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Correlation Between the Entropy Degree and Properties of Multi-component (High-entropy) Film Materials

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A correlation between the degree of entropy and the electrophysical and magnetoresistive properties of film materials with different architecture in the paper establishes. It is established that the gradual decrease in thermal coefficient of resistance (TCR) during the transition from low-entropy (LEA) to high-entropy (HEA) alloys is explained by the fact that the resistivity in the direction of LEA → HEA increases as a result of the decrease of the atoms mobility during the formation of basic phase and solid phase. It is shown that the temperature sensitivity of the resistance almost does not change depending on the entropy degree. The magnetic field dependences in all three measurement geometries differs only in amplitude and has all the GMR characteristics. It is concluded that the elements of granular state are realized in HEA films. At the same time, anisotropic magnetoresistance is observed for all cases of film material architecture under certain conditions which is caused not by spin-dependent electron scattering but by spin-orbital electron interaction, that is, the architecture of the samples does not play a prominent role.

Keywords: Entropy of mixing, Entropy degree, Homogenization, High-entropy film alloys, Thermal coefficient of resistance, Giant magnetoresistance.

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1. INTRODUCTION

According to the conventional classification (see, for example, [1-3]) two-component alloys in the form of solid solution (s.s.) refer to low-entropy alloys (LEA), with $n = 3\text{-}4$ stabilized alloys of medium entropy (MEA), and at $n = 5\text{-}14$ - high-entropy (HEA). High-entropy materials are formed based on Co, Ni, Fe and Cu, Cr, Al or Co, Ni, Fe and Ti, Zr, Hf or V, Nb, Ta et al., which, unlike the traditional 2-3 component containing not less than 5 components, and the atomic concentration is from 5 to 35 % [1]. The formation of a practically single-phase s.s. substitution in a multicomponent system is contrary to the Gibbs phase rule, but is possible when the requirements for certain entropy and enthalpy values are mixed and the atomic size difference parameter (see, for example, [2, 3]). The electrophysical properties of two- or three-component film systems were studied in [4-7].

Under the influence of temperature, strain and external magnetic field, the interaction of charge carriers with the boundaries, the atoms magnetic moments, granules, domains and phonons are revealed. Determining the peculiarities of the influence of various factors on the physical properties of multilayers and multicomponent film materials is necessary for the creation of sensitive elements of electronic equipment with different functional purpose, devices of opto-electronics and spintronics.

Today, a many experimental results have been accumulated concerning the electrophysical (resistivity, temperature coefficient of resistance – TCR) and magnetoresistive (anisotropic magnetoresistance – AMR, giant magnetoresistance - GMR, Hall effect) properties of multicomponent metals (see, for example, [8, 9] and the cited literature).

At the same time remains relevant of more effective elements of microelectronic and low-studied ones - problems with regard to mechanisms and conditions of formation of solid solutions, granular state and influence of phase formation processes and degree of non-entropy of film systems on their properties. Despite the large volume of experimental studies HEA in a bulk state, studies of s.s.films only started [10-13].

The purpose of the work was to study in more detail the magnetoresistive effect, which has all the features of a giant magnetoresistance, and was first observed in film alloys by the authors [12] and to establish the correlation between the entropy degree and electrophysical and magnetoresistive properties.

2. METHOD OF SAMPLE FORMATION AND PROPERTIES MEASUREMENT

The samples were formed by the layer-by-layer condensation method of metals in a vacuum chamber VUP-5M (pressure of a residual atmosphere - 10^{-4} Pa) and annealed (homogenized) in the range temperature of 300-800 K. After annealing is homogenized phase composition based on fcc lattice Cu ($a = 0.355\text{-}0.365$ nm) or Al ($a = 0.402\text{-}0.406$ nm), depending on which component is redundant. Electrophysical properties (resistivity and TCR) were studied using the standard method. The total thickness of the multilayer films is 60-80 nm, the working current when measuring the resistance is 10 mA.

The magnetoresistance (MR) was measured in three geometries: longitudinal (the vector of current and induction of the magnetic field are parallel and lie in the plane of the film ($\vec{J} \,\Box\, \vec{B}$)), transverse ($\vec{J} + \vec{B}$) and perpendicular ($\vec{J} \perp \vec{B}$).

