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ISOTHERMAL EXPANSION OF THE $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ AMORPHOUS ALLOY

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ABSTRACT

Structural changes of the $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ amorphous ribbon that result in its isothermal expansion have been studied by sensitive dilatometrical method and X-ray diffraction (XRD) analysis. Thermal expansion of the ribbon samples exposed to the constant strain degrees σ_1 = 130 MPa, σ_2 = 300 MPa and σ_3 = 475 MPa at temperatures T_1 = 653 K, T_2 = 673 K and T_3 = 693 K was measured. The results of the study suggest that the thermal expansion of the ribbon was induced by the process of the structural relaxation, and these inferred that the process included two stages. The first stage is characterized by the linearity of logaritmical dependence of isothermal expansion of the ribbon on time, which implies that this stage of the structural relaxation is a rapid kinetic process. The second stage of the structural relaxation process is characterized by the linear dependence of the isothermal expansion on the square root of the process duration ($\Delta l = f(\tau^{1/2})$). Such dependence of isothermal expansion on time shows that the structural relaxation process is a slow diffusion process. In both stages of the structural relaxation process, the rate constants were determined, as it follows: $k_1' = 6{,}25 \cdot 10^{-3}\ s^{-1}$, $k_1'' = 9{,}56 \cdot 10^{-3}\ s^{-1}$, $k_1''' = 14{,}59 \cdot 10^{-3}\ s^{-1}$, $k_2' = 2{,}82 \cdot 10^{-4}\ s^{-1}$, $k_2'' = 6{,}11 \cdot 10^{-4}\ s^{-1}$, $k_2''' = 16{,}48 \cdot 10^{-4}\ s^{-1}$. *The results of the XRD analysis suggest that the alloy maintains its amorphous stucture through all processes, whereas both defect density and internal strain remain reduced.*

Keywords: Amorphous alloy, thermal expansion.

1. INTRODUCTION

Annealed glassy alloy is far from the equlibrium state. By heating, 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) [1, 2, 3]. Thermal expansion and viscosity of the glassy alloys are structural relaxation-sensitive [4]. When annealed isothermally, the entire glassy alloy shows practically a linear increase in viscosity with the rise of annealing temperature [4]. Viscosity is expected to attain the constant value when the metal glass reaches the metastable state at the isothermal expansion temperature. Measuring of isothermal thermal expansion is suitable for the obtainment of quantitative data related to the next major parameters of the glassy state: activation energy of relaxation, activation energy of the diffusion flow, frequency factor, and the initial defect concentration.

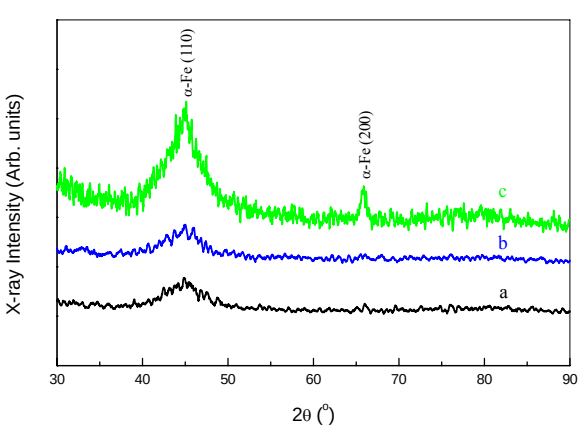
2. EXPERIMENTAL

The amorphous ribbons with composition $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ has been investigated. The ribbon samples were 20 cm long, 2 mm wide and 3 μm thick. Both nonisothermal and isothermal expansion of the ribbon were measured at the following strain degrees and temperatures respectively: σ_1 = 130 MPa, σ_2 = 300 MPa and σ_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} sensibility dilatometer. X-ray diffraction (XRD) analysis of the initial and relaxed samples was performed by the K_α radiation of the copper anticathode.

