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CHANGES OF PROPERTIES OF $Co_{66}Ni_{12}Si_9B_{13}$ METALLIC GLASS IN PROCESS DEVITRYFICATION

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ABSTRACT

Isochronal annealing during 4h at different temperatures (573 ÷ 823 K) of samples of $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass leads to the creation in the amorphous matrix three crystalline phases, i.e. at the temperature 673K phases α –(Co,Ni) and at the temperature 773K phase $(Co,Ni)_3B$ and $(Co,Ni)_2B$. The result of the applied thermal treatment of the samples was their complete crystallization. The process of the annealing of the alloy leads to the systematic decrease of the electrical resistivity, Hall resistivity and the spontaneous Hall coefficient, and the creation of the crystalline phase is related to abrupt value decrease of these parameters. The calculations by quantum chemistry method confirm sequence and verify the composition of the created phases. The growth of grain sice of formed phases were observed by the optical microscope.

INTRODUCTION

Amorphous metallic glasses are well known for their superior magnetic properties, improved mechanical strength and corrosion resistance, but their amorphous structure is metastable. All types of the structural changes are accompanied by the physical properties changes. The occuring of these changes is understandable, because their atoms transiting from the liquid to the solid state did not occupy the equilibrium position, where they would have the minimal energy. The composition and method of their production influence their structural and energetic initial state and they result in type and rate of the occuring structural changes.The latter changes evolve through the changes in the chemical and topological short range order (CSRO and TSRO), later on through the changes in the intermediate state with the medium range order (MRO), leading finally to the policrystalline state with the long range order[1,2]. For some applications it is important to maintain the stable amorphous state and for others either partially or completely crystalline. Therefore, the investigation explaining the influence of different factors on the initiation of the crystallization process and the kinetics crystallization is carried out. The crystallization mechanism depends on various factors and particularly on the way of crystallization, number of "frozen" crystallization centres, activation energy of diffusion, and hence the determined crystallization temperature is not a universal parameter. All types of the structural changes are accompanied by the physical properties changes. Some of them are particularly sensitive to the structural changes, e.g.: elasticity (Young modulus), volume, magnetic coercion, Curie temperature, specific heat, electrical resistivity

[3,4]. The aim of the paper is to investigate thermally stimulated modification of the structural order of $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass by the methods of X- ray diffraction, electrical and Hall resistivities, and optical microscopy. To verify created phases the quantum chemical calculations of the total energy were done. The stimulation of the structural changes was carried out by isochronal (4h) annealing at different temperatures to obtain the complete crystallization.

EXPERIMENT

The investigated metallic glass $Co_{66}Ni_{12}Si_9B_{13}$ was prepared by the roller quenching method in the Institute of Materials Engineering of Warsaw Technical University, Poland. The metallic glass ribbons were 13 mm wide and 27 μm thick. 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 3 K/min. The measurements of the electrical and Hall resistivities and the X-ray diffraction were performed for the as-received as well as annealed samples. The samples were annealed isochronally during 4h at the temperatures : 573, 673, 723, 773, and 823 K. Each sample has been annealed in inert argon atmosphere. The X-ray studies were performed using a DRON-2.0 diffractometr with a horizontal goniometr of the GUR-5 type. The X-ray tube used had a molybdenium target ($\lambda_{K\alpha}$ = 0.71069 x 10^{-10} m) and a graphite monochromator in the primary beam. 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 asymetry. The samples were prepared by selective etching using photolitography.
The electrical resistivity was also measured within a d. c. regime. 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 growth of grain sice of formed phases were observed by the JENAVERT optical microscope with camera CCD.

RESULTS AND DISCUSSION

The temperature of start of annealing were stated on the basis of DSC investigation. The result of investigation of non-isothermal crystallization process carried out for $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass by DSC at constant heating rate of 3 K/min. shows that devitryfication of alloy consists of two main stages. In the exoterm peaks in DSC curve are resolved by a wide temperature range. The peak responsible for the first stage of crystallization is wide and second one is sharp. In our research the onset of the crystallization is especially important. Therefore in the Table 1 their values denoted by T_0 are listed together with the positions of the maximum of the peaks T and also the enthalpy H, referring to the first and second stage of crystallization.
Stimulation of the structural changes was started by annealing at the temperature 573K.The temperature 573K is much smaller than the temperature of the onset of the first stage of the crystallization – Table1.

