Functional Materials 12, No.2 (2005)

Anomalous behaviour of electric resistivity in Co–Si–B based metallic glasses

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Temperature dependences of electric resistivity have been investigated in 300–950 K temperature range for $Co_{65.5}Me_{6.5}(Si,B)_{28}$ metallic glasses (Me = Fe, Cr). Several characteristic temperature intervals have been distinguished in $\rho(T)$ dependences. The minimum of resistivity has been shown to be directly related with the presence of chromium and to be of magnetic nature.

Исследованы температурные зависимости электрического сопротивления металлических стекол $Co_{65.5}Me_{6.5}(Si,B)_{28}$ (Me = Fe, Cr) в интервале 300–950 К. Обнаружены особенности поведения электросопротивления $\rho(T)$ в определенных температурных интервалах. Показано, что минимум электросопротивления непосредственно зависит от наличия примесей хрома и имеет магнитную природу.

Co–Si–B based metallic glasses (MGs) were the subject of several investigations due to their interesting magnetic properties [1, 2]. The magnetic properties depend heavily on composition and on chemical short-range ordering [3]. Meanwhile, the transport properties of these MGs are of great importance for industrial applications, since the eddy current losses depend strongly on the value of resistivity. The doping of basic MGs is known to result in essential variation of their performance properties [4]. Recently, we have reported our data on the influence of Cr and Fe dopants on thermomagnetic behavior and thermal stability of $Co_{72}(Si,B)_{28}$, which was shown to be caused by formation of different types of magnetic clusters [5, 6]. The aim of this work is to analyze the temperature behavior of resistivity of $Co_{72}(Si,B)_{28}$ based amorphous alloys containing small amounts of Fe and Cr with respect to their magnetic properties. Co-based metallic glasses of the general composition $Co_{65.5}Me_{6.5}(Si,B)_{28}$ (Me = Fe, Cr) have been prepared in a form of 10 mm wide and 20–30 μm thick ribbons by single-roll quenching technique using the initial materials of high purity. The melt temperature before ejecting through rectangular nozzle was 100–150 K higher the liquidus temperature, the speed of the quenching disk made from chromic bronze (600 mm in diameter) was 820–850 min^{-1}. The ejection pressure was varied within limits of 15–25 kPa, depending on the casting conditions. Thus, the gap between nozzle and disk was 0.25–0.3 mm. The MGs contents were controlled by X-ray fluorescence. Three $Co_{65.5}Me_{6.5}(Si,B)_{28}$ MGs with different Co:Fe:Cr ratio have been produced, namely, the basic MG with Me = Fe,Cr marked symbolically as #1 and two model MGs with Me = Cr (#2) and Me = Fe (#3).

All samples were analyzed by X-ray diffraction before resistometric and magnetometric measurements. The results obtained prove the amorphous structure of all

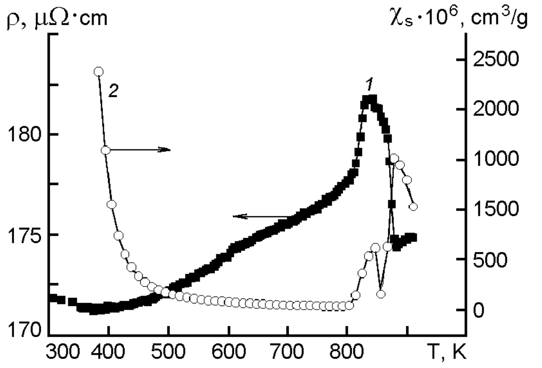

Fig. 1. Temperature dependence of electrical resistivity ρ (*1*) and magnetic susceptibility χ (*2*) for the MG #1.

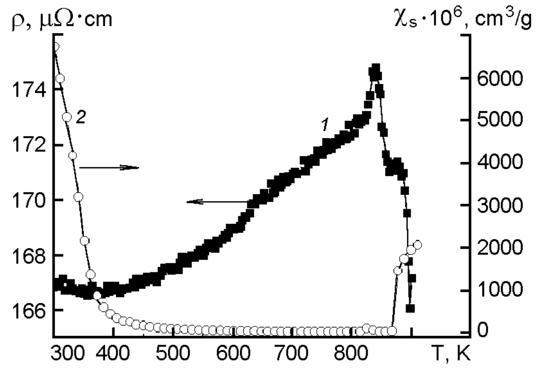

Fig. 2. Temperature dependence of electrical resistivity ρ (*1*) and magnetic susceptibility χ (*2*) for the MG #2.

as-quenched ribbons. No crystalline inclusions were detected. The electrical resistivity $R(T)$ was studied in the temperature range 300–950 K under argon atmosphere using four-probe method being realized in computer-controlled experimental technique. The heating rate was 8 K/min in all experiments. Magnetometric investigations were carried out in the temperature range 300–950 K in the field of 550 kA/m under purified argon medium using Faraday-type magnetometer with microbalance. The accuracy of the susceptibility measurements $\Delta\chi/\chi$ was better than 1.5 % and that of the temperature, $\Delta T < 0.5$ K.

