STRUCTURAL PHASE TRANSITION
OF Co–Ni–Si–B AMORPHOUS ALLOY

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Structural changes of Co_{66}Ni_{12}Si_{9}B_{13} amorphous alloy, stimulated by isochronal and isothermal annealing, were observed by means of the methods: electrical resistivity, Hall effect, and X-ray diffraction. In the amorphous matrix at the temperature 673 K phases α-Co and (Co,Ni)_{3}Si_{2}B are created, while at the temperature 773 K the phase (Co,Ni)_{3}B is formed. The structural phase transitions are related to abrupt decrease in electrical and Hall resistivities at the background of systematic decrease in these parameters values during the alloy transition from the amorphous to the crystalline state.

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1. Introduction

Considering some applications of metallic glasses, a very important problem is the maintenance of the amorphous state. The amorphous structure of the metallic glasses is a metastable state. Their composition and the method of production influence their structural and energetic initial state and result in the type and rate of the occurring structural changes. The structural changes proceed 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 leading finally to the polycrystalline state with the long-range order [1]. For the application purposes of the metallic glasses, the investigations explaining the crystallization mechanisms are performed. The knowledge of these mechanisms could be used to control the crystallization process and determine the intervals of the efficient metallic glass application, as well as to obtain some special structures, either partially or completely crystalline, which cannot be obtained from the liquid state.

The crystallization kinetics depends on various factors, and particularly on the way of crystallization, number of “frozen” crystallization centres, diffusion
activation energy, and hence the determined crystallization temperature is not a universal parameter.

This paper investigates thermally stimulated modification of the structural order of Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ metallic glass by the methods of electrical resistivity, Hall effect and X-ray diffraction. The annealing of the samples was performed isochronally (4 h) at different temperatures to obtain the complete crystallization, and isothermally (673 K) during the first stage of the crystallization.

2. Experiment

The investigated metallic glass Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ was produced by the roller quenching method in the Institute of Materials Engineering of Warsaw Technical University (Poland). The amorphous ribbon of Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ alloy was 13 mm wide and 27–28 μm thick.

For as-received sample of this alloy the investigation of the differential thermal analysis (DTA) was carried out under an argon stream using STA-409 NETZSCH apparatus. The DTA curve was obtained for heating rate of 3 K/min.

The electrical resistivity, the Hall resistivity and the X-ray diffraction measurements were performed for the as-received as well as annealed alloys. The samples were exposed to the following two types of thermal treatment:

— isochronal annealing for 4 hours at the temperatures: 573, 673, 723, 773, and 823 K;

— isothermal annealing at the temperature 673 K in the time intervals: $10^2$, $5 \times 10^2$, $10^3$, $1.44 \times 10^3$, and $2 \times 10^4$ s.

Each as-received sample has been annealed in an inert argon atmosphere.

The Hall voltage was measured by a constant current method at a 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 photolithography.

The electrical resistivity was also measured within a d.c. regime.

The X-ray studies were performed using a DRON-2.0 diffractometer with a horizontal goniometer of GUR-5 type. The X-ray tube used had a molybdenum target ($\lambda_{K_{α}} = 0.71069 \times 10^{-10}$ m) and a graphite monochromator in the primary beam.

3. Results and discussion

The obtained DTA curve for the investigated metallic glass Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ has two peaks at the temperatures 665.6 K and 804.6 K. The occurrence of the peaks proves that this alloy becomes completely crystallized in two stages. The determined temperatures allowed to preserve the same temperatures of the thermal treatment as for the investigated earlier metallic glasses from the family (Fe,Co)$_{78-x}$(Co,Ni)$_x$Si$_9$B$_{13}$ [2–4].
**Structural Phase Transition**

![Figure 1](image1.png)

**Fig. 1.** The relative electrical resistivity, $\Delta \rho/\rho_0$, as a function of annealing temperature, $T$, for Co$_{66}$Ni$_{12}$Si$_{9}$B$_{13}$ alloy.

Figure 1 shows results of the resistivity measurements, presented as a relative change of the electrical resistivity $\Delta \rho/\rho_0$ (i.e. referred to the resistivity of the as-received sample: $\rho_0 = 1.18 \pm 0.02 \ \mu\Omega \ \text{m}$), as a function of the annealing temperature. The obtained results indicate the decrease in the electrical resistivity with the increase in the annealing temperature. Moreover, these results prove that annealing above the temperature 573 K leads to distinct changes with a particular decrease in the electrical resistivity at temperatures 673 K and 773 K.

**Figure 2** shows the results of investigation of the Hall resistivity $\rho_H$ as a function of the external magnetic field $B_0$, for the samples undergoing the same thermal

![Figure 2](image2.png)

**Fig. 2.** The Hall resistivity, $\rho_H$, as a function of the applied magnetic induction, $B_0$, for Co$_{66}$Ni$_{12}$Si$_{9}$B$_{13}$ alloy annealed at different temperatures.
treatment. The magnetic field \( B_0(0, 0, B_0) \) and the electrical field \( E(E_x, 0, 0) \) create in the sample the transverse field \( E_y \), called the Hall field. The quotient of the Hall field \( E_y \) and the current density \( J_x \) is the Hall resistivity
\[
\rho_H = \frac{E_y}{J_x}.
\] (1)

In case of the ferromagnetic substances the so-called anomalous Hall effect occurs, \( \rho_H \) is then a non-linear function of \( B_0 \) [5, 6]:
\[
\rho_H = R_0 B_0 + R_s M(B_0),
\] (2)

where \( R_0 \) and \( R_s \) are ordinary and spontaneous Hall coefficients, and \( M(B_0) \) magnetization of the sample.

