

## Influence of structural relaxation on the performance of Co-based amorphous metallic alloys

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The influence of structural relaxation on the electric resistivity  $\rho$  and structure parameters of low-alloyed Co–Cr–Si–B amorphous metallic alloys has been studied. These materials show a minimum in  $\rho(T)$  dependences. It has been shown that the structural relaxation of the studied alloys does not change the general shape of  $\rho(T)$  curves, but affects essentially the position of minimum  $T_{min}$ . The high values of  $T_{min}$  are due most likely not only to the presence of alloying component but also by a special composition of the metalloid group. The variation of  $T_{min}$  during structural relaxation is caused by variation of the short-range ordering character.

Исследовано влияние структурной релаксации на электросопротивление  $\rho$  и параметры структуры низколегированных аморфных металлических сплавов (АМС) Co–Cr–Si–B, для которых наблюдается минимум на зависимостях  $\rho(T)$ . Установлено, что структурная релаксация исследованных АМС не изменяет общего вида кривых  $\rho(T)$ , однако существенно влияет на положение минимума  $T_{min}$ . Наиболее вероятно, что высокие значения  $T_{min}$  обусловлены не только наличием легирующих компонентов, но и особым составом металлоидной группы, а изменение  $T_{min}$  при структурной релаксации вызвано изменением характера ближнего порядка.

Amorphous metallic alloys (AMAs) obtained by rapid solidification are known to be metastable systems [1, 2]. Their non-equilibrium extent depends on the quenching conditions, in particular, on the cooling rate. Since the as-quenched materials are characterized by a rather high free volume and relatively low values of short-range ordering parameter, the high-temperature annealing results in a reduction of AMA intrinsic energy due to relaxation towards a more stable state within the range of amorphous structure. According to the modern conceptions, the structural relaxation occurs due to decrease of the free volume, changes of the topological and chemical short-range ordering and residual stress reduction [3, 4]. The result of structural relaxation consists in the evolution of some AMAs functional properties sensitive to the atomic structure (e.g., mechanical, electrical, magnetic, etc.). Very often, the optimal

combination of the AMA functional properties is achieved just in result of structural relaxation. Therefore, AMAs should be preliminary annealed to improve the stability of their performance properties.

The Co-based AMAs are known to be materials of good prospects for industrial applications in magnetic elements and modules of the electronic engineering. Besides, a specific feature of the AMAs based on the Co–Cr–Si–B system is the anomalous behavior of electric resistance vs. temperature  $\rho(T)$ , in particular, the presence of a minimum which may be located even above room temperature. The nature of such behavior have been analyzed in detail in [5]. So, the aim of this work is to study the transport properties of Co–Cr–Si–B AMAs during the structural relaxation.

The investigated samples of Co–Cr–Si–B AMA (10 mm wide and 30–40  $\mu\text{m}$  thick)

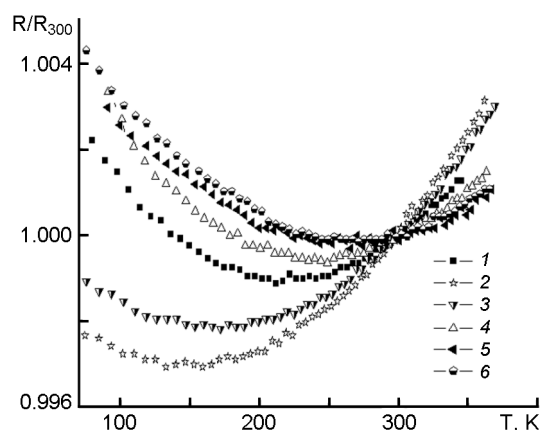


Fig. 1.  $\rho(T)$  dependences for  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMA after heat treatment; 1 – init, 2 – 491 K, 3 – 541 K, 4 – 590 K, 5 – 686 K, 6 – 780 K.

were prepared by single-roll quenching technique using high purity initial materials (better than 99 %). The  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  and  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMAs were studied in most detail. Generally, the structural relaxation of AMAs is realized either by isothermal or isochronal annealing. However, in our work, the relaxation was performed by an alternative procedure, namely by the heating up to a certain temperature at 15 K/min rate and subsequent rapid cooling down to room temperature. To that end, the about 1.2 mm wide and 20 mm long samples were cut out of the ribbons. The samples were placed into high temperature block for  $\rho(T)$  measuring with automatic control of the heating rate. The sample of  $5 \times 7 \text{ mm}^2$  size for the diffraction experiments was also located in the same block close to the sample for resistive studies. After the heat treatment, the standard four-probe method has been used to measure the  $\rho(T)$  dependences in 77–400 K temperature range. The X-ray diffraction investigation was performed using a DRON-4 diffractometer in  $\text{CdK}_\alpha$  radiation.