Measurements of the electric resistivity ρ at room temperature (T = 300 K) have shown that its values increase at decreasing chromium content: for MG #2 ρ = (167±2) μΩ·cm, for MG #1, ρ = (172±9) μΩ·cm and for MG #3, ρ = (182±9) μΩ·cm.

Fig. 1 presents the temperature dependence of electric resistivity $\rho(T)$ for the basic alloy #1. Some characteristic temperature intervals are distinguishable in the $\rho(T)$ dependences: I — ρ decreases slightly with temperature elevation ($T \approx$ 290 to 380 K); II — ρ increases nonlinearly ($T \approx$ 380 to 605 K); III — $\rho(T)$ dependence becomes almost linear at T = 605 to 750 K; IV — ρ value increases sharply ($T \approx$ 750 to 835 K); V — a drastic decrease of electric resistivity ($T >$ 835 K).

Fig. 2 presents the temperature dependence of electric resistivity $\rho(T)$ for the MG #2. Similar peculiar intervals are also observed at this dependence: I — $T \approx$ 290 to 350 K; II — $T \approx$ 350 to 640 K; III — $T \approx$ 640 to 790 K; IV — $T \approx$ 790 to 840 K; V — $T >$ 840 K. A specific feature of $\rho(T)$ dependence for MG #2 as compared to the basic composition is the relatively low resistivity increase within the interval IV. The drastic two-stage decrease of ρ is observed at the subsequent heating.

$\rho(T)$ dependence for sample #3 (Fig. 3) differs radically from those presented in Figs. 1 and 2. No resistivity minimum has been revealed. Besides, nonlinearity within the interval II (T = 290 to 505 K) is manifested weakly. The linear part of $\rho(T)$ dependence in this case is expanded enough and is ranged from 505 K to 790 K. A slight decrease of ρ occurs at temperatures exceedingr 790 K. Then, the resistivity increase and abrupt decrease are observed. Such a behaviour is inherent of typical transition metal based MGs at crystallization.

Figs. 1 through 3 present also the temperature dependences of magnetic susceptibility $\chi(T)$ obtained at the same heating rate, since the heating rate influences essentially the crystallization temperature of amorphous alloys. This permits to compare the peculiar regions obtained from magnetic and resistivity measurements. Besides, the obtained $\chi(T)$ dependences permitted us to determine the values of ferromagnetic Curie temperature T_c: 400, 370, and 507 K for specimens #1, #2 and #3, respectively. Magnetic properties of these alloys are discussed in [5, 6] in more detail. Comparison of $\rho(T)$ and $\chi_s(T)$ dependences allows to state the peculiarities of resistivity at $T >$ 750 K, $T >$ 790 K and $T >$ 790 K for #1, #2 and #3, respectively, occur due to crystallization. An additional arguments for the above statement follows from the X-ray diffraction studies of the MGs annealed at the appropriate temperatures. Before, we

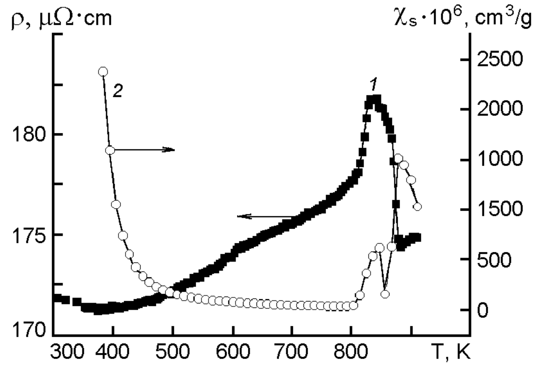

Fig. 3. Temperature dependence of electrical resistivity ρ (*1*) and magnetic susceptibility χ (*2*) for the MG #3.

