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KINETIC OF CRYSTALLIZATION OF Co-Si-B METALLIC GLASS

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The $Co_{78}Si_9B_{13}$ metallic glass was annealed during 4h at different temperatures (573-823 K) and the result of this is the gradual transition from the amorphous to the crystalline state. The crystallization process proceeded in two stages and this investigated by methods: DSC, Hall effect, electrical resistivity and X-ray diffraction. The phases α-Co and Co_2B are the result of the first and second stages respectively and were identified by method X-ray diffraction. The phases were also verified by calculations of the quantum chemistry. The creation of the crystalline phases corresponds the distinct decrease of the Hall and electrical resistivities.

Key words: metallic glass, crystallization, phase transitions, activation energy, Hall and electrical resistivities.

The amorphous solids are in the thermodynamical metastable states and they evolve into more stable states. Crystallization is a transformation during which amorphous phase crystallizes into one or more metastable or stable polycrystalline phases. The amorphous solids may crystallize to polycrystalline phases when are subjected to thermal annealing (including additionally conditions e.g. magnetic field, stress), irradiation [1]. But the conventional thermal annealing is the technique most commonly utilized in investigation on crystallization of amorphous solids. The dimension of crystallites ranges from a few micrometers to a few nanometers, is strongly dependent on the chemical compositions of the amorphous solids, the method of the preparation and as well as its parameters and naturally annealing conditions. The metallic glasses are obtained by the rapid solidification from the liquid state and it leads to the formation of the metastable amorphous structure. They evolve through the changes of the chemical and topological short range ordering (CSRO and TSRO) and next the changes of medium range ordering (MRO), to a polycrystalline state [2,3]. The transformation out the amorphous to crystalline state can occur by the following typical reactions: polymorphous, eutectoid, primary and peritectoid crystallization [4]. The type of transformation depends mainly on the alloy composition. The aim of this paper is determination of the temperature range of the structural stability and at the same time the stability of the properties for the $Co_{78}Si_9B_{13}$ metallic glass. The studies of the structural

changes of the $Co_{78}Si_9B_{13}$ alloy were performed as result thermally stimulated modification of structure caused by isochronal annealing at different temperature. The structural changes coincide with the changes of physical properties, and the latter ones are especially significant when a phase transition occurs. In this paper to study of the phase transitions the standard methods are applied, i.e. DSC (differential scanning calorimetry), X-ray diffraction, electrical resistivity as well as the investigation of the Hall effect which can give the possibility to determine the order of phase transition and also the type scattering of charge carriers [5–7].

The ribbon of the $Co_{78}Si_9B_{13}$ metallic glass were prepared by the roller quenching method.

DSC measurements were carried out using a STA-409 NETZSCH apparatus under an argon stream at different heating rates of 5, 10, 15 and 20 K/min.

Measurements of the electrical and Hall resistivities and X-ray diffraction were done at room temperature for the as-received as well as isochronally (4 h) annealed samples at the different temperatures (573 – 823 K) in inert argon atmosphere.

The X-ray studies were performed using DRON-2,0 diffractometer with MoK_α radiation. The Hall voltage was measured by a constant current method in the field up to 3,26T. The electrical resistivity was also measured within a, d, c. regime. The samples for measurements of the Hall and electrical resistivities were prepared by selective etching using photolitography. Each sample had five electrodes. Two of them were used for supplying the sample with a constant current along its length and three of them were used for the Hall voltage measurements to eliminate any electrode asymmetry.

The quantum chemical calculations of the total energy of the created phases were done using a semi-empirical method of HyperChem 6.0 program.

The thermal stability and kinetics of crystallization of $Co_{78}Si_9B_{13}$ metallic glass was investigated by DSC measurements. The results of the non-isothermal crystallization process carried out for alloy at heating rate 5, 10, 15 and 20 K/min. Fig. 1, a shows the DSC curves of alloy taken at different heating rates. It is clearly seen that all the DSC curves display two exothermic peaks indicating that the transformation out of amorphous to polycrystalline state proceed through two main stages. The temperature of both peaks increases with the increase of the heating rate.

Based on the Kissinger equation it can be estimated the activation energy E_a for crystallization of phases [8–9].

$$\frac{d[\ln(v/T_p^2)]}{d[1/T_p]} = -\frac{E_a}{R} \tag{1}$$

where v, T_p, R are the heating rate, pik temperature and gas constant, respectively.