3. RESULTS AND DISCUSSION

In our previous paper [5] we showed that the amorphous alloy $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ cristalize within the temperature range from 803 K to 900 K. Therefore, the process of the structural relaxation was studied at temperatures for 100 – 150 K lower than the former range. XRD patterns of samples of the investigated alloy exposed to the strain degrees σ_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 bellow (Fig. 1).



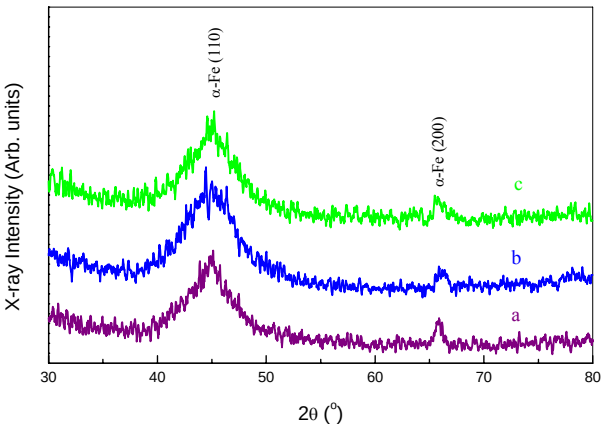


Fig. 1 (left) XRD patterns of samples of the alloy $F_{e89.8}N_{i1.5}S_{i5.2}B_3C_{0.5}$ exposed to the strain degrees σ_1 = 130 MPa and isothermally annealed for 30 minutes at temperatures a) T_1 = 653 K, b) T_2 = 673 K, and c) T_3 = 693 K.

Fig 2 (right) XRD patterns of samples of the alloy $F_{e89.8}N_{i1.5}S_{i5.2}B_3C_{0.5}$ isothermally annealed for 30 minutes at temperatures T_3 = 693 K, and exposed to the strain degrees: a) σ_1 = 130 MPa, b) σ_2 = 300 MPa, and c) σ_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 ($2\cdot\theta > 80^o$) 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 σ_1 = 130 MPa, σ_2 = 300 MPa and σ_3 = 475 MPa. Analysis of the XRD patterns given in Fig. 1 and Fig. 2 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 σ_1 = 130 MPa, σ_2 = 300 MPa and σ_3 = 475 MPa. Low temperature linear dependence of the ribbon length $l_0(T)$ is expressed by the formula:

$$l_o(T) = l_o(T_P)\left[1+\alpha_l^o\left(T-T_P\right)\right], \quad (1)$$

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

Digression $\Delta l_f(T)$ of the actual temperature dependence $l_f(T)$ of the ribbon length $l_0(T)$ may be presented by the formula:

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

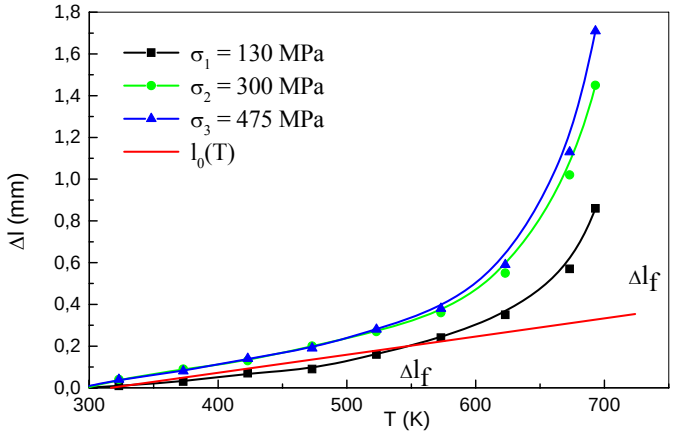


Fig. 3 Dependence of the thermal extension of the ribbon obtained at the constant heating rate of 20 K/min. at strain degrees σ_1 = 130 MPa, σ_2 = 300 MPa and σ_3 = 475 MPa.

The results presented in Fig. 3 show that the most intensive digression $\Delta l_f(T)$ occurrs witin the field of glass transition temperature, whereas the digression for sample exposed to the strain degree σ_1 = 130 MPa is also observed at temperatures $T < T_g$.

