EVOLUTION OF PROPERTIES OF $CO_{66}NI_{12}SI_9B_{13}$ METALLIC GLASS INDUCED BY ISOCHRONA ANNEALING

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INTRODUCTION

Application of metallic glasses requires the stable as-quenched state most often. From the scientific point of view, transitions into a partially or completely crystallized state are always interesting .Therefore, different factors influencing the kinetics of structural order of short (CSRO, TSRO), medium or long range are often investigated [1,2].The crystallization processes are observed mainly by methods like DSC, electrical resistivity, X-ray diffraction [3-7]. In this paper Hall effect measurements were also applied, because the dependence of the Hall voltage on the magnetic induction reflects magnetic properties. The aim is to investigate the thermally activated modification of the structural order of the metallic glass $Co_{66}Ni_{12}Si_9B_{13}$ by the methods of DSC, X-ray diffraction, electrical resistivity and Hall effect.

EXPERIMENT

A ribbon of the metallic glass $Co_{66}Ni_{12}Si_9B_{13}$ (13 mm wide and 27 μm thick) was prepared by the roller quenching method in the Institute of Materials Engineering of Warsaw Technical University, Poland. Differential scanning calorimetry (DSC) was carried out using a STA-409 NETZSCH apparatus under an argon stream.The DSC curve was obtained at a constant heating rate of 5 K/min. Measurements of the electrical and Hall resistivities and X-ray diffraction were made at room temperature for as-received as well as isochronally (4 h) annealed (in an inert argon atmosphere) samples at the temperatures: 573, 673, 723, 773, and 823 K. The X-ray studies were performed using a DRON-2.0 diffractometer with FeKα radiation.The Hall voltage was measured by a constant current method at constant magnetic field. 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 samples were prepared by selective etching using photolitography. The electrical resistivity was also measured within the d.c. regime.

RESULTS AND DISCUSSION

Devitrification of the $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass consists of two main stages , as shown by two resolved exoterms peaks in the DSC curve, obtained at a constant heating rate (Fig.1). The crystallization onsets, at 5 K/min, occur at 662 K and 805 K, respectively, for the first and second crystallization stages. The crystallization parameters derived from the DSC curve, i.e. temperature T and enthalpy ΔH of each transition, are shown in Fig.1.

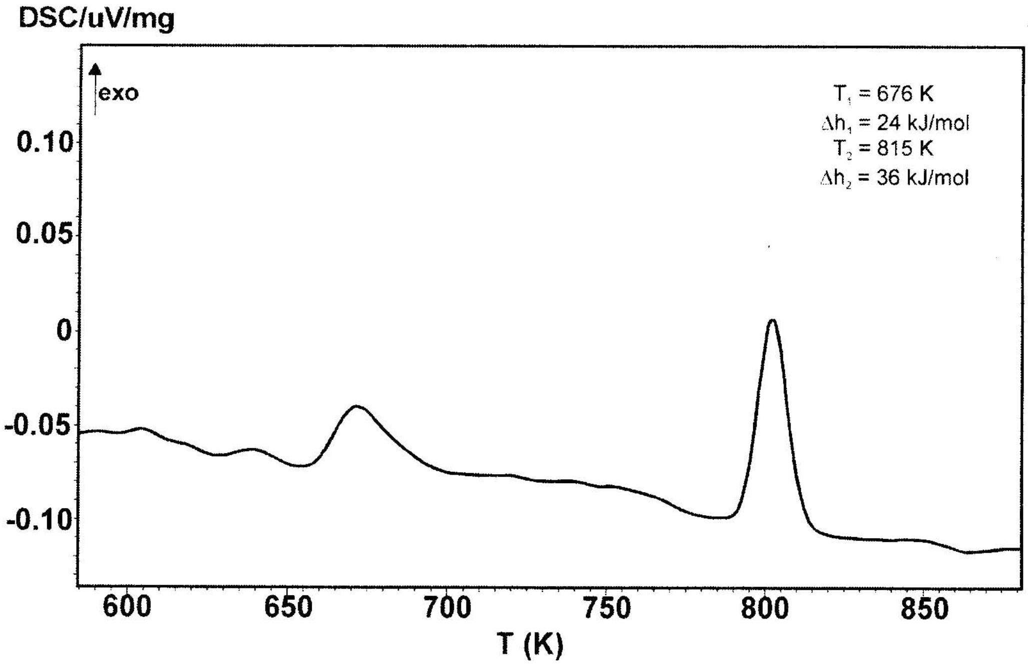

Figure 1. DSC curve for $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass.