The first component of the equation is connected with the Lorentz force acting on the current carriers and the slowly growing part of \( \rho_H = f(B_0) \) curve above the magnetization saturation is referred to it. The second component is the result of the ferromagnetic state of the sample and it can be related to the initial part of \( \rho_H = f(B_0) \) curve. This component is the effect of different mechanisms: skew scattering, side jump mechanism, spin-dependent scattering and the transition from the low-field regime to high-field regime.

The slopes of \( \rho_H = f(B_0) \) curve below and above the magnetization saturation are determined by the spontaneous \( R_s \) and ordinary \( R_0 \) Hall coefficients, respectively.

As can be observed, all the curves from Fig. 2 are typical of the ferromagnetic substances, and moreover the curves related to higher annealing temperatures have lower values of \( \rho_H \). For each \( \rho_H = f(B_0) \) curve from Fig. 2 the spontaneous Hall coefficient \( R_s \) was calculated
\[
R_s = \left( \frac{\partial \rho_H}{\partial B_0} \right)_{B_0=0}.
\] (3)

Figure 3 shows a graph of dependence \( R_s \) on the annealing temperature \( T \). The
decreasing $R_s$ value is analogous to the changes of the electrical resistivity (Fig. 1) and it is the result of decreasing $\rho_{H}$ values of particular curves related to increasing annealing temperatures (Fig. 2). The temperature referred to the sharp drop of $R_s$ values with the constant growth of the sample temperature: $\Delta T/\Delta \tau = \text{const}$ is known as the Curie temperature \([7]\). The changes of the function $R_s = f(T)$ observed in Fig. 3 should be explained by structural changes leading to the decrease in the asymmetrical scattering of the carriers on the substance magnetic atoms. The effect of these changes are phase changes of the first type, because Fig. 2 shows the preservation of the ferromagnetic state of the sample after each annealing.

Fig. 4. The relative electrical resistivity, $\Delta \rho/\rho_0$, as a function of annealing time at the temperature of 673 K.

Fig. 5. The Hall resistivity, $\rho_{H}$, as a function of the applied magnetic induction, $B_0$, for Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ alloy annealed at temperature of 673 K during different time intervals.
At the temperature 673 K the isothermal annealing of the samples was performed to determine which extreme changes of the Hall and electrical resistivities are the result of the first stage of crystallization. The distinct changes of the electrical resistivity (Fig. 4) and the Hall resistivity (Fig. 5) can be observed after annealing of the samples during $10^5$ s and $5 \times 10^3$ s. Annealing during $10^4$ s leads to stabilization of these parameters.

For all the samples undergoing isochronal and isothermal treatment the structural röntgenographic investigations were performed. The obtained X-ray diffraction patterns are shown in Fig. 6 and 7. The X-ray diffraction patterns

![X-ray diffraction patterns](image)

**Fig. 6.** X-ray diffraction patterns for samples of Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ alloy annealed at different temperatures for 4 hours.
referred to the isochronal annealing during 4 h (Fig. 6) prove the creation of the crystalline phase in the amorphous matrix after the annealing at temperatures 673 K and 773 K. For the samples annealed at the temperature 823 K during 4 h and at the temperature 673 K during $2 \times 10^3$ s the quality phase analysis was carried out. To determine the structure of the formed crystalline phases the following computer programs were applied: TREOR 90, LATCON, LAZY PULVERIX and the reference data related to the binary and ternary compounds with a big amount of cobalt [8–11]. It was stated that in the process of crystallization of Co$_{66}$Ni$_{12}$Si$_9$B$_{13}$ metallic glass from the amorphous matrix at the temperature 673 K crystalline phases are created: $\alpha$-Co, (Co, Ni)$_3$Si$_2$B, while at the temperature 773 K, (Co, Ni)$_3$B crystalline phase. Table presents parameters of elementary
cells of the identified crystalline phases and parameters of such phases from the reference data. A good agreement between lattice constants for the phases created from the investigated alloy compared to model pure phases denotes the correct identification of the formed phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Co</td>
<td>2.498</td>
<td>–</td>
<td>4.060</td>
<td>2.505</td>
<td>–</td>
<td>4.070</td>
</tr>
<tr>
<td>(Ni,Co)3Si2B</td>
<td>8.722</td>
<td>–</td>
<td>4.355</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Co5Si2B</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8.6150</td>
<td>–</td>
<td>4.2500</td>
</tr>
<tr>
<td>(Co,Ni)3B</td>
<td>5.193</td>
<td>6.649</td>
<td>4.412</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Co5B</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.229</td>
<td>6.631</td>
<td>4.432</td>
</tr>
<tr>
<td>Ni3B</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.21573</td>
<td>6.61841</td>
<td>4.39159</td>
</tr>
</tbody>
</table>

4. Conclusions

— The crystallization of the metallic glass Co_{66}Ni_{12}Si_{9}B_{13} proceeds in two stages, which — considering performed investigations — may be related to temperatures 673 K and 773 K. The result of the crystallization first stage is the creation of the crystalline phases: α-Co and (Co,Ni)_{3}Si_{2}B, whereas (Co,Ni)_{3}B phase is formed in the second stage.

— The isothermal annealing at the temperature 673 K during 10^4 s leads to the complete crystallization of the α-Co and (Co,Ni)_{3}Si_{2}B phases in the amorphous matrix. Thus, it finishes the first stage of the crystallization.

— During the alloy transition from the amorphous to the crystalline state a systematic decrease in the electrical and Hall resistivities can be observed, while the creation of the crystalline phase is referred to the abrupt decrease in these parameters.

— During the crystallization each alloy state maintains macroscopic ferromagnetic arrangement. The decrease in the spontaneous Hall coefficient denotes the decrease in the amount of asymmetrical scattering of current carriers.

References