A plot of $\ln(v/T_p^2)$ versus $1/T_p$ yields a straight line with a slope $-E_a/R$. The dependence between $\ln(v/T_p^2)$ and $1/T_p$ is shown in Fig.1b. The calculated activation energy for the first and second stages of crystallization for $Co_{78}Si_9B_{13}$ metallic glass are listed in Table.

The above results are also verified by means others investigations presented in this paper.

Fig. 2 show the results of investigation of the Hall resistivity ρ_H as a function of external magnetic field B_0 for samples in as-received state and samples annealed isochronally at different temperatures. With the increase of the annealing temperature the ρ_H decreases. The first lowering of the curves $\rho_H = f(B_0)$ occurs after annealing at 623 K and the next distinct lowerings of the curves are observed after annealing at 673 and

773 K. The investigated alloy is the ferromagnetic materials and therefore the Hall resistivity must be written as [5–7]; [10]:

$$\rho_H = R_0 B_0 + \mu_0 R_S M \quad (2)$$

where R_0 and R_s are ordinary and spontaneous Hall coefficient respectively, and M is the magnetization of the sample.

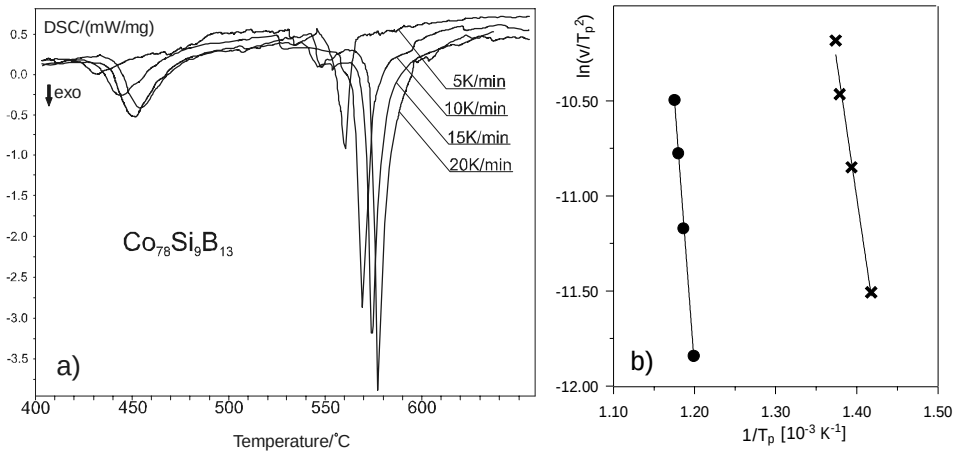

Fig. 1. Dependences for $Co_{78}Si_9B_{13}$ metallic glass: *a* – DSC curves at different heating rates; *b* – relationship between $\ln(v/T_p^2)$ and $1/T_p$ for both stages of crystallization (• - first and × - second)

Table

The activation energy for first E_{a1} and second E_{a2} stages of crystallization for $Co_{78}Si_9B_{13}$ metallic glass

E_{a1} [kJ/mol]	E_{a2} [kJ/mol]
241,43	472,26

Each curve from Fig. 2. has the typical character of ferromagnetic substances. It demonstrates that during the crystallization process the macroscopic ferromagnetic ordering of alloy is conserved. The first term of the equation (2) is the ordinary Hall resistivity ($\rho_{H0} \propto B_0$). It is related to the action of the Lorentz force on the current carriers and corresponds to the slowly growing part of the $\rho_H = f(B_0)$ curve above the magnetization saturation. The second term is the spontaneous Hall effect ($\rho_{HS} \propto M$) and is represented by the initial part of the $\rho_H = f(B_0)$ curve.

