Correlation Between the Crystallization Process and Change in Electron Density of States in Amorphous Powder of the Ni$_{80}$Co$_{20}$ Alloy

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Abstract:
The method of differential scanning calorimetry (DSC) was employed to examine the crystallization process of amorphous powder of the Ni$_{80}$Co$_{20}$ alloy in the temperature interval from room temperature to 1000 K. It is shown that the crystallization process of this alloy's powder proceeds in two stages at temperatures $T_1 = 690$K and $T_2 = 790$K. The relative changes in the electron density of states in the vicinity of Fermi level were determined from the changes in the slope of the thermo-electromotive force (TEMF) temperature coefficient before and after each stage of crystallisation process. The obtained results show that the relative change in the electron density of states is 34.9% after the first crystallization stage and 38.9% after the second one. The changes in the specific electrical resistance of the pressed powder as a function of temperature are fully correlated with the change in the electron density of states and results of the DSC method. The observed rapid decrease in the specific electrical resistance after each crystallization stage is caused by the increase of the mean free electron path and increase in the electron density of states.

Keywords: Amorphous metal, Ni-Co alloys, Electron density.

Introduction

Special attention is being paid to amorphous metal alloys (AMA) in the fields of solid state physics and advanced materials, particularly in term of their application in electronics and electrical engineering [1-4]. They are obtained not only by ultra rapid cooling of alloy melts, but also electrochemically [4,5] resulting in the obtainment of powders with a defined chemical composition and appropriate physical properties.

However, certain AMA specificities have not been completely clarified, yet. Intensive examinations of kinetic properties of AMA indicate a correlation between the physical nature of the anomalous behavior of the electron state density at the Fermi level, heat capacitance, thermal conductivity and electrical resistivity, on the one hand and structural inhomogeneities in these materials, on the other. During annealing of amorphous alloys at temperatures about 50 to 100 K lower than the crystallization temperature two competitive processes take place: on the one hand, free volume decreases, at the same time decreasing the rate of diffusion mass...
transport, and the arranging processes, on the other hand, bring the alloy closer to the crystallized state increasing its readiness for crystallization [8, 9, 10].

Most experimental results on the electron structure [11] refer to determination of the electron state density N(E) or the electron state density at the Fermi level N(E_f).

Nevertheless, due to an impossibility to investigate the Fermi-surface for AMA based on transition metals, the experimental results on the electron structure contain far less information than the ones on crystal materials. Today, correlation between the electron structure and AMA properties could not be (completely) solved on the basis of experimental results.

Certain physical properties of amorphous alloys (AMA) are irreversibly changed during the process of their heating, in the crystallization temperature range. This has been a subject matter of our research for several years and the results obtained have been published in a considerable number of scientific journals [1,6,7].

Experimental

Ni/Co alloy powder was obtained in a glass electrochemical cell of 1.0 dm^3 volume containing a special part with a Lugin capillary and a saturated calomel electrode. The anode used was a RuO_2/TiO_2 electrode of 9 cm^2 surface area, and the cathode was a titanium plate of 5 cm^2 surface area and 0.2 cm thickness. The cell was in a thermostat. The working temperature was maintained within ±0.5°C. A solution was obtained from p.a. chemicals and triple-distilled water. It contained 34 g dm^{-3} NiSO_4 and CoSO_4 , 170 gdm^{-3} NH_4Cl and 450 cm^3 18 % NH_4OH. A standard electric circuit was used. The nickel and cobalt alloy powder was deposited galvanostatically at current densities ranging from 50 to 450 mAcm^{-2}. Following electrolysis, the obtained powder was washed several times with distilled water. After being washed with water, in order to prevent oxidation, the powder was washed with 0.1 % benzoic acid solution and dried at 118°C.

