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Influence of the Changes of Free Electron Density on Electrical and Magnetic Properties of the $Co_{70}Fe_5Si_{10}B_{15}$ Amorphous Alloy

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Abstract:

In this study we present the results on structural relaxation of the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy investigated by measuring the thermo-electromotive force (TEMF) during isothermal annealing (for 600 s). A mechanical junction of the investigated alloy and a copper conductor has been constructed for measuring the thermo-electromotive force (ε). Annealing was performed at temperatures $T_1 = 430°C$, $T_2=460°C$ and $T_3=480°C$ which are about 50 to 100°C lower than the crystallization temperature. At these temperatures structural relaxation occurred only in the amorphous alloy. The activation energy E=224 kJ/mol and rate constants $k_1=6.66·10^{-5}$ s^{-1}, $k_2=33·10^{-5}$ s^{-1} and $k_3=76·10^{-5}$ s^{-1} at temperatures T_1, T_2 and T_3, respectively, have been determined for the process. Each isothermal annealing has been followed by determination of the relative change of the electronic state density at the Fermi level as $\Delta n_1/n$=2.36%, $\Delta n_2/n$ =3.21% and $\Delta n_3/n$= 9.80%, respectively.

Keywords: Amorphous alloy, Free electron density, Electrical properties, Magnetic properties.

1. Introduction

Physical features of amorphous metal alloys are irreversibly changed in the process of structural relaxation. This has been the subject of our research for several years [1-4].

The process of structural relaxation is usually studied under conditions of non-isothermal heating at a constant rate up to temperatures slightly below the crystallization temperature and under conditions of non-isothermal cooling. Kinetic features of amorphous alloys show a correlation between the physical nature of the anomalous behavior of electronic states density at the Fermi level, thermal conductivity, heat capacitance and electrical resistivity on the one hand and structural inhomogeneities in these materials on the other. At temperatures up to 100 ºC lower than the crystallization temperature two competitive processes take place during annealing of amorphous alloys: on the one hand, free volume decreases, which lowers the rate of diffusion mass transport, and on the other hand, arranging processes bring the alloy closer to the crystallized state increasing its readiness for crystallization [5-7].

Most experimental investigations based on the electronic structure [8, 9] are about determination of free electron density $N(E)$ or free electron density at the Fermi level $N(E_F)$. However, due to the impossibility of investigating the Fermi-surface of amorphous metal alloys based on transition metals, experimental results contain less information than the same experiments on crystal materials. Correlation between the electron structure and properties of

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amorphous metal alloys can not be completely solved on the basis of experimental results.

2. Theoretical model

At the junction of materials, with different Fermi levels, electrons move from the material with a higher Fermi level to the material with a lower Fermi level due to the thermodynamic tendency of equalizing Fermi levels in these two materials. As a result of these processes, a so-called constant external potential difference exists, caused by the difference of output work of the electrons (A_1 and A_2) in the two materials, when the electrons move from the material with lower output work into the material with higher output work ($A_2 < A_1$ corresponds to $n_2 > n_1$, where n is the concentration of free electrons in the material):

$$U_e = \frac{A_1 - A_2}{e} \tag{1}$$

A potential difference also exists between inward points of the contact surface. Due to equalizing of the Fermi levels of the two materials, potential energies of electrons in the other material are lower than the ones in the first one for E_{F2}-E_{F1}, so the following internal contact potential difference occurs:

$$U_i = \frac{E_{F_2} - E_{F_1}}{e} \tag{2}$$

in other words,

$$U_i = \frac{h^2}{2me}\left(\frac{3}{8\pi}\right)^{2/3}\left(n_2^{2/3} - n_1^{2/3}\right) \tag{3}$$

Therefore, the internal potential difference is a consequence of the difference in the concentration of electron gases in conducting materials in contact. The temperature dependence of U_i is hidden, because the Fermi level E_f is also temperature dependent.

