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Possible conversion of the charge carriers in high-entropy alloy $Al_{0.5}CoCuCrNiFe$

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A complex study of the temperature dependences of electrical conductivity, thermo-EMF and thermal conductivity in the high-entropy alloy $Al_{0.5}CoCuCrNiFe$ have been carried out in order to established the nature of the anomalies of the kinetic coefficients in the temperature range ~ 300...77 K. It is shown that, as the temperature is lowered from ~ 210 K to ~ 170 K, these characteristics exhibit anomalies, the signs of which indicate an increase in the rate of growth of electrical conductivity and a slowdown in the decrease in thermoelectric power and thermal conductivity. A concept is proposed to explain the discovered anomalies by the hole-electron ($h \rightarrow e$) conversion in the carrier system. Data on the effect of rolling deformation on kinetic coefficients have been obtained.

Keywords: high-entropy alloy, kinetic coefficients, conversion and mobility of charge carriers, plastic deformation.

Можлива конверсія носіїв заряду у високоентропійному сплаві $Al_{0.5}CoCuCrNiFe$.
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Проведено комплексне вивчення температурних залежностей електропровідності, термоерс і теплопровідності високоентропійного сплаву $Al_{0.5}CoCuCrNiFe$ з метою встановлення природи аномалій кінетичних коефіцієнтів в інтервалі ~ 300–77 К. Показано, що при зниженні температури від ~ 210 К до ~ 170 К вказані характеристики демонструють аномалії, знаки яких свідчать про прискорення росту електропровідності і зниження спаду термоерс і теплопровідності. Запропоновано концепцію пояснення виявлених аномалій дірково-електронною ($h \rightarrow e$) конверсією у системі носіїв заряду. Отримано дані про вплив деформації прокаткою на кінетичні коефіцієнти.

Проведено комплексное изучение температурных зависимостей электросопротивления, термоэдс и теплопроводности высокоэнтропийного сплава $Al_{0.5}CoCuCrNiFe$ с целью установления природы аномалий кинетических коэффициентов в интервале ~ 300–77 К. Показано, что при понижении температуры от ~ 210 К до ~ 170 К указанные характеристики демонстрируют аномалии, знаки которых свидетельствуют об увеличении скорости роста электропроводности и торможении спада термоэдс и теплопроводности. Предложена концепция объяснения обнаруженных аномалий дырочно-электронной ($h \rightarrow e$) конверсией в системе носителей заряда. Получены данные о влиянии деформации прокаткой на кинетические коэффициенты.

1. Introduction

When predicting the operational properties of a new class of functional materials-high-entropy alloys (HEAs) [1–3], one should take into account the possibility of structural and electronic transformations in them which can affect the thermophysical, electrophysical and mechanical charac-

teristics. The purpose of this work is to clarify the nature of the anomalies in the kinetic and acoustic coefficients of HEA $Al_{0.5}CoCuCrNiFe$ known from literature sources, which arise at temperatures significantly exceeding the expected operating temperature range (cryogenic) where high strength is combined with high plasticity [4]. The interest to the problem was due to the following circumstances. Earlier, the anomalies of mechanical, acoustic and kinetic properties HEA $Al_{0.5}CoCuCrNiFe$ were observed in the temperature interval ~ 200–150 K [4–8] (inserts a, b in Fig. 1). Despite all this, according to [4], the strength of $Al_{0.5}CoCuCrNiFe$ increases nonlinearly below T ~ 200 K (Fig. 1, inset a), which may be associated with a response to a certain transformation. On the other hand, the absence of structural features below ~ 230 K [5, 6] gave hope to discover an exclusively electronic transformation and its effect on mechanical properties, which, in addition to practical interest, was also of theoretical interest.

To register structural-electronic transformations in extended temperature ranges, methods of studying fundamental kinetic characteristics — electric, thermoelectric, magnetic, electromagnetic, thermal, thermodynamic and their various combinations are usually used, since any such transformation changes the electronic configuration of the material [9]. The most complete information about the electronic subsystem, along with the Hall coefficient, is provided by the thermoelectric coefficient, S, which characterizes the charge transfer under the action of the temperature gradient. In this work, the emphasis was placed on the study of the dependence $S(T)$, which made it possible to track the processes occurring in the system of charge carriers, in particular, those caused by distortions of the crystal lattice. An impressive picture of the influence of the latter on thermo-EMF is a change in the sign of S in copper as a result of rolling deformation [10]. According to [11], such a change of sign of charge carriers is classified as "conversion of charge carriers". Taking into account that the crystalline structure of HEA is distorted in a scale of the unit cell even in the state of structural relaxation, we do not exclude the possibility of transformation processes in the $Al_{0.5}CoCuCrNiFe$ charge carrier system, which manifest themselves in the features of the temperature dependence $S(T)$. As for the fundamentally possible effects associated with the difference in the scattering of