Crystallization of the powder was investigated by the differential scanning calorimetry (DSC) method. Measurements were done in nitrogen atmosphere. Amorphous powder of the Ni_{80}Co_{20} alloy was pressed under a pressure of 800 MPa into samples of 40x1.2x0.5 mm^3 dimension. By mechanical junction of the pressed powder sample and a copper conductor a Cu- Ni_{80}Co_{20} thermocouple was formed. The Cu- Ni_{80}Co_{20} junction was placed into a specially constructed furnace and the loose end of the sample was soaked into a pot with a mixture of water and ice. The thermo-electromotive force induced by the thermocouple thus created during heating was measured using a ISKRA TZ 4200 voltmeter with 10^{-5}V susceptibility. Powder X-ray diffractograms were recorded on a X-ray diffractometer ( Cu-Kα radiation).

Results and discussion

During heating of the initial powder of the nickel and cobalt amorphous alloy, the process of structural relaxation took place followed by the crystallization process. A DSC thermal diagram of the Ni_{80}Co_{20} amorphous powder is shown in Fig. 1

Two strongly distinguished exomaxima are noticable on the thermal diagram, the first one with the peak temperature of 690 K and enthalpy of 66.73 J/g released and the second one with the peak temperature of 790 K and enthalpy of 56.03 J/g released.The DSC analysis results show that the NiCo amorphous powder crystallizes in two phases. The first and second crystallization phases terminate at temperatures of about 730 K and 950 K, respectively.
Fig. 1. DSC thermogram of amorphous powder crystallization (80 mol.%Ni, 20 mol.%Co). Heating rate of 20°C·min⁻¹.

For the purpose of investigating structural changes of the powder, an XRD analysis was used to select the samples of the initial powder, the powder heated up to 730 K when the first crystallization phase terminated and the powder heated to 950 K when the second crystallization phase terminated.

Fig. 2. X-ray diffraction patterns of Ni₈₀Co₂₀ powder samples: 1-amorphous powder, 2-heat-treated at 730 K, 3-heat-treated at 950K

The amorphous nature of the alloy particles was confirmed by X-ray diffraction
patterns [12,13]. The XRD-patterns for amorphous Ni$_{80}$Co$_{20}$, as well as the heated samples heat-treated at 730 K (first crystallization phase terminated), and heat-treated at $T_1=950$K (second crystallization phase terminated) are depicted in Fig.2. The X-ray diffractogram of the amorphous sample shows a broad peak [Fig.2(1)]. With the increase in the heating temperature, the percentage of the crystalline phase within the powder increased. The XRD-patterns for samples 2 and 3 show the crystalline structure of the powder, with all crystalline phases present in it. The diffractogram [Fig.2(3)] has considerably more intensive peaks than the diffractogram [Fig.2(2)]. The lines characteristic of Ni-Co appear [Fig.2(2) and 2(3)].

The TEMF measurement results for the same sample during multiple heatings are presented in Fig. 3.

![Fig.3. Temperature dependence of TEMF during multiple heating of the sample of the pressed powder of Ni$_{80}$Co$_{20}$ alloy: 1-first heating, 2-second heating, 3-third heating](image)

It was determined that after each heating of the powder at temperatures $T_0=490$K, $T_1=730$K and $T_2=950$K, a change in the temperature coefficient TEMS ($\alpha$) occurred. The temperature coefficient TEMS is a function of the electron density of states at the Fermi level and is described as follows:

$$\alpha = \frac{h^2}{2m_e} \left( \frac{3}{8\pi} \right)^{2/3} \left( N_{1(E_F)}^{2/3} - N_{2(E_F)}^{2/3} \right)$$

where $h$ is – Planck’s constant, $m_e$ – mass of the electron, $(N_{1(E_F)})$ – electron state density in copper, and $(N_{2(E_F)})$ – electron state density in the Ni$_{80}$Co$_{20}$ powder.

The electron density of states in copper remained approximately constant during the heating of the powder up to 1000 K, which implies that the change of the temperature coefficient TEMS after each heating was the result of a change in the electron density of states at the Fermi level in amorphous Ni$_{80}$Co$_{20}$ of the thermocouple.