Table 1. Temperature of the onset crystallization T_0 and position of the peak T and enthalpy H of both stages of crystallization.

Parameters / No. of stage	T_0 [K]	T [K]	H [J/mol]
I stage	651.96	665.76	23.99
II stage	795.16	804.76	35.73

In order to analyse the structural changes and identify the formed phases out of the matrix the X-ray investigations for the samples: as-received and isochronally annealed during 4 h at different temperatures were performed. The result of the qualitative phase analysis were made by means of PowderCell and LATCON programs are presented in Table2 [5-7]. The analysis of these patterns proved the creation of three crystalline phases. The nucleuses of these phases form after the annealing at the temperature 673 K and 773 K. The first peaks appear on the X-ray diffraction patterns only after annealing at the temperature of 673 K therefore for the series of samples with the initial as-received state, the annealing was performed at this temperature at different time: $10^2 \leq \tau \leq 2 \cdot 10^4$ s. The obtained X-ray diffraction patterns, for the isothermal annealing, show the first peaks after the annealing during 10^3 s. They intensify with the increase of the annealing time. 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) [8]. Annealing of the $Co_{66}Ni_{12}Si_9B_{13}$ glass at 673 K leads to crystallization with formation of the phase α-(Co,Ni). 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.

Table 2. 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

The occuring structural changes during annealing were confirmed by changes in the electrical resistivity and Hall effect for the samples undergoing the same thermal treatment.

The results of investigation of electrical resistivity as a function of the annealing temperature as a relative change of electrical resistivity (i.e. related to the resistivity of the as-received sample $\rho_0 = 1.18 \pm 0.02$ $\mu\Omega$m) $\Delta\rho/\rho_0 = f(T)$ are presented in Fig.1.

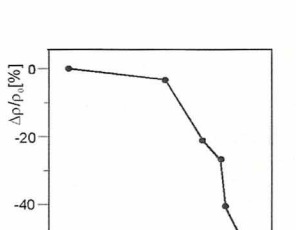

Figure 1. The relative electrical resistivity, $\Delta\rho/\rho_0$, as a function of annealing temperature, T, for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy.

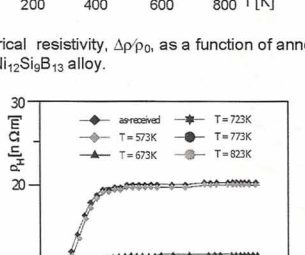

Figure 2. The Hall resistivity, ρ_H, as a function of the applied magnetic induction, B_0, for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy annealed at different temperatures.

The results of the investigation of Hall effect presented Fig.2 as Hall resistivity ρ_H versus the induction of the external magnetic field B_0. Fig.2 contains family of curves for the particular structural states, i.e. for the as-received state and states determined by isochronal (4h) 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. is analogous with the as-received state. Each curve from Fig. 2 has a typical character for the ferromagnetic substances and is described by the equation [9-11] :

$$\rho_H = R_0 B_0 + R_s M(B_0) \tag{1}$$

where R_0 and R_s are ordinary and spontaneous Hall coefficient and $M(B_0)$ is the magnetization of the sample. The first component of the equation (1) is related to the action of Lorentz force on the current carriers and slowly growing part of the $\rho_H = f(B_0)$ curve above the magnetization saturation is responsible for it. The second component characterises the ferromagnetic state of the sample and the initial part of $\rho_H = f(B_0)$ curve relates to it. 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 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 calculated using the method of the linear regresion

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

Figure 3 presents dependence of R_s as a function of the annealing temperature T.

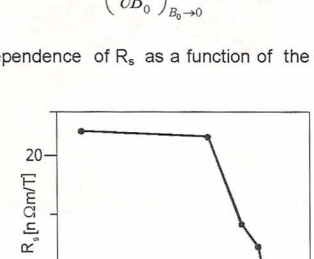

Figure 3. The spontaneous Hall coefficient, R_s, as a function of the annealing temperature, T, for samples of $Co_{66}Ni_{12}Si_9B_{13}$ alloy.