TCR i MR were calculated based on rations:

$$TCR = \frac{R(T) - R(300K)}{R(300K)\cdot(T - 300K)} \text{ and } MR = \frac{R(B) - R(0)}{R(0)},$$

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where $R(T)$ and $R(B)$ – resistance at a certain temperature and magnitude of the magnetic field.

The atomic fractions components was calculated according to the ratio:

$$c_i = \frac{D_i d_i \mu_i^{-1}}{\sum_{i=1}^{n} D_i d_i \mu_i^{-1}},$$

where D_i – metals density; d_i – thickness i-layer; μ_i – molar mass, and then refined by the EDS (SEO-SEM Inspect S50-B scanning electron microscope).

The mixing entropy was calculated according to the ratio:

$$\Delta S_{\text{mix}} = -R\sum_{i=1}^{n} c_i \ln c_i .$$

3. ELECTROPHYSICAL PROPERTIES OF FILMS WITH DIFFERENT ENTROPY DEGREE

Investigation of the properties of two-component systems in the condensed state allows to expand the possibilities of their practical application in modern technology.

In a three-layer film systems, the magnetic layers (M) are separated by a layer of nonmagnetic (NM) material (eg, Cu, Ag, Au, Pd, Pt, Ge). If the magnetic layers have antiparallel vectors of magnetization, then the conditions for the occurrence of spin-dependence scattering of electrons (SDSE) appear in the three-layer system. The advantage of such structures is the relatively low values of the saturation fields at which the GMR effect is observed. In granular film alloys, under certain conditions, the AMR and GMR phenomena may occur, since in a nonmagnetic matrix the excess magnetic atoms form nanosized granules with a radius of 1 to 10 nm, some of which are in a ferromagnetic or superparamagnetic state and causes the SDSE.

The results obtained by us are summarized in Fig. 1, which shows the correlation between TCR and ΔS_{mix}. The gradual decrease in TCO in the transition from low-entropy to high-entropy alloys is explained by the fact that the resistivity in the LEA → HEA direction increases as a result of the decrease in the mobility of atoms in the formation of the MEA or HEA base phase and homogeneity s.s. At the same time the temperature sensitivity is almost unchanged. On Fig. 1 also shows data for two-layer Me1/Me2/S films in which no processes of mixing atoms and phase state homogenization occurred (such materials cannot be attributed to LEA).

4. CORRELATION BETWEEN MAGNETORESISTANCE AND MIXING ENTROPY

The study of MR on the example of the same film systems as the case of the study of electrophysical properties (Fig. 1) gave the following results.

In all cases (LEA, MEA, and HEA) magnetoresistance amplitude at $T = 300$K has a relatively small value (generally at 0.2-0.4 %), which is typical of film systems belonging to the MEA or HEA class (see, for example, [9]).

Only in some cases [7, 13] does the MR amplitude increases to the value 0.8-1.0 %. The MR is quite small in the case of HEA. The characteristics of the film materials and the measurement results of the MR are shown in Table 1.

It is necessary to emphasize that the MR field dependence in three geometries of measurement externally has a completely identical character (except for the magnitude of the amplitude) and all features of the GMR.