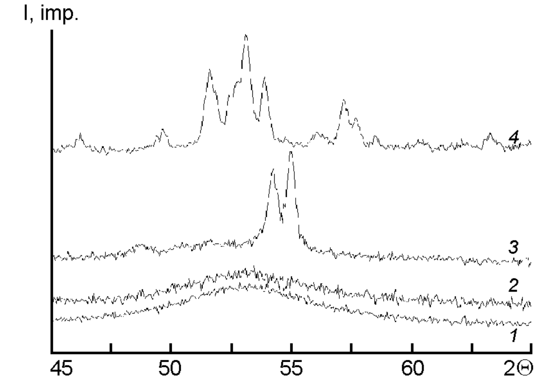

Fig. 4. Parts of the X-ray diffraction patterns for the MG #1 as-quenched (*1*) and annealed at 750 K (*2*), 820 K (*3*) and 870 K (*4*).

have found [5, 6] that the crystallization is two-stage for these MGs. α-Co_2Si phase (Ni_2In-type crystalline phase; space group $P6_3/mmc$, a = 0.3881 nm and c = 0.4850 nm is formed at first stage; β-Co_2Si (space group *Pnmm*, a = 0.49255 nm, b = 0.37445 nm, c = 0.71082 nm) and distorted $(Co,Me)_3B$ (space group *Pmmm*) phases are formed at the second stage. Fig. 4 displays as an example the parts of diffraction patterns for MG #1 obtained for different annealing temperatures. So, the anomalous behaviour of ρ in the near-crystallization region is caused by the formation of α-Co_2Si phase with relatively high resistivity. The subsequent decrease of ρ is caused due both to formation of $(Co,Me)_3B$ and polymorph α-Co_2Si → β-Co_2Si transformation.

The ρ(T) behavior near room temperature is especially unusual. A low minimum of electric resistivity is observed in this region for the alloys containing Cr (#1 and #2). Such type of minimum for the non-ferromagnetic MGs with magnetic impurities is conditioned by the Kondo effect [7, 8]. In some cases, this minimum occurs at a relatively high temperature (T_{min} ~ 500 K for Pd–Cr–Si amorphous system at a high chromium content [7]). The "modified" theory of the Kondo effect has been developed to explain the nature of such ρ behaviour in a case of ferromagnetic glasses [9]. The essence of this theory conditioned by the fact that the distribution of effective local magnetic fields H acting on magnetic ions in some amorphous systems could be essentially widely tailing down to zero or even negative H values. As a result, an extremely low magnetic field acts on some spins, so they could be involved into the Kondo scattering. Though the experimental temperature values corresponding to resistivity minimum are quite low (are equal to several tens of Kelvins) for the majority of ferromagnetic metal-metalloid systems [10], the value of $T_{min} \approx 210$ K was reported for $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ MG [11].

Nevertheless, even this value is noticeably lower than the values of T_{min} observed for the studied Cr-containing MGs. A certain correlation between the values of T_{min} and T_c, namely, the higher is T_c, the higher is T_{min}, could be detected just for these alloys. Taking this into account, the origin of resistivity minimum could be supposed to be of magnetic nature. According to calculations presented in [9], the required distribution of the local magnetic fields is not reached if only the direct exchange between neighboring magnetic ions and long-range RKKY interaction are considered under reasonable values of involved parameters. Only the accounting for additional strong indirect antiferromagnetic exchange between the magnetic ions separated by the metalloid atoms could provide the compensation of strong direct exchange and result in the required result. Therefore, it looks reasonable to suppose that it is just chromium admixtures that provide the strong indirect antiferromagnetic exchange in the studied MGs and results in high values of T_{min}. This is confirmed by the formation of Cr-based antiferromagnetic clusters in such alloys [6] and by the absence of the resistivity minimum for MG with Me = Fe (#3).

Here, we discuss one of the possible reasons for the origin of resistivity minimum. Meanwhile, the alternative explanations (refer, e.g. to [12]) could not be totally excluded. Finally, it is worth to note that the decrease of ρ values at room temperature with increasing chromium content could be of the similar nature as for MGs on the base of Fe–Si–B system we have studied before [13]. This is caused by the shift of the Fermi level to the left toward the maximum of *d*-band state density at partial Co substitution by Fe and Cr atoms, which possess lower number of *d*-electrons.

Thus, temperature dependences of electric resistivity have been investigated in 300–950 K temperature range for $Co_{65.5}Me_{6.5}(Si,B)_{28}$ metallic glasses (Me = Fe, Cr). Several characteristic temperature intervals are distinguished at $\rho(T)$ dependences. The resistivity minimum has been shown to be directly related with the chromium admixture and to be of magnetic nature.

Acknowledgement. The cordial assistance of Dr.O.Nakonechna is highly appreciated by the authors.

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Аномальна поведінка електроопору металічних стекол на основі Co–Si–B

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Досліджено температурні залежності електричного опору металічних стекол $Co_{65.5}Me_{6.5}(Si,B)_{28}$ (Me = Fe, Cr) в інтервалі 300–950 К. Виявлено особливості поведінки електроопору $\rho(T)$ в певних температурних інтервалах. Показано, що мінімум електроопору беспосередньо залежить від наявності домішки хрому і має магнітне походження.