The identification of the crystalline phases formed during crystallization was carried out by X-ray diffraction. The structure determination was performed using PowderCell and LATCON programs [8,9]. These results were also compared with reference data related to the binary and ternary compounds with a big amount of Co [10-12]. The crystalline phases identified are presented in Table 1.

Because the investigation by DSC, performed by means of non-isothermal heating of an as-received sample, proved the crystallization at 676 K, the isothermal annealing for different time intervals was performed at a temperature of 673 K.The crystallization begins at temperature 673 K after annealing during 10^3s.

Table 1. The parameters of the elementary cells of crystalline phases formed during the devitrification of $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass.

Phase	Space group	Structure type	Lattice parameters (nm)		
			a	b	c
α-(Co,Ni)	$P6_3/mmc$	Mg	0.2489	-	0.4116
$(Co, Ni)_2B$	I4/mcm	$CuAl_2$	0.5002	-	0.4197
$(Co, Ni)_3B$	Pnma	CFe_3	0.5193	0.6649	0.4412
$(Co, Ni)_5Si_2B$	I4/mcm	W_5Si_3	0.857	-	0.425

The $Co_{78}Si_9B_{13}$ metallic glass investigated earlier, also from the same family $Co_{78-x}Ni_xSi_9B_{13}$, has a lower temperature of the onset of crystallization (648 K) [7]. Annealing of the $Co_{66}Ni_{12}Si_9B_{13}$ glass at 673 K leads to eutectic crystallization with formation of the phases α-(Co,Ni) and $(Co,Ni)_5Si_2B$. As a result of this crystallization the amorphous matrix enriches with B, and after the annealing at 773 K the phases $(Co,Ni)_2B$ and $(Co,Ni)_3B$ crystallize.

The structural changes, occuring as a result of isochronal annealing, were confirmed by changes in the electrical resistivity and Hall effect for samples undergoing the same thermal treatment.The results of investigation of electrical resistivity as a function of the annealing temperature are presented in Fig.2 as relative change $\Delta\rho/\rho_0$ = f (T) (i.e. related to the resistivity of the as-received sample $\rho_0 = 1.18 \pm 0.02$ μΩm). Distinct falls of the electrical resistivity are seen after annealing at 673 K and 773 K, which correlates with the X-ray investigations. The electrical resistivity of the investigated as-received metallic glass is lower compared with $Co_{78}Si_9B_{13}$ [7]. Addition of Ni to the alloy causes an increase of the conduction electron concentration.

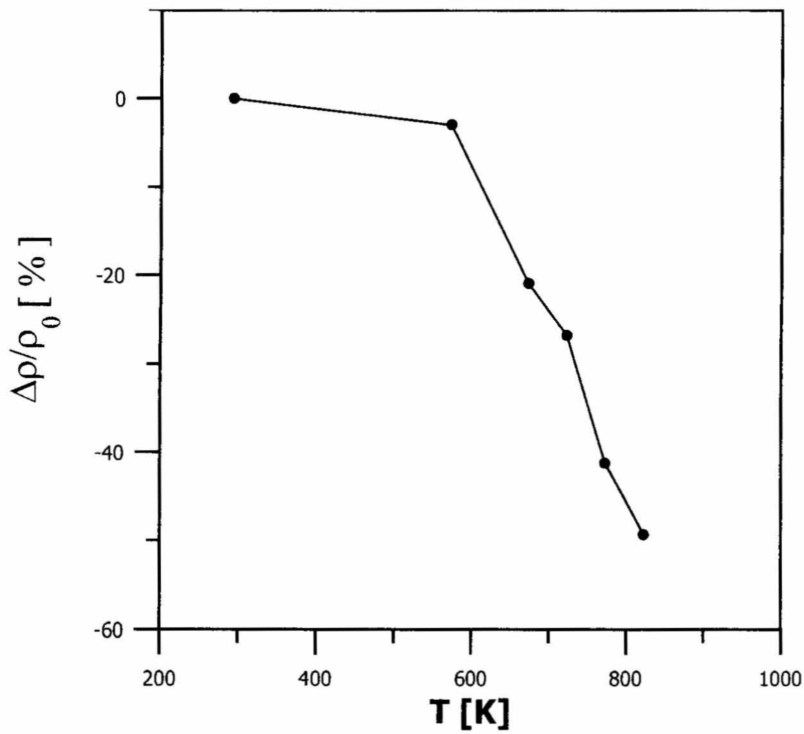

Figure 2. The relative electrical resistivity, $\Delta\rho/\rho_0$, as a function of annealing temperature, T, for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy.

The results of the investigation of the Hall effect are shown in Fig.3 as the Hall resistivity ρ_H versus the induction of the external magnetic field B_0. Fig.3 contains a family of curves for the particular structural states, i.e. for the as-received state and the states determined by isochronal (4 h) annealing at different temperatures. The curves related to higher annealing temperatures have lower values of ρ_H. The shape of the curves is conserved, i.e. analogous to the as-received state.