Changes of R_s are analogous to the changes of the electrical resistivity – Fig. 1 and changes of $\rho_H = f(B_0)$ curves – Fig.2. The results of these investigation are

given in Figs.1,2 and 3 and prove distinct changes and they are bigger when in the sample the crystalline phase is formed [8,12].
It is known that the investigation of the spontaneous Hall coefficient as a dependence on the annealing temperature of the same sample allows to calculate the Curie temperature T_c of the substance [13,14]. The sharp drop $R_s = f(T)$ with the constant rate of annealing: $\Delta T/\Delta\tau$ = const is responsible for the transition of the ferromagnetic substance to the paramagnetic state . The values of the Hall coefficient R_s below T_c are almost independent on the temperature. The investigation of R_s for the isochronally pre-annealed samples at different temperatures above Curie temperature show change of T_c . Values of changes ΔT_c are a monotonic function of the annealing temperature. Presented in Fig.3 dependence $R_s = f(T)$ show sharp drops, which are caused by structural changes in the range of phase transition of the first type. Fig. 2 shows that each state of the sample during transition from the amorphous to the crystalline state is a ferromagnetic state, and the structural changes decrease the asymetrical scattering of the carriers on the magnetical moments of the substance.

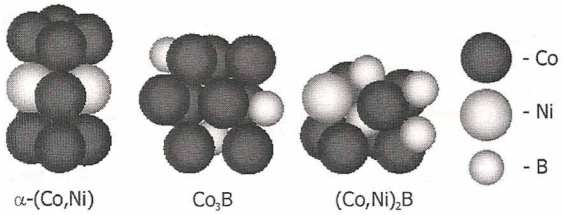

Figure 4. The model clusters of the formed phases.

Quantum chemistry calculations of total energy carried out by semi-empirical method (ZINDO/1) for 12 atoms cluster proved Ni atom to build only into α-Co and Co_2B phases (Fig.4.). The energy of these clusters after replacing Co with Ni decreased the values for α-Co from -228327.7 to -241105.1kcal/mol and for Co_2B from -161397.0 to - 167773.9 kcal/mol. The obtained values of the total energy for particular phases verify sequence of the created phases, determined on the basis X-ray diffraction too.

The microstructure of samples as-received as well as annealed are presented in Fig.5.As seen during the annealing follow the growth density of sites nucleation and growth of grain sice of formed phases out of amorphous matrix.

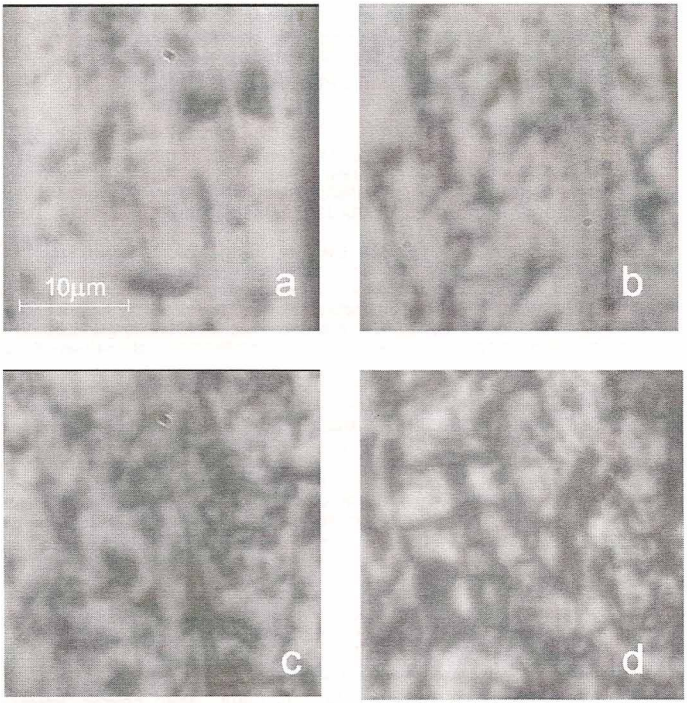

Figure 5. The microstructure of alloy $Co_{66}Ni_{12}Si_9B_{13}$: a) as-received and annealed at the temperature b)673 K, c)773 K, d)823 K.

CONCLUSIONS

The process of crystallization of $Co_{66}Ni_{12}Si_9B_{13}$ metallic glass has two stages and proceeds according to the following scheme:

$$Co_{66}Ni_{12}Si_9B_{13} \xrightarrow{673K} \alpha\text{-}(Co,Ni) + (Co,Ni)_5Si_2B + \text{amorphous}$$

$$\text{amorphous} \xrightarrow{773K} (Co,Ni)_2B + (Co,Ni)_3B$$

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 and Hall resistivities , spontaneous Hall coefficient. This is caused by the increase of the mean free path of the carriers.

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