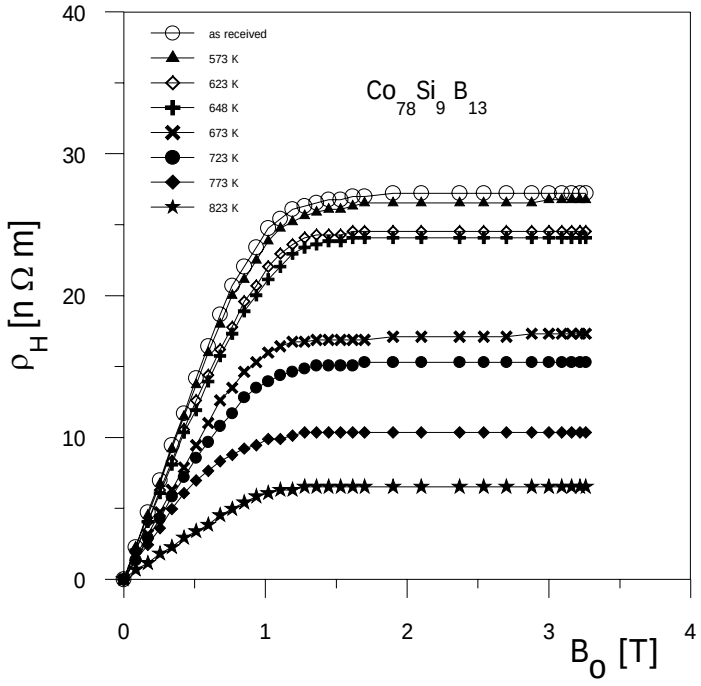

Fig. 2. The Hall resistivity, ρ_H, as a function of the applied magnetic induction, B_0, for samples of $Co_{78}Si_9B_{13}$ alloy annealed at different temperatures

The ρ_{HS} is connected with a ferromagnetic state and determined by following mechanisms: a spin-orbit interaction, a skew scattering and a side jump [5,6]. These mechanisms decrease the mean free path of carriers. For the initial part of the $\rho_H = f(B_0)$ curves the spontaneous Hall coefficient R_s was calculated using the linear regression $R_s = (\partial \rho_H / \partial B_0)_{B_0 \to 0}$.

Fig. 3 shows the relative changes of the electrical resistivity (related to the resistivity of the as-received state) vs. the annealing temperature. The decrease of the electrical resistivity during the crystallization is caused by the increase of the free path of the carriers in ordered structure in medium and long range.

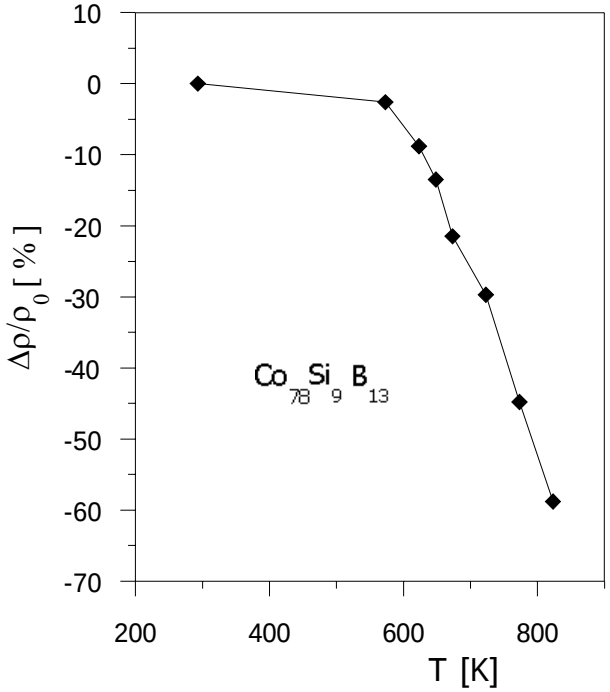

Fig. 3. The relative electrical resistivity, $\Delta\rho/\rho_0$, as a function of annealing temperature, T, for samples of $Co_{78}Si_9B_{13}$ alloy

According to Berger and Bergmann the spontaneous Hall coefficient R_s is described by dependence [5-7]:

$$R_s = a\rho + b\rho^2 \tag{3}$$

where a and b are constans roughly independent of temperature and ρ is the resistivity.

The first term of equation (3) is responsible for the classical asymmetric scattering of charge carriers and the second term describes the quantum effect and corresponds to the lateral displacement of the charge carrier trajectory at the point of scattering , i.e. the side jump. The dependence of $\lg R_s$ on $\lg\rho$ gives the exponent n in relation $R_s \propto \rho^n$ and by its means it can be concluded which type of scattering is dominant for the spontaneous Hall effect. Fig.4 represents these dependence. The calculated exponent n is 1.58. The value n indicate that during the crystallization process the charge carriers are mainly scattered by nonclassical mechanism, i.e. side jump.

To analyse the structural changes and identify the crystalline phases formed out of the amorphous matrix the X-ray investigations for the as–received as well as annealed samples were performed. The X-ray diffraction prove that the first stage of the crystallization begins after the annealing at the temperature of 648 K and second at the temperature 773 K. The qualitative analysis proves that is related with the creation of the phases α-Co and Co_2B, respectively [11–14]. The first stage of crystallization of alloy occurs as a result of the primary crystallization and the second stage as a result of the polymorphous crystallization. The structural changes appear in the measurements of the

electrical and Hall resistivities after annealing at temperatures lower than in X-ray diffraction studies and DSC. It demonstrates that the methods involving the electronic transport are more sensitive on the structural changes.