According to the diffraction data, all the samples have the X-ray amorphous structure even after heat treatment up to 780 K. This indicates that the revealed changes in resistivity are conditioned just by the structural relaxation rather than by the alloy crystallization.

We have stated before [5] that a specific feature in  $\rho(T)$  dependences for AMAs of the Co–Si–B system is the appearance of a minimum when AMA of the basic composition is doped with chromium. The position of this minimum depends essentially on the

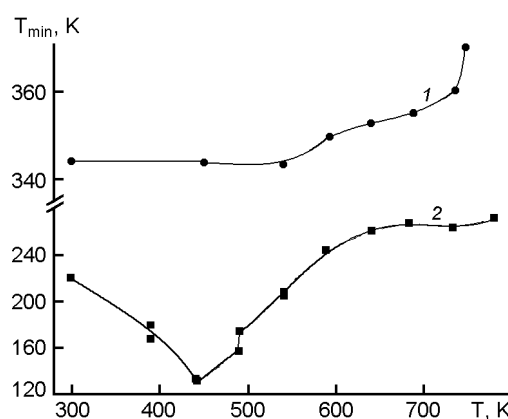


Fig. 2. The dependences of  $T_{min}$  on the annealing temperature  $T_h$  for  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  (1) and  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  (2) AMAs.

Cr content and sometime may exceed the room temperature [5]. Fig. 1 illustrates the influence of the relaxation annealing on the  $\rho(T)$  dependence of the  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  (with the lowest chromium content among the investigated AMAs). It is seen that the structural relaxation of the investigated AMAs does not change the general character of  $\rho(T)$  curves, while affecting strongly the position of minimum  $T_{min}$ . The dependences of  $T_{min}$  on the annealing temperature  $T_h$  for  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  and  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMAs are presented in Fig. 2. The heat treatment even at a temperature lower than 400 K is seen to cause a lowering of  $T_{min}$  for  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMA. It decreases first from 220 to 120 K and then increases up to 260 K reaching the saturation at  $T_h$  near 700 K. At the same time, the electric resistivity at room temperature is found to be less sensitive to the low-temperature treatment. The values of  $\rho$  remain almost invariable up to  $T_h \sim 650$  K and begin to rise only at the treatment temperatures higher than 690 K (Fig. 3).

The higher  $T_{min}$  values have been found to be inherent in AMAs with higher chromium content. In particular,  $T_{min}$  for as-quenched  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  alloy is 340 K. In this case, in contrast to AMA considered before, the  $T_{min}$  value is almost constant (340 K) up to  $T_h = 540$  K. Only at the further elevation of the annealing temperature it gradually increases up to 375 K at  $T_h = 745$  K. The  $\rho_{300}(T_h)$  dependency for this AMA is presented in Fig. 3. It should be noted that this dependence is similar in general to that for  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}(\text{SiB})_{29}$  AMA. However, the difference consists in a weak

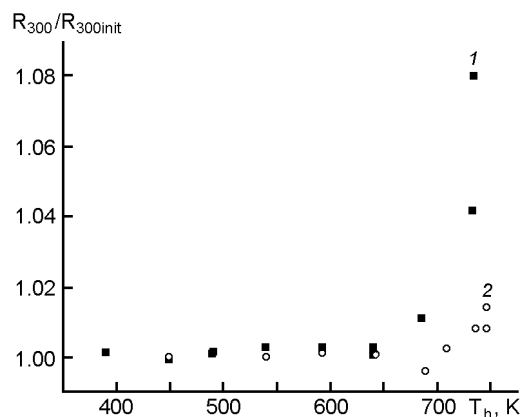


Fig. 3. Normalized resistivity at room temperature as a function of the heat treatment temperature for  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  (1) and  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  (2) AMAs.

reducing of  $\rho_{300}$  at heat treatment of  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  in the range 590–690 K. Besides, the increasing of  $\rho_{300}$  at  $T_h > 700$  K in this case is less pronounced.