The diagram in Fig. 4 presents isothermal dependence of the thermal expansion of the amorphous ribbon samples on 30 min-strain degrees, at temperature T_3 = 693 K.

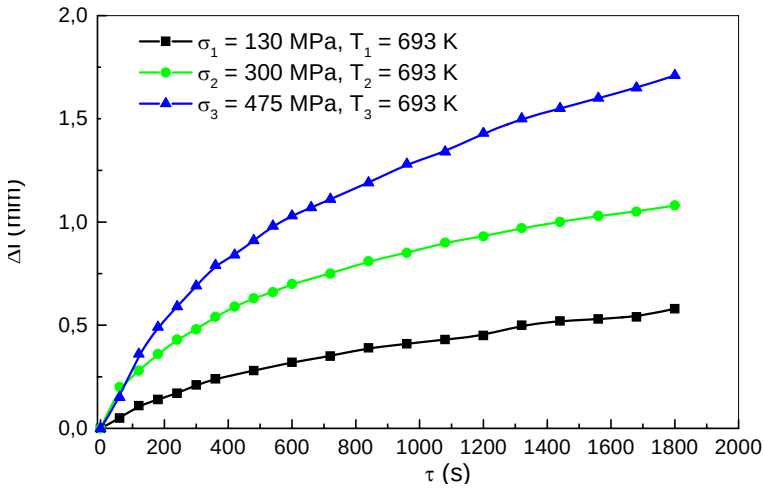


Fig. 4 Dependence of isothermal thermal expansion of the ribbon on 30 min-strain degrees for 30 minutes , at temperature T_3 = 693 K.

The analysis of the results presented in Fig. 4 reveal that structural relaxation process of the amorphous alloy $Fe_{89.8}$ $Ni_{1.5}Si_{5.2}B_3C_{0.5}$ during the isothermal process occurs in two stages. The diagram in Fig. 5 shows logarithmic dependence of isothermal ribbon expansion on time ln (Δl) = f(τ) for the sample exposed to strain degrees σ_3 = 475 MPa at temperatures T_1 = 653 K, T_2 = 673 K, and T_3 = 693 K. Obtained linear dependence ln (Δl) = f(τ) suggest kinetical nature of the first stage of the structural relaxation. The duration of the first stage of the structural relaxation process decreases with the rise of annealing temperature, i.e. at T_1 = 653 K is τ_1 = 180 s, at , T_2 = 673 K is τ_2 = 150 s, and at T_3 = 693 K is τ_3 = 120 s.

The second stage of the structural relaxation process is characterized by the linear dependence Δl = f($\tau^{1/2}$) (Fig. 6). Such dependence suggests that the second stage of the structural relaxation process is a slow diffusion process, whereby the inter-cavity mass moves and the free volume decreases.

Fig. 6 shows incomplete diffusion process during annealing to 1800 s at the stated temperatures. The curves ln Δl (τ) (Fig. 5) and Δl ($\tau^{1/2}$) (Fig. 6) determine the rate constants for both stages of the structural relaxation process: $k_1' = 6{,}25 \cdot 10^{-3}\ s^{-1}$, $k_1'' = 9{,}56 \cdot 10^{-3}\ s^{-1}$, $k_1''' = 14{,}59 \cdot 10^{-3}\ s^{-1}$, $k_2' = 2{,}82 \cdot 10^{-4}\ s^{-1}$, $k_2'' = 6{,}11 \cdot 10^{-4}\ s^{-1}$, $k_2''' = 16{,}48 \cdot 10^{-4}\ s^{-1}$.