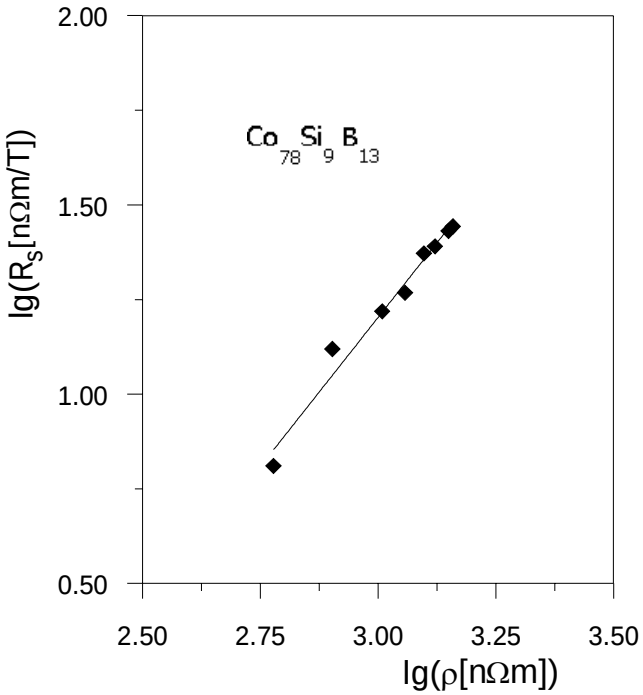

Fig. 4. The dependence lg R_s versus lgρ for $Co_{78}Si_9B_{13}$ alloy annealed at different temperatures

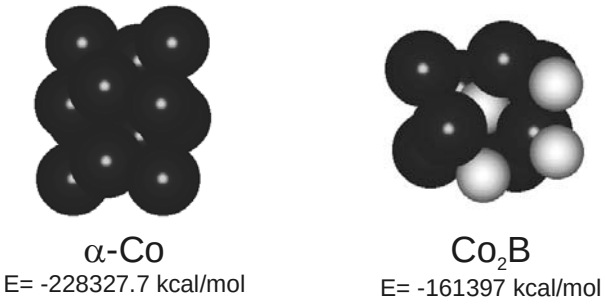

Fig. 5. The clusters of formed phases

To verify the sequence of the created phases determined on the basis of X-ray diffraction, quantum chemistry calculations of the total energy of the model clusters

representing the investigated alloys semi-empirical method (ZINDO/1) were carried out. The values of total energy of α-Co clusters (-228327,7 kcal/mol) are smaller than those of Co_2B clusters (-161397 kcal/mol).These results prove that at first the metal phase crystallize out of amorphous matrix during the annealing because they require lower energy and only after annealing at higher temperatures the borides crystallize. These results confirm the difference between the temperature of crystallization of metal and boride phases and the sequence of the created phases stated in this paper by other methods.

- The crystallization process for $Co_{78}Si_9B_{13}$ metallic glass follows two stages. At the first stage crystallize α-Co and at the second Co_2B.
- During the crystallization process the ferromagnetic order of alloy is conserved. – The dominant scatterings of charge carriers is the side jump.
- The Hall and electrical resistivities decrease abruptly after crystallization of the phase.
- The activation energy for both stages of crystallization as well as the total energy for clusters of created phases calculated from DSC and quantum chemistry method respectively, prove that at the first stage the metal phase is created and at the second the metal borides.

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КІНЕТИКА КРИСТАЛІЗАЦІЇ МЕТАЛІЧНИХ СТЕКОЛ Co-Si-B

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Металічні стекла $Co_{78}Si_9B_{13}$ відпалювали протягом чотирьох годин за температури (573-823 K), в результаті чого простежено поступовий перехід з аморфного в кристалічний стан. Процес кристалізації поділяли на дві стадії і досліджували методами диференціальної скануючої калориметрії, вимірюванням ефекту Хола, електричного опору та методом рентгенівської дифракції. Фази α-Co і Co_2B утворювалися під час першої та другої стадії кристалізації, відповідно і були ідентифіковані методом рентгенівської дифракції. Існування цих фаз було також підтверджене квантово-хімічними розрахунками. Виникнення кристалічної фази спричиняє явне зменшення холівського та електричного опору.

Ключові слова: металічні стекла, кристалізація, фазові переходи, енергія активації, холівський опір, електричний опір.

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