Thermal stabilization of the thermocouple (pressed metastable part) was performed by null heating to 490K. This was followed by the first heating to $T_k1 < T_1=730$K$< T_k2$ and the temperature coefficient ($T_k$) of the TEMS slope had the following value $\alpha_1=41\mu$V/K. After the second heating to the temperature $T_2=950$K$> T_k2$ and completion of the first crystallization stage, the value of the temperature coefficient of the TEMS slope was $\alpha_2=26.7\mu$V/K in the temperature interval from 293K to 600 K. From the change in slope of the temperature coefficient, the relative change in the electron density of states, caused by the first crystallization stage, was determined to be $\Delta n_1/n_2=34.9\%$. After the third heating to the temperature of 600K and termination of the second crystallization stage, the value of the
The temperature coefficient TEMS was $\alpha_T = 16.3 \mu V/K$. The corresponding relative change in the electron density of states, caused by the second crystallization stage, was $\Delta n_{22}/n_2 = 38.9 \%$. The overall change in the electron density of states, caused by the first and the second crystallization stages combined, was $\Delta n_{22}/n_2 = 60.2 \%$.

The results of measurement of the temperature dependence of electrical resistivity are shown in Fig. 4.

![Fig. 4. Temperature dependence of specific electrical resistance $\rho(T)$.](image)

The dependence $\rho(T)$ shows that each crystallization stage was accompanied by a decline in electrical resistivity. The occurrence of a new powder structure during the first crystallization stage, resulting in the obtainment of a metastable crystal structure, probably gave rise to partial overlapping of 3d and 4s orbits, creating a conductivity zone. In the second crystallization stage 3d and 4s orbits maximally overlapped, which was accompanied by a further decrease in electrical resistivity. The TEMF measurements, on the other hand, showed that each crystallization stage was accompanied by an increase in the electron state density near the Fermi level. Furthermore, the formation of the crystalline structure increased the mean free path of the electrons.

The results obtained indicate that the sudden decrease of electrical resistivity during each crystallization stage was caused not only by the increase of the free electron concentration at the Fermi level but also by the increase of the mean free path of the electrons.

**Conclusion**

Ni$_{80}$Co$_{20}$ amorphous alloy powder was thermally stable (retained amorphous structure) up to the temperature of around 600 K. The crystallization process proceeded in two stages with exomaxima temperatures of $T_{k1} = 690$K and $T_{k2} = 790$K and enthalpy of crystallization $Q_1 = 66.73$ J/g and $Q_2 = 56.03$ J/g. Each crystallization stage was followed by an increase in the electron density of states in the vicinity of Fermi level $\Delta n_{21}/n_2 = 34.9 \%$ and $\Delta n_{22}/n_2 = 38.9 \%$. The total change in the density of states for the transition from amorphous into crystalline state was $\Delta n_{22}/n_2 = 60.2 \%$. The decrease in electrical resistivity during each crystallization stage arises for two reasons: due to the increase in the electron density of states in the vicinity of the Fermi level and due to the increase in the mean free path of the conducting electrons, stipulated by the transition from amorphous into crystalline phase.
Thus, a full correlation between the crystallization process, the change in the electron state density in the vicinity of the Fermi level and the change in electrical resistivity was determined in the case of Ni$_{80}$Co$_{20}$ amorphous powder.

References


Садржај: Методом диференцијалне сканирајуће калориметрије (ДСК) у температурном интервалу од собне температуре до 1000 К испитан је процес кристалнизаје аморфног праха легура Ni$_{80}$Cu$_{20}$. Показано је да прах ове легуре кристалише у два ступња у области температура $T_1=690$ $K$ за први ступањ и $T_2 = 790$ $K$ за други ступањ. Промене густине стања електрона на Фермијевом нивоу после сваког ступања кристалнизаје одређене су методом мерења специфичне електричне стање електрона (ТЕСМ). Утврђено је да релативно повећање густине електрона после првог ступања кристалнизаје износи $\Delta n_1/n_1 = 34.9\%$, a после другог $\Delta n_2/n_2 = 38.9\%$. Резултати мерења промене специфичне електричне стање електрона у зависности од температуре у потпуној су корелацији са резултатима ДСК методе и промене густине електрона. Нагли пад електричне стање електрона после првог ступања кристалнизаје управљан је порастом концентрације слободних електрона на Фермијевом нивоу и порастом средње дужине слободног пута електрона.

Кључне речи: аморфни метал, легура NiCo, густина стања електрона.