RELAXATION PROCESSES IN AN AMORPHOUS $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ ALLOY IN THE PRE-CRYSTALLIZATION TEMPERATURE INTERVAL

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The variations of the structurally dependent characteristics of an amorphous $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ alloy, which had undergone a thermal treatment within the pre-crystallization temperature interval, have been studied. Substantial changes in the behaviors of the mechanical stress relaxation parameter, temperature coefficient of resistance, coercitivity, and residual magnetization of an amorphous ribbon, provided the annealing temperature is within the indicated interval, have been discovered. The phenomena observed have been explained by the existence of two substantially different mechanisms of structural relaxation: the low-temperature local mechanism and the high-temperature diffusion-governed one. The relation for calculating the critical temperature of the relaxation mechanism changeover has been proposed.

1. Introduction

Amorphous, magnetically soft, “metal—Co-based metalloid” ribbons possess the properties which provide their wide use in instrument- and transformer-making industries. One of the technological stages in fabricating the magnetically soft ribbons is their annealing in order to reduce hardening-induced stresses which influence negatively the magnetically soft properties of the ribbons [1]. The character of modifications of the physical properties of amorphous materials due to their thermal treatment is known [2, 3] to be governed by the processes of structural transformation. It is rather difficult to study structural changes in amorphous multicomponent alloys, which are being subjected to a thermal action, experimentally in a straightforward way. Nevertheless, the processes of structural relaxation in such materials can be investigated indirectly, making use of their structurally sensitive properties. Such researches are challenging, because they enable an optimal choice between the regimes of thermal treatment to be made in order to improve the operational characteristics of amorphous ribbons. Therefore, this work is aimed at studying the variations of the structurally sensitive characteristics of amorphous, magnetically soft $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ ribbons subjected to thermal treatment.

2. Materials and Methods

Following the Luborsky method [4], we studied the relaxations of mechanical stresses in an amorphous cobalt-based ribbon 20 μm in thickness and 9 mm in width. The ribbon was fabricated by spinning in the argon atmosphere. According to the method, a ribbon specimen was curled onto and fixed at a cylindrical holder of the radius $R_0 = 5$ mm. In so doing, the mechanical stresses, the amplitude of which depended on the curvature radius of the holder, arose in the ribbon. After the isothermal annealing of the holder together with the specimen fixed at it for a given time interval, the final radius of the specimen R was measured. The quantity $\alpha = 1 - R_0/R$ was adopted as the parameter that characterized the relaxation of mechanical stresses. The durations of the isothermal annealing were 10, 20, and 30 min.

The ribbons, which had been annealed at the same temperatures, were used to determine the residual magnetization and the coercive force at a magnetic reversal frequency of 500 Hz and the maximal strength of the magnetic field of 100 A/m, as well as to measure the variation of the electrical resistance while heating them at a rate of 0.2 K/s.

3. Results and Their Discussion

In Fig. 1, the dependence of the parameter of mechanical stress relaxation in the initial alloy on the temperature of isothermal annealing is depicted with an absolute error of 0.02 (curve *1*). From the figure, one can see that the experimental points obtained for the specimen under isothermal annealing for 10, 20, and 30 min practically lie along a single curve. Some deviations from this curve started at temperatures higher than 590 K. Therefore, a reduction of mechanical stresses occurred rather quickly, reaching a certain, depending on the temperature, value of the parameter α for several minutes. Curves *2*, *3*, and *4* in Fig. 1 correspond to the specimens that had been annealed for 10 min at temperatures of 518, 568, and 603 K, respectively, before their deformation. Annealing the alloy at the indicated temperatures, which are considerably lower than the crystallization one (770 K [5]), resulted in substantial changes of the relaxation curves: there appeared a plateau, which corresponded to $\alpha = 1$, followed by a drastic reduction of the parameter α. Nevertheless, the temperature, at which the relaxation parameter becomes zero, remained constant. It should be noted that the drastic reduction of the relaxation parameter started at a temperature that was somewhat lower than the temperature of the previous annealing. Such a temperature difference may be caused by the intermediate process of cooling after the previous annealing.

Curve *5* in Fig. 1 describes the relaxation of mechanical stresses in specimens that had been annealed beforehand for 10 min at a temperature of 643 K, which corresponded to the minimal temperature, at which α decreased to zero (curve *1*). In this case, the occurrence of a plateau ($\alpha = 1$) was accompanied by a displacement of the point, at which $\alpha = 0$, towards higher temperatures.

