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The Correlation of Processes of Crystallization and Changes of Free Electron Density Amorphous Alloy Powder $Co_{80}Ni_{20}$

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Abstract: Great attention is being given today to investigations on the capabilities and structural changes of amorphous and nanocrystal materials.

Structural changes of the amorphous cobalt and nickel alloy powder obtained by electrochemical deposition were investigated in this paper. The crystallization process, as determined by the DSC method, occurred in two steps. The temperature dependence of electrical resistivity and magnetic susceptibility in isothermal and non-isothermal conditions within the temperature range of room temperature to 700ºC was determined for the powder samples pressed under pressure of 800 MPa. The X-ray structural examinations results correlate with those of the DSC analysis and the electrical resistivity measuring.

Keywords: Crystallization, Amorphous alloy, Nanocrystal materials.

1 Introduction

Amorphous metal alloys are being given special attention in the fields of solid state physics and advanced materials, particularly in terms of their application in electronics and electrical engineering [1-4]. They are obtained not only electrochemically but also by ultrarapid cooling of alloy meltings [4, 5] resulting in the obtainment of powders with a defined chemical composition and appropriate physical properties.

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].

However, certain AMA specificities have not been completely clarified, yet. Intensive examinations of kinetic properties of AMA indicate the correlation

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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 by about 50 to 100K lower than 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 of the experimental results on electron structure [11, 12] refer to determination of the electron state density $N_{(E)}$ or of 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.

2 Experimental

The amorphous powder of $Co_{80}Ni_{20}$ alloy was pressed under pressure of 800 MPa into samples of 40×1.2×0.5 mm^3 dimension. By mechanical junction of the pressed powder sample and a copper conductor a Cu-$Co_{80}Ni_{20}$ thermocouple was formed. The Cu-$Co_{80}Ni_{20}$ junction was placed into a specially constructed furnace and the loose end of the sample was soaked into a pot with the mixture of water and ice. The thermo-electromotive force induced by the thermocouple thus created during heating was measured using the ISKRA TZ 4200 voltmeter of 10^{-5} V susceptibility.

Crystallization of the powder was investigated by differential scanning calorimetry (DSC) method. The measurements were done in the nitrogen atmosphere.

3 Results and Discussion

The DSC thermogram of the pressed amorphous powder of the $Co_{80}Ni_{20}$ alloy is presented in Fig. 1.

The thermograms show three exo-maxima. The first one in the temperature interval from 420 to 520K refers to the thermal stabilization of the sample structure after powder pressing. The other two exo-maxima are typical of the powder crystallization process. Namely, crystallization of the powder is

performed in two stages with crystallization maximum peak temperatures being $T_{K1} = 688.32\,K$ and $T_{K2} = 761.87\,K$. The energy released for each crystallization stage was $Q_1 = 160\,J/g$ and $Q_2 = 4.69\,J/g$, respectively. The TEMF measurement results for the same sample during multiple heatings are presented in Fig. 2.

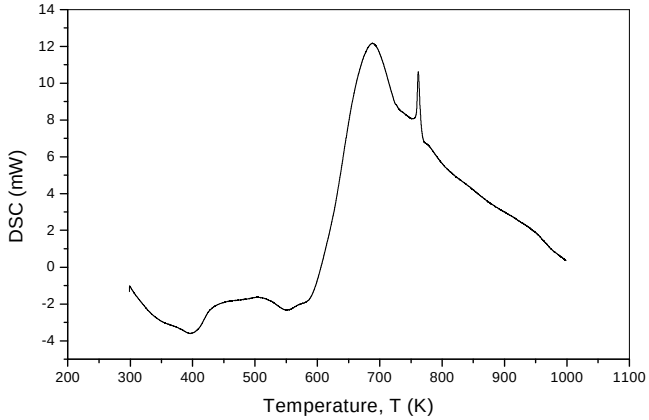

Fig. 1 - *DSC thermogram of the pressed amorphous powder of the $Co_{80}Ni_{20}$ alloy.*

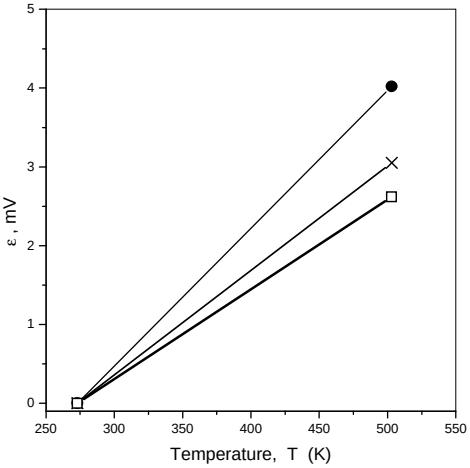

Fig. 2 - *Temperature dependence of TEMF during multiple heating of the sample of the pressed powder of $Co_{80}Ni_{20}$ alloy:* ●- *first heating,* x.- *second heating,* □- *third heating.*

Each heating is followed by a change of the temperature coefficient of TEMF (α) being a function of the difference of electron density at the Fermi level $N_{(E_F)}$:

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

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 $Co_{80}Ni_{20}$ powder.