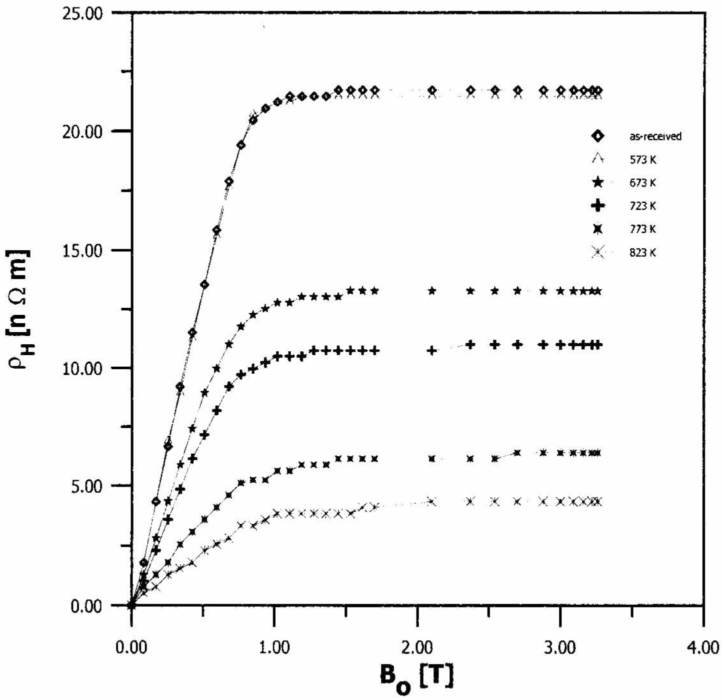

Figure 3. The Hall resistivity, ρ_H, as a function of the applied magnetic induction, B_0, for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy annealed at different temperatures.

Each curve from Fig.3 has the typical character of ferromagnetic substances and is described by the equation [13-15]:

$$\rho_H = R_0B_0 + R_sM\,(B_0) \qquad (1)$$

where R_0 and R_s are ordinary and spontaneous Hall coefficient respectively, and $M(B_0)$ is the magnetization of the sample. The first component of the equation (1) 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 component characterises the ferromagnetic state of the sample and is represented by the initial part of the $\rho_H = f(B_0)$ curve. This component is a result of different mechanisms: skew scattering, side jump mechanism, spin-dependent scattering and the transition from the low field regime to the high field regime. The spontaneous R_s and ordinary R_0 Hall coefficients, respectively, determine the slope of the $\rho_H = f(B_0)$ curve below and above the magnetization saturation.

For the initial, linear part of the $\rho_H = f(B_0)$ curve the spontaneous Hall coefficient R_s was coefficient R_s was calculated using the method of the linear regression

$$R_s = \left(\frac{\partial \rho_H}{\partial B_0}\right)_{B_0 \to 0} \qquad (2)$$

Fig.4 presents the dependence of R_s as a function of the annealing temperature T.The changes of R_s are analogous to the changes of the electrical resistivity (Fig.2) and those of the $\rho_H = f(B_0)$ curves (Fig.3), which show an abrupt decrease when in the sample the crystalline phases are formed [6,7]. The spontaneous Hall effect is more sensitive to structural changes than the electrical resistivity (Fig.2 and Fig.3). The abrupt decrease of R_s