The dependence of the relaxation parameter on temperature for the alloy specimens that had not been annealed beforehand (curve *1*) can be approximated rather exactly by the square-law function of the annealing temperature T:

$$\alpha(T) = 1 - \left(\frac{T - T_0}{T_K - T_0}\right)^2. \quad (1)$$

Here, $T_0 = 293$ K is the room temperature, and T_K is the minimal temperature, which corresponds to $\alpha = 0$ (for curve *1* in Fig. 1, $T_K = 643$ K).

Supposing a similar dependence of the relaxation parameter for other amorphous alloys, relation (1) can be applied to determine the temperature of complete relaxation T_K, making use of only a single experimental value $\alpha(T)$,

$$T_K = T_0 + \frac{T - T_0}{\sqrt{1 - \alpha(T)}}, \quad (2)$$

or taking into account the definition $\alpha = 1 - R_0/R(T)$,

$$T_K = T_0 + (T - T_0)\sqrt{R(T)/R_0}. \quad (3)$$

The obtained experimental data can be explained if one assumes that stresses do not relax in the whole volume of the specimen, but relax only in those regions, where the sum of mechanical stresses (induced by both the bending and the hardening of the ribbon) exceeds a certain threshold value. Such a threshold stress, in its turn, decreases as the annealing temperature grows. Therefore, the growth of the annealing temperature is also accompanied by the increase in the number of regions, where stresses are reduced through a local rearrangement of atoms.

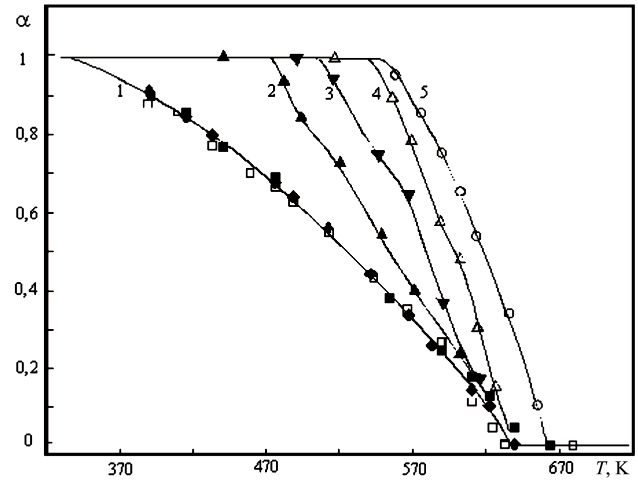

Fig. 1. Influence of isothermal annealing on mechanical stress relaxation in amorphous alloy $Co_{68}Fe_4Cr_4Si_{13}B_{11}$: annealing for 10 (solid squares), 20 (diamonds), and 30 min (hollow squares); preliminary annealing of the specimens at 518 (solid deltas), 568 (grey nablas), 603 (hollow deltas), and 643 K (circles)

Hence, stresses relax at the initial stage of annealing, until all the regions, where mechanical stresses exceed some threshold value at this temperature, disappear.

This supposition allows also the appearance of the plateau in the temperature dependence of the mechanical stress relaxation for preliminarily annealed specimens to be explained. The elastic deformation of a ribbon annealed beforehand and its following annealing do not bring about the change of the ribbon shape until the annealing temperature reaches the values that are sufficient for the residual stresses to relax. The mechanism specified agrees with the model of the amorphous alloy structure proposed in work [4]. According to this model, the amorphous alloy consists of liquid-like regions with an enhanced free volume and crystal-like regions with a small free volume; the dimensions and the number of the crystal-like clusters grow as the temperature decreases. At temperatures well below the glass-transition one T_g, the crystal-like regions

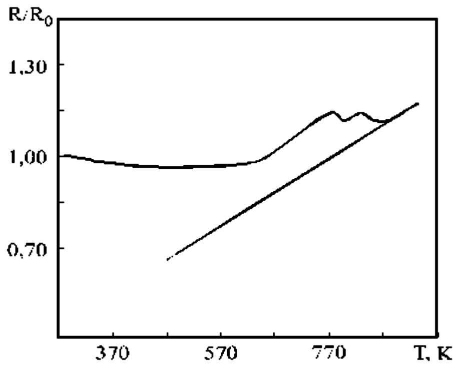

Fig. 2. Dependence of the electroresistance of alloy $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ on temperature while heating the specimen at a rate of 0.2 K/s

form a rigid matrix (skeleton) which separates liquid-like regions from one another.

