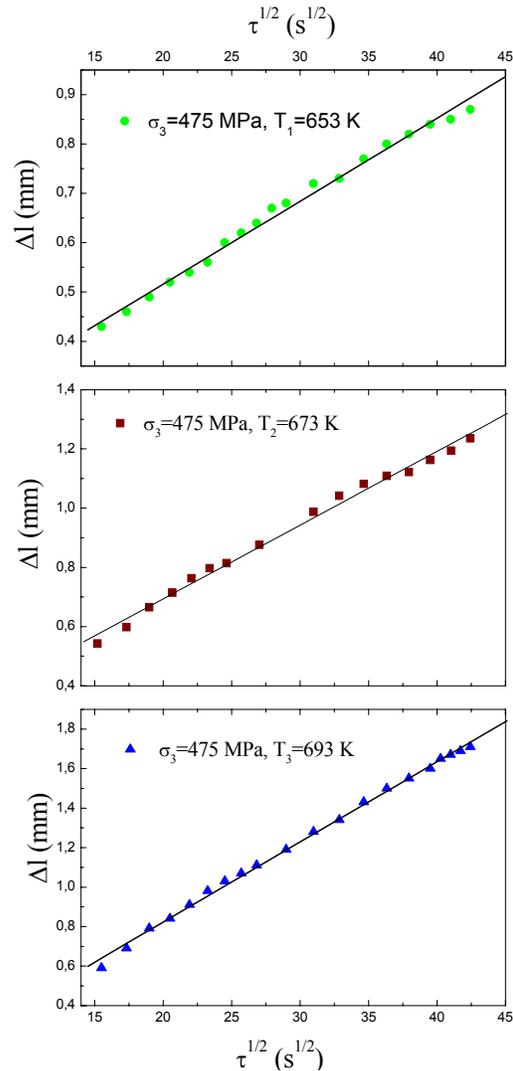


Fig. 6. Dependence of the isothermal expansion $\Delta l = f(\tau^{1/2})$ on the square root of the process time for the samples exposed to the strain degree $\sigma_3 = 475$ MPa at temperatures $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K.

Fig. 7 shows the dependences $\ln(k) = f(1000/T)$. Activation energy for kinetic (E_1) and diffusion (E_2) processes

of structural relaxation were determined from the slope $\Delta \ln k / \Delta(1/T)$ according to equation:

$$E = R \frac{\Delta \ln k}{\Delta \left(\frac{1}{T} \right)}, \quad (3)$$

R - being universal gas constant.

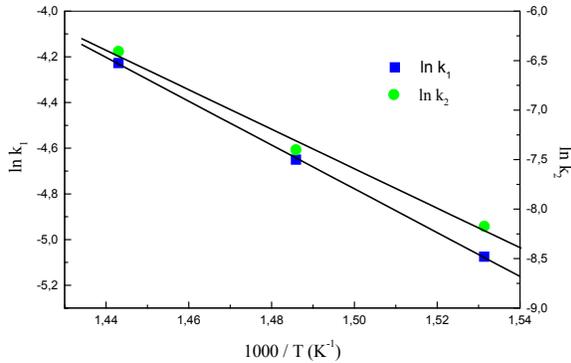


Fig. 7. Dependence $\ln k$ on $1/T$ of the samples of alloy $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ exposed to the strain degrees of 475 MPa and annealed at temperatures 653 K, 673 K and 693 K for 30 minutes ($\ln k_1$ – the first stage, $\ln k_2$ – the second stage of structural relaxation process).

The obtained values for kinetic parameters are shown in Table 1.

Table 1. Kinetic parameters for structural relaxation process of the samples of alloy $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ annealed at temperatures 653 K, 673 K and 693 K and exposed to the strain degree of 475 MPa

σ (MPa)	T (K)	$k_1 \cdot 10^{-3}$ (s ⁻¹) 1)	$k_2 \cdot 10^{-4}$ (s ⁻¹)	E_1 (kJ/mol)	E_2 (kJ/mol)
475	653	6.25	2.82	79.72	165.80
	673	9.56	6.11		
	693	14.59	16.48		

4. Conclusions

Experimental investigation of as-cast and annealed samples of alloy $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ confirmed that all the annealed samples have a relaxed amorphous structure, characterized by the onset of α -Fe phase crystal grain formation. The results of isothermal expansion of the amorphous ribbon exposed to strain degree of 475 MPa at temperatures $T_1 = 653$ K, $T_2 = 673$ K and $T_3 = 693$ K show that the structural relaxation process occurs in

2 stages. Linear dependence $\ln(\Delta l) = f(\tau)$ shows that in this time interval structural relaxation is activationally-controlled process. The duration of this interval decreases with the rise in annealing temperature, i.e. at $T_1 = 653$ K is $\tau_1 = 180$ s, at $T_2 = 673$ K is $\tau_2 = 150$ s, and at $T_3 = 693$ K is $\tau_3 = 120$ s. The second time interval of the structural relaxation process is characterized by the linear dependence $\Delta l = f(\tau^{1/2})$, which leads to the conclusion that the second stage is a slow diffusion process. Fig. 6 shows incomplete diffusion process during 30 minute measuring time. The paper has shown that dilatation method may be successfully used in the analysis of structural relaxation process of amorphous ribbons, which is not possible by means of X-ray and DSC methods.

Acknowledgements

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