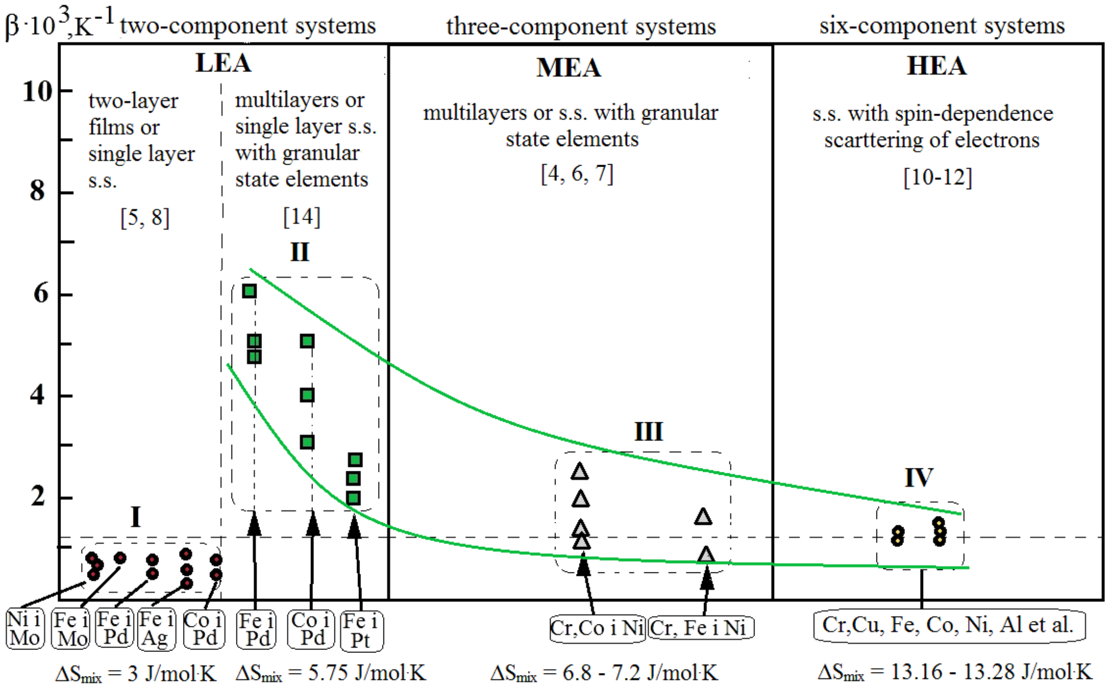

Fig. 1 – Correlation between TCR and ΔS_{mix} for films with different enropy degree

Table 1 – General characteristics of the samples and measurement results MR at the T = 300 K

№	Elemental composition of samples after annealing (concentration, at.%)	T_a, K	R, Ohm at the B = 0 T	MR, %	ΔS_{mix}, J/mol·K
Low-entropy alloys					
1	$Pt_{0,28}Fe_{0,72}$/S	800	–	0.30 (ǀǀ) 0.32 (+) 0.28 (⊥)	4.93
2	$Co_{0,53}Au_{0,47}$/S	800	–	0.25 (ǀǀ) 0.20 (+) 0.18 (⊥)	5.75
3	$Pd_{0,50}Fe_{0,50}$/S	800	–	0.35 (ǀǀ) 0.32 (+) 0.26 (⊥)	5.76
Middle-entropy alloys					
1	$Cu_{0.15}Pd_{0.70}Fe_{0.15}$/S	780	–	0.60 (ǀǀ) 0.45 (+) 0.32 (⊥)	6,80
2	$Fe_{0.60}Co_{0.22}Cu_{0.18}$/S	550	–	0.80 (ǀǀ) 0.95 (⊥)	7,20
High-entropy film alloys					
1	$Cu_{0.15}Ni_{0.25}Fe_{0.20}Co_{0.25}Al_{0.15}$/S	800	152.0 152.2	0.08 (+) 0.05 (⊥)	13.16
2	$Co_{0.20}Ni_{0.14}Cu_{0.20}Fe_{0.28}Al_{0.18}$/S	800	33.0 25.0 25.0	0.15 (ǀǀ) 0.17 (+) 0.20 (⊥)	13.16
3	$Co_{0.20}Ni_{0.25}Cu_{0.20}Fe_{0.20}Al_{0.15}$/S	800	47.0 48.0 48.4	0.15 (ǀǀ) 0.17 (+) 0.30 (⊥)	13.27
4	$Cu_{0,15}/Ni_{0,23}/Fe_{0,22}/Co_{0,22}/Al_{0,18}$/S	750	134.0	0.30 (⊥)	13.28

Since this effect is realized by spin-dependent scattering of electrons at magnetic interfaces or granules, it can be concluded that in HEA films in the form of s.s. single-layer elements of the granular state are realized, which will cause the GMR.

At the same time, it should be noted that in all cases of the film materials architecture, the properties of which we studied, under certain conditions anisotropic magnetoresistance is observed, which is caused not by SDSE, but by the spin-orbital interaction of electrons. Its amplitude is relatively small, since even in bulk samples of AMR no more than 4%, which can be ten times smaller than the GMR. In this case, the architecture of the samples does not play a prominent role.

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