Proceeding from this model and taking into account the results obtained, one may assume that the skeleton would “collapse” at the initial stages of the annealing into the regions, where the stresses are maximal, i.e. the separation degree of the regions with the enhanced free volume reduces. It provides a certain relaxing of mechanical stresses, the coalescence of the free volume regions, and, in due time, the “ restoration” of the skeleton. The growth of the annealing temperature up to that, at which the separation of individual liquid-like regions disappears leads to the complete relaxation of mechanical stresses.

It should be noted that the alloy specimens that were annealed at temperatures above 600 K become brittle and can be broken in pieces relatively easily. We have estimated the influence of the annealing duration on the embrittlement temperature, which was defined as the minimal annealing temperature of the ribbons, at which the specimen, being bent over the safety razor blade, broke in pieces. This temperature fell down from 660 K at the 10-min isothermal annealing to 630 and 620 K at the 20- and 30-min annealings, respectively.

According to the results of work [6], the enhancement of the embrittlement of amorphous alloys belonging to the metal—metalloid system is caused by the change of their chemical short-range order and the formation of regions which are inhomogeneous by chemical composition. At the same time, in works [7, 8], the enhancement of the embrittlement was explained by the coalescence of the free volume regions and the formation of micropores which stimulate the formation of cracks.

In order to gain a better insight into the processes that take place in an amorphous ribbon subjected to heating, the studies of the dependence of the electroresistance on temperature were carried out (Fig. 2). From the figure, one can see that, at low temperatures, the alloy was characterized by the temperature coefficient of electroresistance close to zero. At a temperature above 640 K, the curve $R(T)/R_0$ demonstrates a sharp turn, i.e. the temperature coefficient of electroresistance starts to grow. At higher temperatures, up to those when the crystallization commences on, a linear growth of electroresistance was observed. In this case, the temperature coordinate of the knee point is practically equal to the temperature of complete relaxation T_K.

The crystallization of $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ alloy in the course of isothermal annealing was shown earlier [5] to differ substantially from that under pulse laser heating. Supposing that the amorphous alloy “inherits” its structure from the melt before hardening and taking into account that, in contrast to the isothermal annealing conditions, the pulse laser heating cannot provide a sufficient duration of the thermal influence for extended diffusion processes to run, one may put forward an assumption concerning the pre-crystallization stratification of the amorphous matrix in the course of isothermal annealing. Such a stratification, which might occur at temperatures not lower than 640 K, could ensure the difference between the crystallization processes under the conditions of thermal influence specified above and, obviously, could predetermine the drastic growth of the thermal coefficient of electrical resistance.

The validity of our assumption concerning the variation of the character of structural relaxation processes at temperatures close to T_K could be verified by confronting them with the corresponding variations in the behavior of the temperature dependences of other structurally sensitive properties of the alloy. The results of measurements of the magnetic characteristics of isothermally annealed specimens of $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ alloy are presented in the table.

Coercive force and residual magnetization of alloy $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ after the isothermal 30-min annealing

Annealing temperature, K	Initial state	493	513	533	533	573	593	613	633	653	673
H_c, A/m	10,8	10.9	10.8	8.8	8.6	8.3	7.9	7.5	7.4	7.6	7.6
B_r, Tl	0.16	0.16	0.16	0.16	0.16	0.16	0.17	0.18	0.21	0.24	0.24

Isothermal annealing at temperatures up to 513 K inclusively did not affect the coercive force $H_c = 10.8$ A/m and the residual magnetization $B_r = 0.16$ T measured for the initial specimen. Annealing at temperatures within the interval 533 to 633 K resulted in reducing the coercive force and growing the residual magnetization. The coercive force and the residual magnetization of the specimens annealed at temperatures of 653 and 673 K amounted to 7.6 A/m and 0.24 T, respectively.

It is of interest that while measuring either the mechanical stress relaxation or the electroresistance, the changes in the character of the dependences of H_c and B_r on the annealing temperature were observed at a temperature of about 643 K. The authors of work [9], where the specimens of amorphous alloys $(Co_{0.95}Fe_{0.05})_{75}Si_{10}B_{15}$ and $(Co_{0.92}Fe_{0.08})_{75}Si_{15}B_{10}$ were annealed by energizing them, also pointed out the existence of a critical temperature, at which the influence of the annealing duration on the magnetic properties of the specimen changed its character. This temperature was 613 K for the former alloy, and 629 K for the latter. Hence, the values of the critical temperatures obtained in work [9] are close to that obtained in this work for alloy $Co_{68}Fe_4Cr_4Si_{13}B_{11}$.