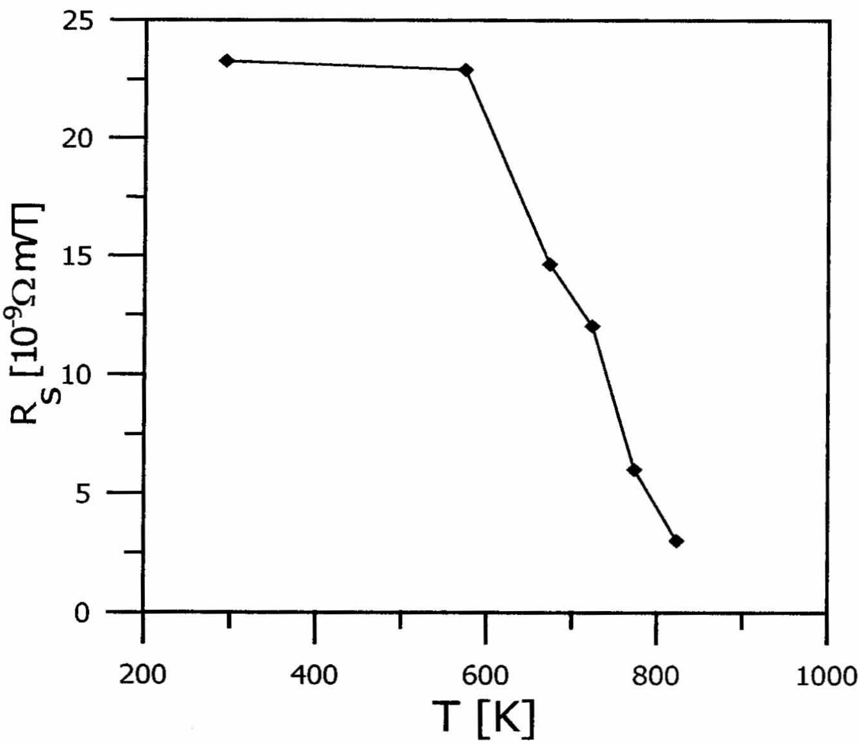

Figure 4. The spontaneous Hall coefficient, R_s, as a function of the annealing temperature, T, for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy.

value after annealing at 673 K and 773 K is caused by structural phase transitions. In the ferromagnetic alloys the proportionality of R_s to ρ^2 proves both their amorphism as well as majority participation of side-jump scatterings among spin-orbit interactions [16].

Fig.5 presents the dependence of ρ^2/R_s as a function R_s. The plot allows to determine the range of the existence of the amorphous state. The function is constant in the amorphous range. As seen the crystallization process begins after the annealing at the temperature T=673 K and it confirms the results obtained from DSC and X-ray diffraction methods, even though they do not base on the transport carriers phenomena.

The creation and growth of the crystalline phases from the amorphous matrix causes a decrease of structural and spin disorder. As a result, the mean free path of the carriers increases which leads to the decrease of the electrical resistivity and gives proportionality R_s to ρ.

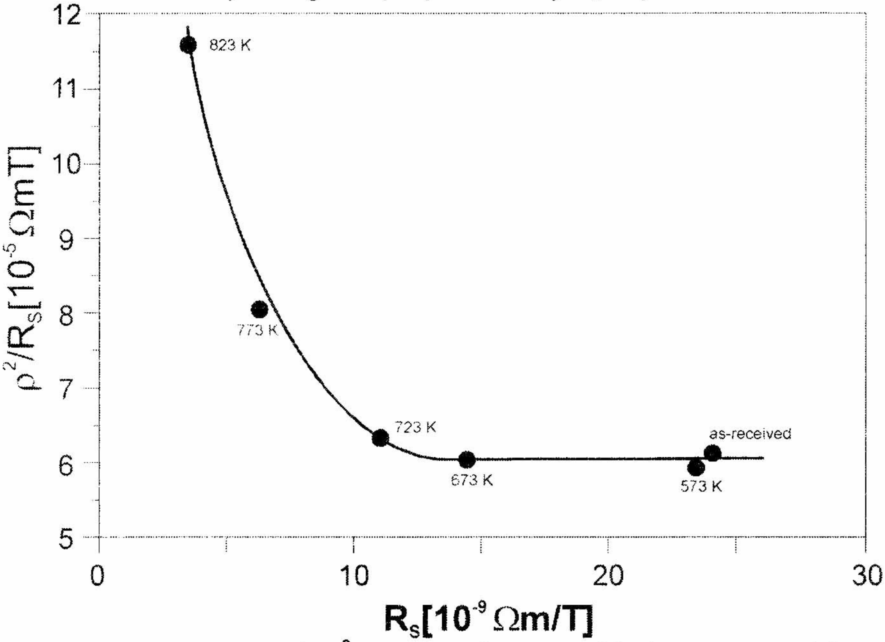

Figure 5. Dependence of ρ^2/R_s as a function of R_s for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy annealed at different temperatures (ρ – electrical resistivity, R_s – spontaneous Hall coefficient).

The carried out quantitative phase analysis (based on the X-ray diffraction pattern of the sample after annealing at T=823 K) proved that 70% and 15% of the sample are the ferromagnetic phases of α-Co and Co_2B, respectively [17]. The α-Co phase dominates in the first (673 K) and Co_2B in the second (773 K) stage of the crystallization and therefore the alloy is still ferromagnetic (see Fig.3).

CONCLUSIONS

The crystallization begins after the annealing at temperature 673 K during 10^3s.

Formation of the crystalline phases out of the amorphous matrix leads to the abrupt decrease of electrical (ρ) and Hall (ρ_H) resistivities , spontaneous Hall coefficient (R_s).

For the investigated metallic glass R_s is proportional to ρ^2 when the temperature of annealing is lower than 673 K, i.e. when the structure of the alloy is amorphous.

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