Along with the changes of transport properties at relaxation annealing, an evolution of the parameter characterizing the AMA atomic structure was observed. As an example, Fig. 4 presents the variation of the first maximum position of halo  $2\theta$  and its half-width  $w$  as a function of  $T_h$  for  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  (Fig. 4a) and  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  (Fig. 4b) AMAs. The character of these dependences is seen to be somewhat different. The  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMA is characterized by increase of  $2\theta$  value at  $T_h$  up to 490 K and by subsequent reduction at higher temperatures. In contrast, for  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  AMA,  $2\theta$  changes non-monotonously exhibiting a minimum at

$T_h = 590$  K. High-temperature treatment at  $T_h$  exceeding 700 K promotes a considerable decrease of  $2\theta$ . Certain differences between these two alloys are also observed in the  $w(T_h)$  dependences. Moreover, it may be noted that the heat treatment near 750 K causes the structure formation in both AMAs, which is characterized by almost the same values of  $2\theta$  and  $w$ .

It is well known that the first diffraction halo position for amorphous materials is directly related with most probable value of interatomic distance (the higher is the angle, the smaller is the interatomic distance). The half-width reflects the disordering extent and the level of the quench stress (the higher is  $w$ , the higher is the disordering and/or quench stress) [6]. The  $2\theta$  and  $w$  values are  $53.35^\circ$  and  $8.15^\circ$  for as-quenched  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  and  $53.52^\circ$  and  $7.22^\circ$  for as-quenched  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$ , respectively. So, the first AMA can be supposed to be characterized by higher values of either free volume or quench stress. Just this is thought to define some difference in the evolution of the studied characteristics upon structural relaxation. It is known that the doping of Fe based AMAs with chromium results in an increase of structural disordering [7]. Naturally, this should be also expected for the studied AMAs. However, judging from the structural data for (Co,Fe,Cr)–Si–B AMAs with different content of the doping components, it may be supposed that the observed regularities are conditioned not only by difference in AMA composition, but also by a certain difference in the quenching conditions.

The intensity of relaxation, in particular of low-temperature one, is known to be di-

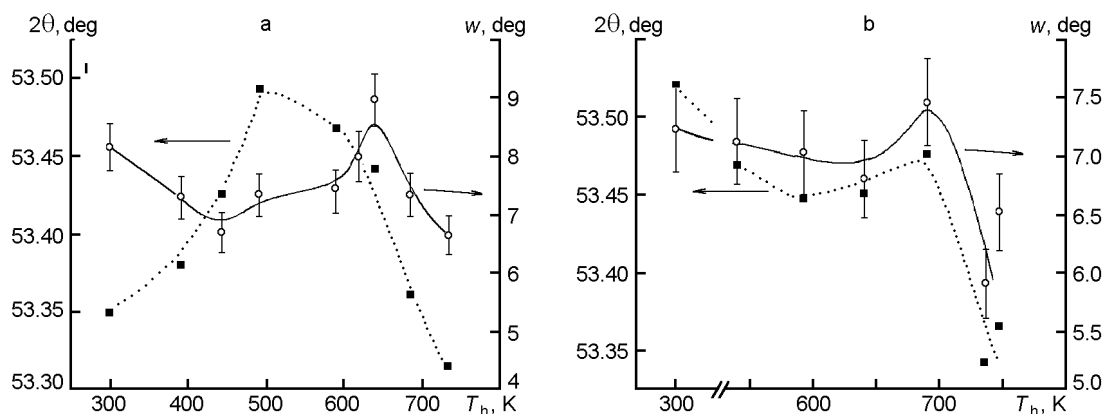


Fig. 4. Variation of the  $2\theta$  halo first maximum position and its half-width  $w$  with  $T_h$  for  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  (a) and  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  (b) AMAs.

rectly defined by the free volume presence in the AMAs [8]. The metalloid atoms essentially govern this process. Their displacement during structural relaxation causes a modification in the short-range ordering and, respectively, formation of a more compact structure (due to free volume exhausting). Since the bonds of chromium with metalloid atoms are stronger in comparison with those for cobalt atoms, the mobility of metalloid atoms turns out to be inhibited at Cr doping. This, respectively, improves the thermal stability of the amorphous structure [9]. An increase of  $2\theta$  value (i.e., a decrease of mean interatomic distance) has been observed upon annealing of  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMA up to  $T_h \sim 500$  K. In other words, a more compact amorphous structure is formed. At the same time, the half-width of the diffraction halo decreases. This implies that free volume reduces and could reflect the variation of the short-range ordering. In contrast, the relaxation annealing of  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  AMA (characterized by a higher structural ordering in the as-cast state) at a temperature lower than  $T_h \sim 600$  K slightly decreases the value of  $2\theta$ . This cannot be ascribed unambiguously to the free volume exhausting, however, may be conditioned by the micro-stress reduction. The latter is confirmed by a slight decrease of the diffraction halo half-width. However, the structural relaxation process at higher  $T_h$  (600–700 K) is controlled mainly by the structure densification that results in a reduction of the mean interatomic distance (the increasing  $2\theta$ ). The revealed difference in the temperature behavior of structural parameters at low annealing temperatures for these two AMAs is caused most likely not only by the difference in structural state of the as-cast samples, but also by the different chromium content [9]. The rising of  $T_h$  above 650 K for  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMA and above 700 K for  $\text{Co}_{69}\text{Cr}_3\text{Si}_{18}\text{B}_{10}$  AMA results in a sharp decrease of  $2\theta$  and  $w$ . Moreover, the values of these structural parameters for both compositions were found to become almost the same at  $T_h \sim 750$  K. In this case, the occurring changes of the structural parameters are considered to be due to variation of the chemical short-range ordering in the nearest neighbor of metal atoms.