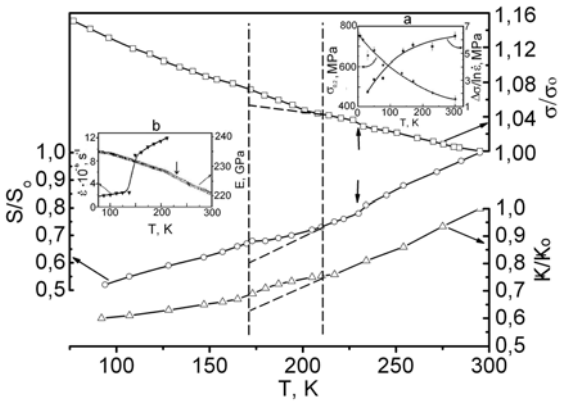

Fig. 1. Solid lines — dependences $\sigma(T)/\sigma_0$, $S(T)/S_0$ and $K(T)/K_0 \propto k(T)/k_0$ for initial samples. Insert (*a*): conventional yield point, $\sigma_{0.2}$, and high-speed perceptibility of normal deforming tension, $\Delta\sigma/\Delta\ln\varepsilon$ at ε ~ 2 % as a function of T [4]. Insert (*b*): creep rate ε [8] and dynamic Young's modulus E as a function of T [5, 6]. The use of dashed lines is explained in the text.

charge carriers of different signs by phonons — electrons (electron-like) and holes (hole-like), additional information for interpretation of the results can be the temperature dependences of two more kinetic coefficients — electrical conductivity σ and thermal conductivity k.

It was also interesting to establish the effect of plastic deformation on kinetic coefficients of $Al_{0.5}CoCuCrNiFe$. For this purpose the rolling deformation was applied.

2. Experimental

HEA plates of $Al_{0.5}CoCuCrNiFe$ (~ 50×3×0.7 (mm^3) were cut out from a billet obtained by rolling ingot which was manufactured by alloying the components (wt. %: Al — 4.46; Co — 19.48; Cu — 21.01; Cr — 17.18; Ni — 19.4; Fe — 18.46 with a purity of 99.9 %) in an argon atmosphere [5, 6]. The plates were annealed during 12 h at T = 975°C. The structural state formed as a result of annealing is referred below as the initial one. The experiments began by measuring the predicted dependences on the initial samples. After completing these measurements, the samples were deformed by rolling along the long axis at T ~ 295 K to the degree of deformation ε = 43 %. For ε, the ratio of the difference between the initial and final plate thicknesses to the initial value was taken. After this, measurements of similar dependences on deformed samples were repeated. Thus, the results below refer to the same sample.

The temperature T of the samples was measured with an accuracy of ~ 1 K with a copper-constantan thermocouple. Electrical resistivity $r = 1/\sigma$ (σ is the electrical conductivity) was measured with an accuracy of no worse than ~ 1 % by the 4-points method at direct current ~ 1–10 mA. To designate the absolute (specific) thermopower S, the ratio $S = \delta U/\delta T$ is taken, where $\delta U = U_1 - U_2$ is the potential difference between the ends of the sample, which arose due to the presence of a stationary drop $\delta T = (T_1 - T_2)$ (5–10) K. The δU measurement accuracy was ~ 10^{-7} V. The presence of δT was a consequence of the stationary heat flux Q, which was supplied to one of the ends of the sample; δT was measured with a sensitivity of ~ 10^{-3} K by two copper-constantan thermocouples, switched towards each other. An accuracy of determining the absolute value of S was estimated as ~ 5–10 %.

