ELECTRICAL RESISTANCE OF BINARY ORDERED ALLOYS WITH HCP STRUCTURE IN THE PRESENCE OF IMPURITY ATOMS OR THERMAL VACANCIES

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Conditions for crystallization determine largely the crystal structure. They can provide formation of superstructure, such defects like vacancies or impurity atoms. Investigations into scattering of different sorts of waves (X-rays, slow neutrons including conduction electrons in the problem on resistance) by the lattice of metals and alloys allow the detection of imperfections in the crystalline structure; the evaluation of ordering level for alloy and dependence of order parameters on temperature and structure; the determination of the order-disorder transition temperature and its dependence on component concentrations; the evaluation of the vacancy concentration.

The theoretical investigation and the computer calculation of residual resistance for ordered alloys with AB_3 stoichiometry composition and *hcp* structure have been performed in the work presented. These alloys contain inpurity atoms or vacant points in the lattice. Calculations have been performed by the quantun-mechanical method using simplifying assumptions and one-electron approach. Correlation for filling up points in the lattice by atoms of different sorts was disregarded. The lattice is assumed to be geometrically ideal. Vacancies are taken as "atoms" of the third component *C*. Difference in energies for interaction of conduction electrons and A,B,C ions in the lattice are considered to be small. Approximation for almost free electrons is used. The problem is solved using the perturbation theory. The completely ordered alloy containing effective ions was chosen as zero-order approximation.

The electrical resistance of alloy is determined by the conduction electron scattering in the crystal lattice when the potential field of the crystal shows a broken periodicity [1-4]. This scattering is characterized by probability of the electron transition between different equilibrium states. According to the perturbation theory, probability of quantum transitions is determined by the square of modulus of matrix elements of disturbance energy. The matrix elements are constructed on electron wave functions in zero-order approximation for different states. These states are charact erized by values of a wave vector.

Therefore, the problem is reduced to the calculation of the square of modulus of matrix elements of disturbance energy. Disturbance energy is determined by difference in potential electron energies in the crystal field and the energy of zero-order approximation. The latter is a periodical function of coordinates with the lattice constant. Periodicity in potential energy is broken by both disordered A,B atoms in the lattice points and the presence of impurity atoms or vacant points.

Considering *C* vacancies as atoms of third sort and performing calculations, we obtain the following formula for residual resistance of alloy [5-23]:

$$\rho = A_1(P_A^{(1)}P_B^{(1)} + 3P_A^{(2)}P_B^{(2)}) + A_2(P_A^{(1)}P_C^{(1)} +$$
$$+ 3P_A^{(2)}P_C^{(2)}) + A_3(P_B^{(1)}P_C^{(1)} + 3P_B^{(2)}P_C^{(2)}),$$

where A_1, A_2, A_3 are positive constants, $P_\alpha^{(i)}$ are probabilities for substitution of the point of i=1,2 type by atoms of α=A,B,C sort. The latter is determined by the alloy composition, the order parameter η and the concentration *c* of impurity atoms or vacancies using the following formulae:

$$P_A^{(1)} = (a + \frac{3}{4}\eta)(1+c)^{-1},\ P_B^{(1)} = (b - \frac{3}{4}\eta - \delta)(1+c)^{-1},$$
$$P_C^{(1)} = 4c_1(1+c)^{-1},$$
$$P_A^{(2)} = (a - \frac{1}{4}\eta)(1+c)^{-1},\ P_B^{(2)} = (b + \frac{1}{4}\eta + \frac{1}{3}\delta) \times$$
$$\times (1+c)^{-1},\ P_C^{(2)} = \frac{4}{3}c_2(1+c)^{-1},$$

where *a,b* are atom concentrations of A,B components; c_1, c_2 are concentrations of vacant points of the first and the second types or impurity atoms in the points of different types

$$c_1 + c_2 = c,\ \delta = 3c_1 - c_2$$

Considering the latter formulae, the dependence of residual resistance on composition, order and concentration *c*, correct to linear relatively small values *c* and *δ,* is expressed by the formula:

$$\rho = A_1(ab - \frac{3}{16}\eta^2) + c[A_2a + A_3b -$$
$$- 2A_1(ab - \frac{3}{16}\eta^2)] - \frac{1}{4}(A_1 - A_2 + A_3)\delta .$$