Therefore, one may assert that there exist two mechanisms of relaxation processes in the amorphous alloy $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ which run in different temperature intervals. At temperatures lower than 643 K, the structural relaxation occurs, mainly, owing to localized liquid-like regions with high levels of the free volume and the free energy. Certainly, it is impossible to draw a sharp line between crystal-like and liquid-like regions, because it is reasonable to assert that they possess certain distributions of the free energy and the volume values. Therefore, the disconnection of these regions decreases as the temperature grows, which, in its turn, enables the process of mechanical stress relaxation and promotes the coalescence of the free volume regions. In due course, the coalescence results in that the amorphous alloy becomes brittle. As the temperature reaches 643 K, the disconnection of liquid-like regions disappears completely, which enables the concentration stratification, so that structural modifications become more expanded and governed by diffusion.

It is this transition from one mechanism of structural relaxation to the other that causes different characters of the dependences of physical properties on the thermal treatment temperature in low- and high-temperature intervals.

4. Conclusions

1. Two mechanisms of structural relaxation of the amorphous alloy $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ in the pre-crystallization temperature interval have been established: low-temperature local relaxation in the regions with the enhanced free volume and high-temperature diffusion-governed structural relaxation. The mechanism changeover occurs at a critical temperature of 643 K, and the previous low-temperature annealing does not affect the value of the critical temperature.

2. The empirical relation for calculating the critical temperature, at which the mechanism of structural relaxation is changed, making use of a single value of the parameter of mechanical stress relaxation $\alpha(T)$, has been proposed for amorphous cobalt-based alloys of the metal–metalloid system.

1. *Handrich K., Kobe S.* Amorfe Ferro und Ferrimagnetika. — Berlin: Akademie Verlag, 1980.
2. *Graham C.D., Egami T.* // Ann. Rev. Mater. Sci. — 1987. — **8**. — P. 423—427.
3. *Kobe S., Ferchmin A.R., Nose H., Stobiecki F.* // J. Magn. and Magn. Mater. — 1986. — **60**. — P. 1—135.
4. *Amorphous* Metallic Alloys / Ed. by F.E. Luborsky. — London: Butterworth, 1983.
5. *Girzhon V.V., Rudnev Yu.V., Anpilogov D.I., Smolyakov A.V.* // Scr. Mater. — 1998. — **39**, N 6. — P. 815—823.
6. Metallic Glasses / Ed. by J.J. Gilman, H.J. Leamy. — Metal Park, Ohio: American Society for Metals, 1978.
7. *Glezer A.M., Molotilov B.V., Utevskaya O.L.* // Fiz. Met. Metalloved. — 1984. — **58**, N 5. — P. 991—1000.
8. *Betekhtin V.I., Glezer A.M., Kadomtsev A.G., Kipyatkova A.Yu.* // Fiz. Tverd. Tela. — 1998. — **40**, N 1. — P. 85—89.
9. *Gonzalez J., Vazquez M., Barandiaran J.M., Hernando A.* // J. Phys. D: Appl. Phys. — 1988. — **21**. — P. 162—167.

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РЕЛАКСАЦІЙНІ ПРОЦЕСИ В АМОРФНОМУ СПЛАВІ $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ У ДОКРИСТАЛІЗАЦІЙНОМУ ІНТЕРВАЛІ ТЕМПЕРАТУР

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Р е з ю м е

Проведено дослідження зміни структурно — залежних характеристик аморфного сплаву $Co_{68}Fe_4Cr_4Si_{13}B_{11}$ під дією термообробки в докристалізаційному інтервалі температур. Виявлено істотні зміни характеру поведінки параметра релаксації, температурного коефіцієнта електроопору, зміни коерцитивної сили та залишкової намагніченості аморфної стрічки всередині інтервалу. Спостережувані явища пояснено існуванням двох суттєво різних механізмів структурної релаксації сплаву: низькотемпературного локального та високотемпературного контрольованого дифузудією. Запропоновано співвідношення для критичної температури зміни механізму релаксації.