To register the temperatures and signs of anomalies in the thermal conductivity coefficient k, we used a version of the classic method of uniaxial stationary heat flux (USHF) developed by us [8, 12] for the range of 300–77 K [13]. It makes possible to avoid accounting all possible heat losses, that, as known, is a difficult problem. In this method, the adequacy of the results was provided by measuring the temperature dependence of the same characteristic $\delta T = (T_1 - T_2)$, but — this is the essence of the difference from USHF — under conditions of a strictly monotonic change in T in all heat losses. Writing down $\delta T(T) \propto 1/[k(T) \times \Psi(T)]$, where Ψ is the temperature coefficient monotonic in T, and denoting $[k(T) \times \Psi(T)] \equiv K(T)$, where $K(T)$ has the meaning of the coefficient of thermal conductivity monotonically scaled in T, we obtain a visual representation of the changes with T in real k using the curve $K(T)$. All measurements of the dependences were carried out in the mode of a step-by-step T decrease of the sample which was in a thermal field of gaseous nitrogen in a vertically oriented Dewar vessel with liquid N_2.

The configuration of isotherms of this field provides: a monotonic decrease in T as it approaches the level of liquid nitrogen, and simultaneously the monotonic change in the coefficient $\Psi(T)$ [8, 12]. Note also that two thermalizations are required to obtain an adequate result: with a duration of ~ 10 min to stabilize the current temperature of the sample T_i at $Q = 0$, and approximately the same time for the thermalization of the state that was established after connecting Q.

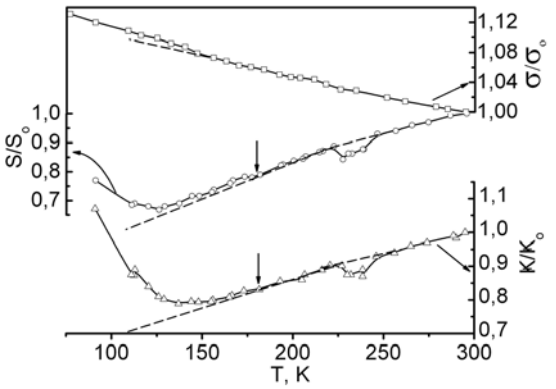

Fig. 2. Solid lines — dependences $\sigma(T)/\sigma_0$, S/S_0 and $K/K_0 \propto k/k_0$ for samples deformed by rolling to $\varepsilon = 43$ %. The use of dashed lines is explained in the text.

3. Results and discussion

The graphs of normalized dependences $\sigma(T)/\sigma_0$, $S(T)/S_0$ and $K(T)/K_0 \propto k(T)/k_0$ ($T_0 = 295$ K) for initial samples are shown in Fig. 1. It can be seen that each curve has an anomalous section in the range of ~ 210–170 K, in which the temperature derivative of the measured value differs markedly from the value above T ~ 210 K. The dashed lines show the linear extrapolation of the sections of the graphs available in the range of 295–210 K to the region of anomalies. The meaning of this operation is to identify the sign of an anomaly, i.e. the sign of the difference between the experimental and extrapolated values, for example, $S(T)^{exp} - S(T)^{extr}$. You can see that all coefficients have an anomaly with the sign "+". The latter means that with decreasing T, the presence of an anomaly increases the growth rate of σ and slows down the rate of decrease in S and K.

There are also weak anomalies in the region of ~ 230 K on the curves $\sigma(T)/\sigma_0$ and $S(T)/S_0$. Their different signs indicated a different nature of this anomaly in comparison with the nature of the previous one.

On graphs of analogous dependences for deformed samples, Fig. 2, one can see a cardinal change in the configurations of the $S(T)/S_0$ and $K(T)/K_0$ curves. Thus, the anomaly in $S(T)/S_0$ near ~ 230 K has become visible. Roughly the same configura-

tion has appeared in the same place of T the anomaly section of curve $K(T)/K_0$.

The extended anomaly inherent in the initial structures in the range of ~ 210–170 K was also significantly transformed. First, the temperature of its upper boundary (indicated by the arrow) dropped to ~ 180 K. Second, below of ~ 130 K the signs of the temperature derivatives of the dependences $S(T)/S_0$ and $K(T)/K_0$ changed from "+" to "–" although the signs of the anomalies themselves remained the same. The latter indicates the same nature of this anomaly as the anomaly in the initial structure.

The coefficients of thermo-EMF of both kinds of samples for the range of ~ 300–77 K are positive ($S > 0$), that indicates predominantly electronic conductivity. In spite of this $S_0(\varepsilon = 0) \approx 3.3$ μV/K, $S_0(\varepsilon = 43\ \%) \approx 6.0$ μV/K.