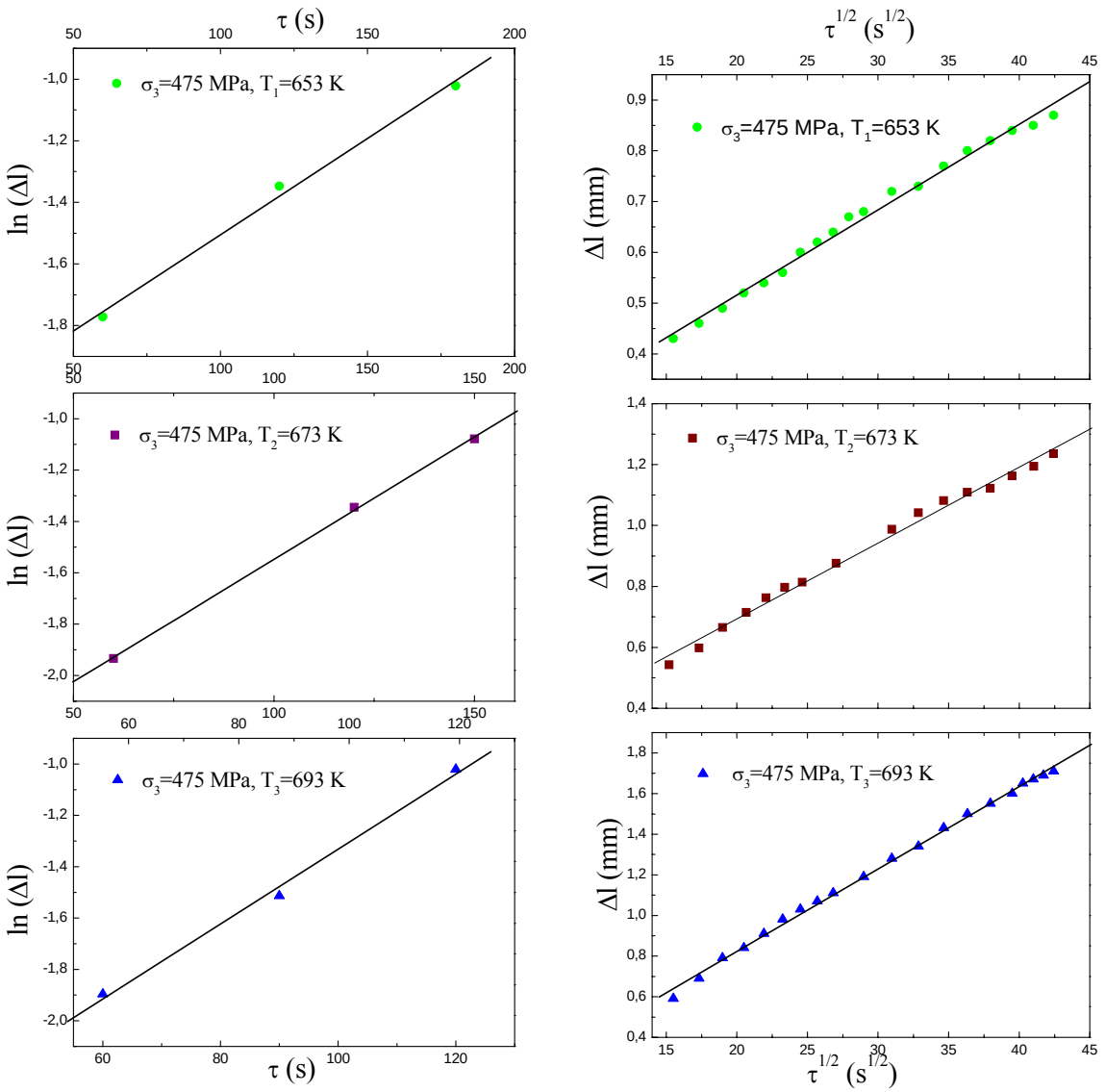


Fig. 5 (left) Logarithmic dependence of isothermal expansion ln(Δl) = f(τ) on time for the sample exposed to strain degrees σ_3 = 475 MPa at temperatures T_1 = 653 K, T_2 = 673 K and T_3 = 693 K.

Fig. 6 (right) Dependence of the isothermal expansion $\Delta l = f(\tau^{1/2})$ on the square root of the process time for the sample exposed to the stain degrees σ_3 = 475 MPa at temperatures T_1 = 653 K, T_2 = 673 K and T_3 = 693 K.

4. ACKNOWLEDGEMENTS

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