Electron state density in copper during the process of heating up to 1000 K remained nearly constant. The changes in the temperature coefficient of TEMF after each heating obviously occur due to the electron state density change in the amorphous (metastable) part of the thermocouple.

Thermal stabilization of the pressed powder sample was performed by zero heating up to 550K. Then, at first heating to $T_1 = 600\,\mathrm{K} < T_{K1}$ the temperature coefficients (TC) of the TEMF direction was $\alpha_1 = 17.5\,\mu\mathrm{V/K}$. Following the second heating, up to temperature $T_{K1} < T_2 = 720\,\mathrm{K} < T_{K2}$, the first crystallization stage terminated. The temperature coefficient of the direction was $\alpha_2 = 13.3\,\mu\mathrm{V/K}$. From the change in the TC of the TEMF direction determination was made of the relative change of the electron state density caused by the first crystallization stage $\Delta n_{21}/n_2 = 24\%$.

After the third heating, up to temperature $T_3 = 800\,\mathrm{K} > T_{K2}$, following the second crystallization stage, the TC of the TEMF direction was $\alpha_2 = 11.4\,\mu\mathrm{V/K}$. The relative change of the electron density induced by the second crystallization stage was $\Delta n_{22}/n_2 = 14.3\%$.

The Fig. 3 presents results on the measurement of temperature dependence of specific electrical resistance.

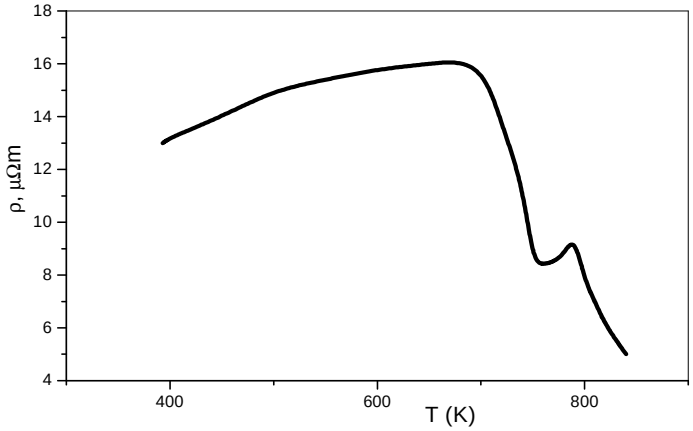

Fig. 3 - *Temperature dependence of specific electrical resistance ρ(T).*

The dependence ρ(T) shows that each crystallization stage is 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 gives rise to a partial overlapping of 3d and 4s orbits, creating a conductivity zone. In the second crystallization stage 3d and 4s orbits maximally overlap, which is accompanied by a further decrease in electrical resistivity. The TEMF measurements, on the other hand, have shown that each crystallization stage is accompanied by an increase in the electron state density near the Fermi level. Furthermore, the formation of the crystal structure increases the mean free path of the electrons.

The results obtained indicate that the sudden decrease of electrical resistivity during each crystallization stage has been 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.

4 Conclusion

The amorphous powder of the $Co_{80}Ni_{20}$ alloy retains its thermal stability up to about 330 ºC. The crystallization process is being performed in two stages with exo-maximum peak temperatures being approximately $T_{K1} = 415°C$ and $T_{K2} = 488°C$. Each crystallization stage is followed by an increase in the electronic state density at the Fermi level: $\Delta n_{21}/n_2 = 24\%$ and $\Delta n_{22}/n_2 = 14.3\%$.

The decline in the electrical resistivity of the powder during each crystallization stage is caused by the increases of electron state density near the Fermi level and of the mean free path of the conductive electrons. Therefore, a complete correlation between the crystallization process, amorphous $Co_{80}Ni_{20}$ alloy powder, electron state density change near the Fermi level and the electrical resistivity change has been determined.

5 References

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