The morphology of the initial structure. The HEA ingot of $Al_{0.5}CoCuCrNiFe$ has a dendrite structure in which the dendrites are enriched in Fe, Cr and Co, and interdendrite gaps (IDG) — by Cu (65 %), Al (up to 15 %) and depleted in Fe, Cr, Co [5, 14, 15]. High-temperature annealing do not change the composition of the dendrites while the Cu and Al contents in the IDG decrease and the contents of other elements increase. For our work it is important that as a result of annealing the particles are formed at the boundaries between dendrites, and IDG are enriched in Ni (~30 %), Al (>20 %) and Cu (>20 %) having an ordered *bcc* lattice of the type B2.

It has been established by several methods that the presence of these particles causes an anomaly in the properties of annealed samples at T ~ 230 K. Thus, the temperature dependence of the dynamic Young's modulus has a weak feature here [5, 6] (marked with an arrow in the inset *b* in Fig. 1), which correlates with the relaxation resonance of acoustic absorption (Koiva-Hasiguchi). In our work, the $\sigma(T)/\sigma_0$ and $S(T)/S_0$ dependences also have features at the same T (indicated by arrows in Fig. 1). Additional attention we focus on one more experimental fact: on the $E(T)$ plot below ~ 210 K, there are no features indicating any structural transformations [5, 6]. Because of this, it can be assumed that the anomaly in the range of ~ 210–170 K has an exclusively electronic nature due to thermal compression.

The working hypothesis and its premises. There are data in the literature on the dependences $S(T)$ for $Al_{0.5}CoCuCrNiFe$ HEAs with equiatomic composition [16, 17], which indicate not only their hole-like conductivity ($S < 0$) at T ~ 300 K, but even the change in the sign of S with decreasing T, i.e. the presence of conversion of free charge carriers, which leads to prevalence of electron-like carriers ($S > 0$). These results may indicate a significant effect of the component composition of the HEA on the type of electrical conductivity in a wide temperature range.

Having no reason to associate the discovered anomalies with structural changes (see above), we considered the possibility of their explanation by the conversion of free charge carriers. In presenting the proposed concept we restrict ourselves to phenomenology of the phenomenon and assume that electrons and holes make independent contributions to σ, S and k [19]:

$$\sigma = n_e|e|u_e + n_h|e|u_h, \tag{1}$$

$$S=|S_e| - |S_h|, \tag{2}$$

$$k = k_e + k_h + k_{ph}. \tag{3}$$

In (1)–(3), density and mobility of electrons and holes are denoted by symbols n and u with corresponding indexes, and the charge-conjugate (e and h) and phonon components of the thermal conductivity k are denoted by symbols k_e, k_h and k_{ph}.

Obviously, the phenomenon of conversion will manifest itself most expressively in the change of total thermoelectric power $S = |S_e| - S_h$. In this case, the changes in the values of σ and k must correspond, in particular, to the degree of change in the concentrations of the carriers included in the ensemble. In this regard, let's consider some variants of temperature behavior of the total thermoelectric power S of a typical metal ($S \propto T$) with mixed electrical conductivity. At the same time, we will remain within the framework of experimental situation available in our work: $|S_e| - |S_h| = |S| > 0$, and $S > 0$.

a) Let no carrier conversion take place in a certain interval $T_0 - T_3$. Then the graph of the dependence $S(T)/S_0$ will be similar to curve *1*, Fig. 3.

b) Suppose further that in the interval T_1–T_2, the conversion of a certain number of holy carriers into the same number of electrons takes place in the system of charge carriers. This situation can occur in the case of a change in the configuration of

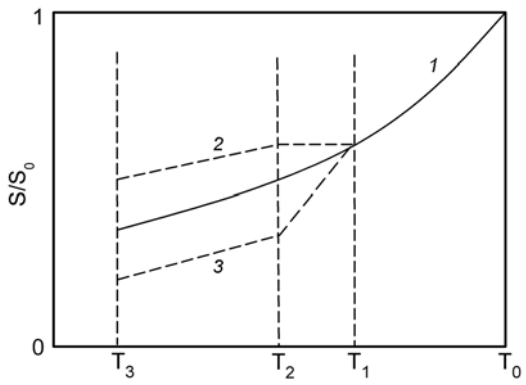

Fig. 3. Schematic picture of possible variants of dependences $S(T)/S_0$ for typical metal that having mixed electric conductivity with predominantly electron-like carriers: *1* — conversion of charge carriers is absent; *2* — in interval $T_1 - T_2$ part of holes transforms in electrons; *3* — in the interval $T_1 - T_2$ part of electrons transforms in holes.