If the joint conductors are held at different temperatures $T_2 > T_1$, a thermoelectric current occurs, as a consequence of the thermo electromotive force:

$$\varepsilon = U_{12} + U_{21} = \frac{h^2}{2me}\left(\frac{3}{8\pi}\right)^{2/3}\left(n_2^{2/3} - n_1^{2/3}\right)\left(T_2 - T_1\right) \tag{4}$$

or $$\varepsilon = \alpha\Delta T \tag{5}$$

where

$$\alpha = \frac{h^2}{2me}\left(\frac{3}{8\pi}\right)^{2/3}\left(n_2^{2/3} - n_1^{2/3}\right) \tag{6}$$

is the thermo electromotive force coefficient depending on the characteristics of the materials in junction and ΔT is the temperature difference of the two junctions.

3. Experimental procedure

A thirty-micrometer-thick ribbon of the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy was used as a sample in our research. A mechanical junction of the investigated alloy and a copper conductor was constructed for measuring TEMF. Measurements of TEMF and the temperature dependence of electric resistance were performed using a double-channel voltage signals recorder with a sensitivity of 1 μV.

The crystallization process was investigated using the DSC method in the temperature

interval from room temperature to 700°C. Measurements of relative magnetic permeability in isothermal and non-isothermal conditions were performed using a modified Maxwell method, based on the action of an inhomogeneous field on the magnetic. Measurements of the magnetic force were performed with a sensitivity of 10^{-6}N. All measurements were done in argon atmosphere.

4. Results and discussion
4. 1. Structural Relaxation Kinetics

Experimentally obtained isothermal dependencies of the TEMF of the Cu-Al amorphous alloy thermocouple on time at temperatures of T_1 , T_2 and T_3 are presented in Fig 1.

The results obtained show a linear dependence of TEMS on time, which can be given as:

$$\varepsilon = kt + \varepsilon_0$$

where ε - is the TEMS at any moment during isothermal annealing, k –is a structural relaxation rate constant at a certain temperature and ε_0 -is the initial TEMS at the annealing temperature . This value is proportional to the temperature of isothermal annealing and inversely proportional to the sample-heating rate to the given temperature.

From the line slopes presented in Fig. 1 structural relaxation rate constants $k_1 = 6.66 \cdot 10^{-5}$ s^{-1}, $k_2 = 33 \cdot 10^{-5}$ s^{-1} and $k_3 = 76 \cdot 10^{-5}$ s^{-1} were determined at $= T_1 = 430°$C, $T_2 = 460°$C and $T_3 = 480°$C, respectively.

The Δln k dependence on 1/T was also linear. From the slopes of linear dependencies *ln k vs. $10^3/T$* the value of activation energy $E_a = 224$ kJ/mol was determined.

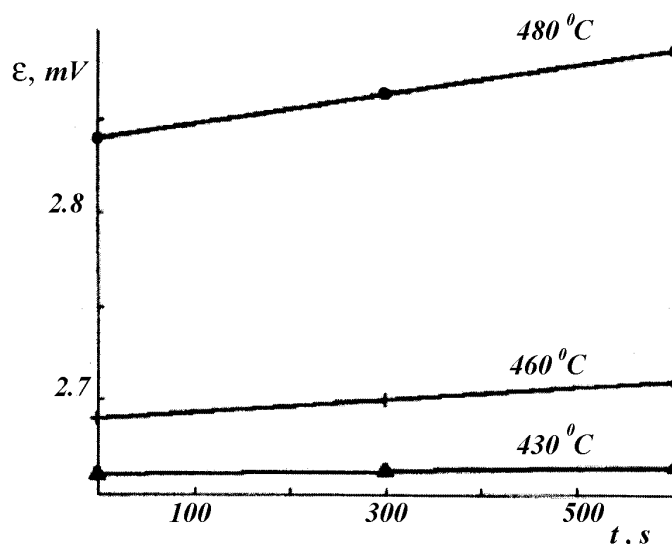**Fig. 1** TEMF dependence on time at temperatures $T_1 = 430°$C, $T_2 = 460°$C and $T_3 = 480°$C

Thus, measurements of the thermo-electromotive force can be used for investigation of the structural state of amorphous metal alloys and changes of the thermo-electromotive force coefficient can be used to evaluate the degree of system heterogeneity.