The first component in this formula

$$\rho_1 = A_1(ab - \frac{3}{16}\eta^2)$$

corresponds to residual resistance of alloy in which impurity atoms or vacancies are absent. This formula can be compared with experimental data on the temperature dependence ρ(T) of resistance for $MgCd_3$ and Mg_3Cd alloys, if an additional term for the linear temperature dependence of resistance is considered. This resistance is

due to the thermal fluctuations. Temperature dependence of the lattice constant is also considered. It is determined by the relation:

$$\ln\frac{(a+\frac{3}{4}\eta)(b+\frac{1}{4}\eta)}{(a-\frac{1}{4}\eta)(b-\frac{3}{4}\eta)}=\frac{2(\omega+\omega')}{kT}\eta,$$

where $\omega + \omega'$ is ordering energy of alloy (ω and ω' correspond to the different interatomic distances between the nearest neighbouring pairs of atoms at $c \neq 1.63\,a$).

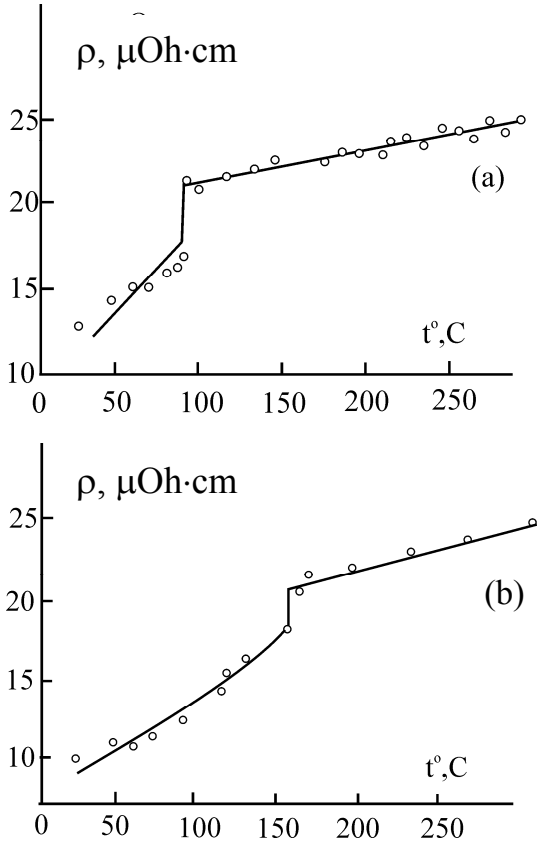

Fig.1. The temperature dependence of electrical resistance for $MgCd_3$ (a) and Mg_3Cd (b) alloys with the stoichiometric composition. Curves correspond to the theory, points correspond to the experimental data.

Fig.1 shows theoretical curves and experimental points which demonstrate dependence of resistance for $MgCd_3$ and Mg_3Cd alloys with the stoichiometric composition on the annealing temperature. The abrupt change in resistance is observed at T_o = 87 °C for $MgCd_3$ and at 155 °C for Mg_3Cd. This jump is due to the first-kind phase order-disorder transition. As seen from Fig.1, agreement between theory and experiment is satisfactory.

The availability of vacancies in alloy can change both the abrupt change in resistance at $T=T_o$ and the slope of $\rho(T)$ plot at $T>T_o$ depending on the values of A_1, A_2, A_3 constants. For alloys with the stoichiometric composition at $2(A_2+3A_3)<3A_1$, the jump in resistance in the point $T=T_o$ is decreased, and the slope of the curve for $\rho(T)$ at $T>T_o$ becomes negative due to vacancies.

It should be noted that at rather high annealing temperatures, besides the linear term, the quadratic component can appear in the formula for the temperature dependence of resistance $\rho(T)$. This component is due to anharmonicity of oscillations. The component $\exp\frac{-Q}{kT}$ proportional to the vacancies concentration can also appear:

$$\rho(T)=\rho_1+B_1T+B_2T^2+B_3\exp\frac{-Q}{kT}$$

(for $MgCd_3$, Mg_3Cd alloys in the range of order-disorder transition temperatures 87 °C, 155 °C these terms did not have a significant effect), Q is energy for the vacancy formation; B_1, B_2, B_3 are positive constants ($B_2 \ll B_1$, B_3).