the holy sheet of the Fermi surface with formation of an electron pocket in another Brillouin zone due to changes in the degree of overlap of the wave functions of neighboring atoms. An example of a complex shape of the Fermi surface of a metal is the holy "monster" for Be and MgB in the review by Kosevich [19]. Within the framework of such a model, $|S|$ will decrease starting from T_1 more slowly than in the case (a), and the curve $S(T)/S_0$ in the $T_1 - T_2$ interval will be located above the corresponding portion of curve *1*, Fig. 3.

c) Suppose finally that in the interval $T_1 - T_2$, part of electrons on the Fermi surface turns into holes. As a result, starting from T_1, $|S|$ will decrease faster than in the absence of the conversion, and the curve $S(T)/S_0$ will be located below the corresponding portion of curve *1*, Fig. 3.

Comparing the graphs $S(T)/S_0$ (Fig. 1 and 2) with the considered variants of the temperature behavior of $S(T)/S_0$ of typical metal, it can be seen that for the initial structures, the behavior of $S(T)/S_0$ in the range of ~ 210–170 K corresponds to the conversion of holes into electrons, i.e. to the case (b). In deformed samples the anomaly of $S(T)/S_0$ below T ~ 180 K also corresponds to the case (b). The subsequent "abnormal" change in $|S|$ increases with decreasing T; and below T ~ 130 K, a strong increase in $|S|$ is observed. Within the framework of the proposed concept, the change in the sign of the temperature derivative dS/dT should be interpreted as an indicator of the intensification of the conversion process. An indirect evidence of the absence of experimental error is the similar character of the temperature dependence $K(T)/K_0$ below T ~ 130 K.

Possible influence of conversion on σ *and* $K \propto k$. It was noted above that it is fundamentally impossible to exclude the influence of conversion on the electrical conductivity σ and the charge-conjugate component of thermal conductivity $k_e + k_h$ by changing the characteristics of scattering of charge carriers of different signs by phonons. In other words, one can expect an effect associated with a change in the ensemble-averaged carrier mobility u. Registering this would be an argument in favor of the conversion hypothesis. Let's turn to the experiment.

In section "*Results*" it was noted that the anomalies present in both annealed and deformed samples in the range of ~ 210–170 K and below ~ 180 K, respectively (Fig. 1, 2), lead to an increase in σ^{exp} and K^{exp} in comparison with the values $\sigma^{extr}(T)$ and $K^{extr}(T)$ extrapolated from the higher-temperature sections of the dependences. Based on this, the following conclusion can be drawn. If the detected anomalies of the kinetic coefficients have really conversion nature of the "$h \rightarrow e$" type, then the signs of the quantities $\Delta\sigma = (\sigma^{exp} - \sigma^{extr}) > 0$ and $\Delta K = (K^{exp} - K^{extr}) > 0$ are indeed associated with an increase in the concentration of electron-like carriers. In this case, electron-like carriers should have a higher mobility u_e (lower effective mass) than the mobility of hole-like carriers.

Data on the ratio of electron-to-hole mobilities in $Al_{0.5}CoCuCrNiFe$ could be a direct confirmation of the stated hypothesis, but they are unknown to us. At the same time, it can be noted that there are alloys, for example, InSb and GaSb, in which the electron mobility is almost two orders higher than magnitude of the hole mobility [11].

4. Conclusions

In the range of ~ 300–77 K, the temperature dependences of electrical conductivity σ, absolute thermoelectric power S and thermal conductivity k of HEA $Al_{0.5}CoCuCrNiFe$ in the annealed state and after deformation by rolling up to ε = 43 % were measured and their comparative analysis was performed. For each of the named structural states, an extended temperature range was found (annealed state ~ 210...170 K, de-

formed one ~ 180... < 77 K) in which the kinetic coefficients demonstrate the correlated anomalies in the form of an excess of σ, S and k in comparison with those extrapolated from the neighboring region of higher temperatures. In both cases, the thermoelectric power was positive ($S > 0$), which indicates predominantly electronic type of electric conductivity.

To explain the observed effects the concept was proposed based on the hypothesis of the conversion of a part of holy charge carriers into electrons, which may be associated with changes in the configurations of the holy and electron sheets of the Fermi surface due to a change in the degree of overlap of wave functions of neighboring $Al_{0.5}CoCuCrNiFe$ atoms with decreasing T. A prerequisite for the correctness of the proposed concept should be the predominance of the electron mobility over the hole mobility.

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