4. 2. Change of electronic state density at the Fermi level during isothermal annealing

It was experimentally determined that a linear TEMF temperature dependence existed before and after each annealing, Fig. 2.

From the line slopes presented in Fig. 1 temperature TEMF coefficients were determined before and after each isothermal annealing at temperatures 430, 460 and 480^0C, being α=5.92 μV/°C and α_1=6.06 μV/°C, α_2=6.11 μV/°C and α_3=6.50 μV/°C, respectively.

From the relation (6) showing the dependence of the TEMF temperature coefficient on the electronic state density difference at the Fermi level of the material in junction, the change of electronic state density at the Fermi level after each isothermal annealing was determined: $\Delta n_1/n$=2.36%, $\Delta n_2/n$ = 3.21 %. The increased value $\Delta n_3/n$=9.8% most likely resulted from partial alloy crystallization at temperature T_3=480ºC.
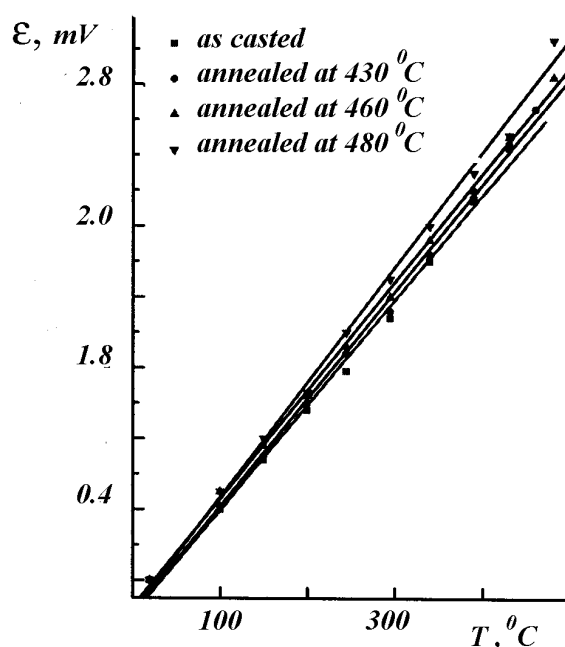
**Fig. 2** TEMF temperature dependence before and after annealing at T_1=430˚C, T_2=460˚C and T_3=480˚C. The duration of annealing was 600 s.

The results obtained show that during isothermal annealing of the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy at temperatures about 50ºC lower than the crystallization temperature, structural relaxation and the process of partial crystallization take place in the material at temperatures T_1 and T_2, and at temperature T_3, respectively. As a result of the process, the electronic state density at the Fermi level increases in the amorphous alloy. These changes directly affect electrical and magnetic properties of the alloy.

4.3 Electrical and Magnetic Properties

Electrical Properties Fig. 3 presents the experimentally obtained dependence of electrical resistivity of the alloy on temperature.

According to DSC measurements, Fig.4, the alloy crystallizes in two stages, at temperature T_1=460˚C for the first stage and at T_2=540˚C for the second one. The temperature