Experimental investigations of $\rho(T)$ dependence at different annealing temperatures may allow the evaluation of Q energy [2].

The concentration dependence of residual resistance $\rho(a)$ can also essentially change in the presence of vacancies in the alloy. Behaviour of this change is determined by the relation between A_1, A_2, A_3 constants and energies for interatomic interaction.

Fig.2 shows the plots of resistance versus concentration $\rho(a)$ for completely disordered and maximum ordered alloys. When the composition is close to the stoichiometric one (especially in ordered alloys), the vacancy concentration is decreased. Vacancies have a stronger effect on resistance at a,b concentrations that differ from a = 1/4; b = 3/4.

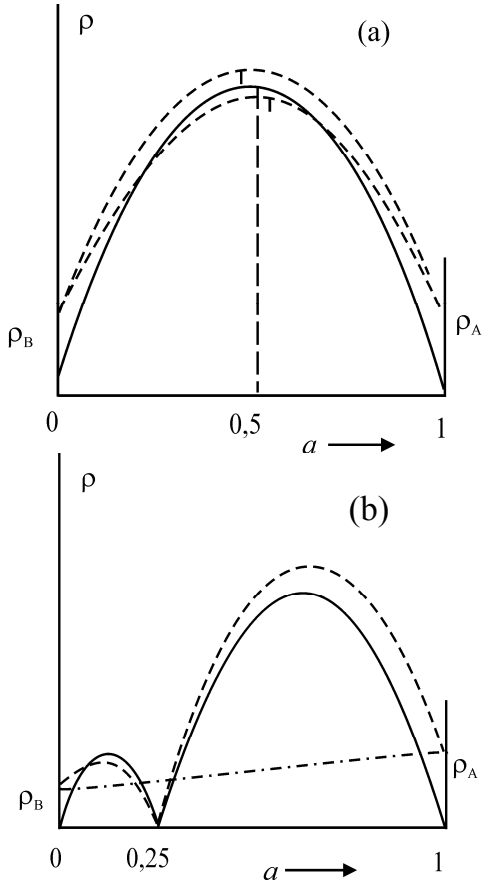

Fig.2. Residual resistance as a function of concentration for completely disordered (a) and

maximum ordered (b) alloys with the *hcp* lattice. Solid curves correspond to the absence of vacancies, the dotted ones correspond to the presence of vacancies.

For disordered alloys which do not contain impurity atoms or vacancies the $\rho(a)$ dependence is a parabola with maximum at $a = 0.5$. Such a dependence is in a good line with experimental data for many alloys. Data on gold-silver and gold-copper alloys show especially good agreement with theory [2]. Impurities or vacancies present in the disordered alloy can essentially change the $\rho(a)$ curve. Depending on the relations for A_1, A_2, A_3 constants, there appears asymmetry in the $\rho(a)$ curve, maximum may shift to both sides from the point $a = 0.5$, the $\rho(a)$ curve can also shift up and down from this point in the absence of impurity or vacancies. Such changes in the $\rho(a)$ curve makes it possible to judge on the presence of impurity atoms or vacancies in the alloy and to evaluate both A_1, A_2, A_3 constants and energy parameters of interatomic interaction.

Resistance of the maximum ordered alloy that does not contain vacancies is determined by the formula:

$$\rho_1 = A_1 \cdot \begin{cases} a(b - 3a) & \text{at} \quad a \le \frac{1}{4}, \\ b(a - \frac{1}{3}b) & \text{at} \quad a \ge \frac{1}{4}. \end{cases}$$

This dependence $\rho_1(a)$ (solid curve in Fig.2(b)) was observed for gold-copper alloys [2]. Impurities or vacancies can cause an interesting effect: residual resistance of pure A,B components, annealed at the same temperature as the alloy, can appear much higher than that of the ordered alloy with the stoichiometric composition. In the case of vacancies this effect is due to their absence in such an ordered alloy. Therefore, appearance of this feature in the $\rho(a)$ curve will show the presence of vacancies in the alloy.

Hence, experiments that will be performed to determine temperature and concentration dependences for residual resistance of alloys can allow us to judge on the presence of impurity atoms or vacancies in the alloy, to evaluate the ordering level of the alloy, its ordering temperature, concentration of vacancies and energy for their formation.

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