A peculiar feature of the studied AMAs is the anomalous behavior of  $\rho(T)$  curves, in particular, the presence of a minimum, which position may exceed the room temperature. The nature of such anomalous be-

havior has been analyzed in more detail in [5]. The nature of this anomaly is thought to be related with the presence of Cr and its position were shown to be determined by the chromium contents or, more precisely, by the presence of atomic inhomogeneities with antiferromagnetic interaction of Cr atoms and neighboring Co atoms. The analysis performed in [5] has shown that the most probable additional mechanism of the scattering is the electron-electron interaction causing the presence of a term in total resistivity decreasing with temperature. Other mechanisms of carrier scattering (the Faber-Ziman, magnon etc.) increase with temperature. So, the common action of these contributions promotes the onset of resistivity minimum.

However, the nature of high  $T_{min}$  values remains currently still unclear. The most probable reason is related with the composition of metalloid group in the studied alloys. For example, the character of  $\rho(T)$  curves for  $\text{Co}_{78}\text{Cr}_x\text{Si}_6\text{B}_{14}$  AMAs is close to linear that is typical of AMAs on the base of transition metals. So, even insignificant changes in the nearest atomic neighboring of chromium atom may modify strongly the scattering parameters and, respectively, the  $T_{min}$  position. According to the structural data, the changes occurring in  $\text{Co}_{66}\text{Fe}_{3.8}\text{Cr}_{1.2}\text{Si}_{17}\text{B}_{12}$  AMA after the low-temperature relaxation annealing are conditioned by the free volume exhausting. This, in turn, results in a substantial change of the short-range ordering degree and, respectively, in a considerable variation of  $T_{min}$  as compared to those for the other studied AMA. This is seen to be the most probable reason for  $T_{min}$  enhancement, since the evolution of the chemical short range ordering takes place for both compositions at sufficiently high annealing temperatures. This confirms an essential role of the atomic neighboring, in particular, of the cluster structure, in the scattering mechanisms. However, the presented experimental data and the lack of the detailed theories of the carrier scattering in such systems does not permit to propose the ultimate explanation of the physical microscopic mechanisms of the revealed regularities.

Thus, the structural relaxation of Co–Cr–Si–B AMAs has been shown to be accompanied by variations in the topological and chemical short-range ordering. This is confirmed by the X-ray diffraction data. The observed regularities may be considered within the routine models of the relaxation

process in amorphous systems. It has been shown that the structural relaxation of the studied AMAs does not change the general shape of the  $\rho(T)$  curves, but affects essentially the position of resistivity minimum. The most probable reason of high  $T_{min}$  values is thought to be caused not only by the presence of alloying component, but also by a specific composition of the metalloid group. The changes of  $T_{min}$  are conditioned by variations of the short-range ordering upon heat treatment.

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## Вплив структурної релаксації на функціональні властивості аморфних металевих сплавів на основі кобальту

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Досліджено вплив структурної релаксації на електроопір  $\rho$  та параметри структури низьколегованих аморфних металевих сплавів (АМС) Co–Cr–Si–B, які виявляють мінімум на залежностях  $\rho(T)$ . Встановлено, що структурна релаксація АМС, що досліджувалися, не змінює загального вигляду кривих  $\rho(T)$ , але суттєво впливає на положення мінімуму  $T_{min}$ . Найбільш ймовірно, що високі значення  $T_{min}$  обумовлені не тільки наявністю легуючих компонентів, а й особливим складом металоїдної групи, а зміна  $T_{min}$  при структурній релаксації викликана зміною характеру ближнього впорядкування.