dependence of electrical resistivity presented in Fig. 3 shows that a sudden decrease of electrical resistivity occurs during each crystallization stage.
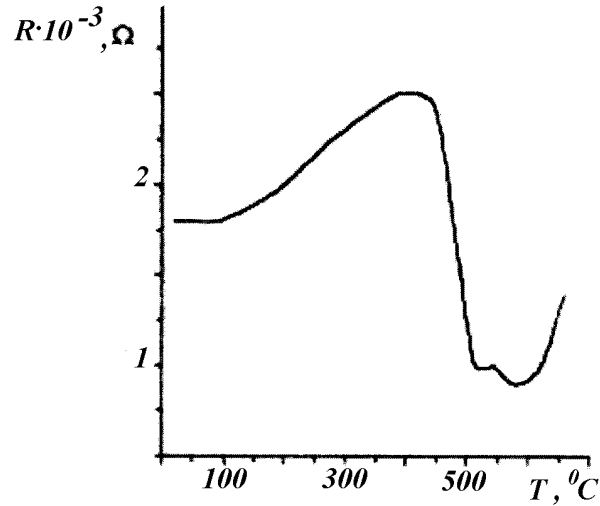
Fig. 3 Temperature dependence of electrical resistivity

The results obtained indicate that the sudden decrease of electrical resistivity during the crystallization process has been caused not only by the increase of the electron mean free path but also by the increase of electronic state density at the Fermi level.
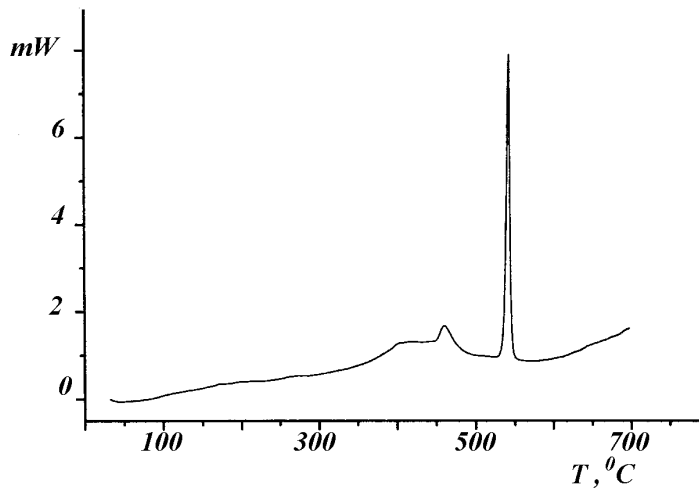

Fig. 4 DSC curve; heating rate 10 K/min

Magnetic Properties   Fig. 5 presents the results of measurements of the change of relative magnetic permeability before and after annealing. The results obtained show that after structural relaxation at T=460°C and 480°C, magnetic properties have changed, being in direct correlation with the change of electronic state density at the Fermi level.

These results show that the relative change of magnetic permeability after annealing is in full correlation with the change of electron state densities at the Fermi level. Namely, electrons responsible for ferromagnetic properties must be located in deeper energy states.

These bands should not be completely full, as the effect of electron spins of full states is cancelled. Thus, internal, partially filled bands have an effect on ferromagnetism. As during structural relaxation of the amorphous alloy atoms move to lower energy states and electron state densities increase in the high energy states, it is obvious that the number of free quantum states in the lower sub-shell increases. Electron spins will then spontaneously orient in the same direction attaining a lower energy state. Due to the Pauli principle only one electron can be present in any quantum state.
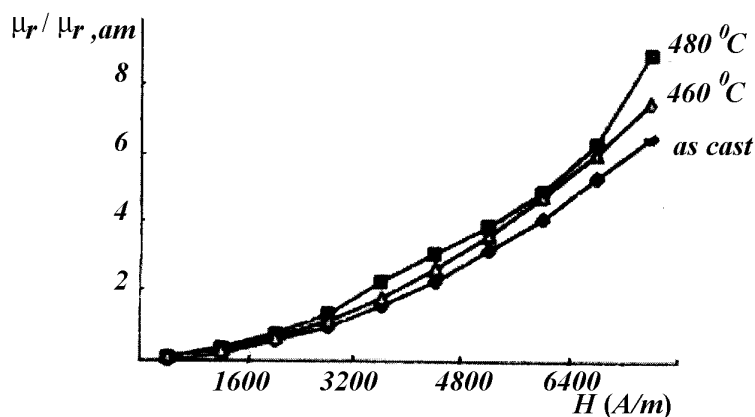
Fig. 5 The effect of annealing on the relative change of magnetic permeability

      This way, the increase of free quantum states in internal partially filled bands increases the number of electrons with parallel-uncoupled spins that finally leads to a higher magnetic permeability of the amorphous alloy after structural relaxation. However, when the amorphous alloy has completely crystallized its ferromagnetism is weaker than in the amorphous state. Reduction of magnetic permeability (ferromagnetic properties) of the amorphous alloy after crystallization can be explained by a reduction of inter-particle distances. The partially filled sub-shell diameter and inter-atomic distance ratio is now significantly smaller than before the crystallization process that has a significant influence on the reduction of ferromagnetic properties.

5. Conclusion

      The $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy retains its amorphous structure up to 400°C. During isothermal annealing, the TEMF increases at temperatures about 50 to 100 °C lower than the crystallization temperature. The electronic state density at the Fermi level increases after each isothermal annealing. The changes of electron density at the Fermi level during structural relaxation cause changes of its electrical and magnetic properties. Direct proportionality between the increase of electronic state density and electrical conductivity has been determined. The dependence of magnetic properties on electronic state density is considerably more complex.

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Резюме: В данной работе представлены результаты структурной релаксации аморфного сплава $Co_{70}Fe_5Si_{10}B_{15}$ *получены измерением термоэлектродвижущей силы при помощи термопары, полученной механическим соединением проводника из меди и исследуемого аморфного сплава в изотермических условиях в течение 600 с при температурах* T_1=430, T_2=460 *и* T_3=480°C. *Эти температуры приблизительно на 50-100° С ниже температуры кристаллизации. Структурная релаксация протекает только в аморфном сплаве. Определены энергия активации процесса Е=224 кдж/моль, константы скорости процесса* (k_1=6,66·$10^{-5}s^{-1}$, k_2=33·$10^{-5}s^{-1}$ *и* k_3=76·$10^{-5}s^{-1}$) *при температурах* T_1, T_2 *и* T_3. *На основании изменения после каждого отжига температурного коэффициента термоэлектродвижущей силы, определено относительное изменение плотности состояний электронов аморфного сплава на уровне Ферми (*$\Delta n_1/n$=2,36%, $\Delta n_2/n$ =3,21% *и* $\Delta n_3/n$= 9,80%.)

Ключевые слова: Аморфный сплав, плотность свободных электронов, электрические свойства, магнитные свойства.

Садржај: У овом раду дати су резултати структурне релаксације аморфне легуре $Co_{70}Fe_5Si_{10}B_{15}$ *праћене мерењем термоелектромоторне силе (ТЕМФ) термопара оствареног механичким спајањем бакарног проводника Cu и испитиване аморфне легуре у изотермским условима, током 600 s, на темпертурама* T_1=430, T_2=460 *и* T_3=480°C. *Ове температуре су приближно за 50 до 100°C ниже од температуре кристализације, тако да се структурна релаксација одвија само у аморфној легури. Одређене су енергија активације процеса, Е = 224 kJ/mol, константе брзине* k_1 =6,66·$10^{-5}s^{-1}$, k_2=33·$10^{-5}s^{-1}$ *и* k_3=76·$10^{-5}s^{-1}$ *на температурама* T_1, T_2 *и* T_3. *Из промене температурног коефицијента термоелектромоторне силе после сваког одгревања, одређена је релативна промена густине стања електрона аморфне легуре на Фермијевом нивоу,* $\Delta n_1/n$=2,36%, $\Delta n_2/n$ =3,21% *и* $\Delta n_3/n$= 9,80%.

Кључне речи: Аморфна легура, густина слободних електрона, електрична својства, магнетна својства.