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STUDY ON DISORDERED BINARY ALLOY

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Abstract. *Using the model of central atom and the method of coordination sphere in statistical physics, we analyse a disordered binary alloy into a combination of two more simple systems (called effective metals) and determine the relation of free energy between these systems. From that we derive the analytic expression of free energy for disordered binary alloy. Numerical calculations for thermodynamic quantities of CuAl alloy with* 8% *Al atoms and CuNi alloy with* 35% *atoms Ni are in good agreement with the experimental data.*

I. INTRODUCTION

The application of statistical physics methods in order to calculate the thermodynamic functions (or thermodynamic potentials) of real systems up to now is a difficult problem and good results only are obtained for some simple systems such as crystals with same type of atom [1, 2, 3]. Complicated systems of many components usually are studied by statistical methods such as the pseudochemical method and the method of density functional [4, 5, 6]. Recently with the support of computer, methods of classical molecular dynamics (CMD) and ab initio molecular dynamics (AIMD) are applied in order to study systems of metals and binary alloys [1, 2, 7]. However, the obtained results usually are quite complex and non-analytic. In present paper, we apply the model of central atom and the method of coordination sphere in order to analyse a disordered binary alloy into a combination of two more simple systems (called effective metals) and to find the relation on free energy between the disordered binary alloy and the effective metals and between the effective metals and component metals. Our obtained results have simple analytic form. Numerical calculations for thermodynamic quantities of $CuAl$ alloy with 8% Al atoms and $CuNi$ alloy with 35% atoms Ni are in good agreement with the experimental data.

II. EQUATION OF STATE AND THERMODYNAMIC QUANTITIES OF DISORDERED BINARY ALLOYS CuAl AND CuNi

II.1. Free energy of disordered binary alloys

We calculate the free energy through the statistical sum Z of system from the following relation:

$$\Psi = -kTlnZ, \tag{1}$$

where k and T are the Boltzmann constant and the absolute temperature, respectively and:

$$Z = \sum_n exp(-E_n^{AB}/kT), \tag{2}$$

where E_n^{AB} is the energy of system and n is the index of state.

Representing the energy E_n^{AB} through the configuration energy E_c^{AB} and the vibration energy $E_m'^{AB}$ [8] and using the model of effective metals [9], we transform (2) into the form:

$$\Psi = c_A\Psi_{A*} + c_B\Psi_{B*} - TS_c, \tag{3}$$

where Ψ_α is the free energy of effective metals $\alpha(\alpha = A, B)$,

$$\Psi_{\alpha*} = -kTln\sum_m exp\left(-\frac{E_{\alpha*}^c + E_m'^{\alpha}}{kT}\right), \tag{4}$$

S_c is the configuration entropy of disordered binary alloy and

$$S_c = klnW = -kN(c_A lnc_A + c_B lnc_B). \tag{5}$$

Representing the parameters $u_{0\alpha*}, k_{\alpha*}$ of effective metals through the parameters $u_{0\alpha}, k_\alpha$ of metals α [9], we obtain the expression of free energy for disordered binary alloy as follows:

$$\Psi = c_A\Psi_A + c_B\Psi_B + \frac{3RTc_Ac_B}{4}\left(\frac{X_A}{k_A} - \frac{X_B}{k_B}\right)(k_B - k_A) - 12Rc_Ac_B\frac{\omega}{k} - TS_c, \tag{6}$$

where Ψ_A and Ψ_B are the free energy of metals A and B, respectively [10].

II.2. Equation of state and thermal expansion coefficient of disordered binary alloys $CuAl$ and $CuNi$.

The equation of state of alloy is determined from the thermodynamic relation:

$$P = -\left(\frac{\partial\Psi}{\partial V}\right)_T = -\frac{a}{3V}\left(\frac{\partial\Psi}{\partial a}\right)_T. \tag{7}$$

Substituting (6) into (7), we obtain the equation of state for disordered binary alloy as follows:

$$-\frac{Pv}{a} = c_A\left(\frac{1}{6}\frac{\partial u_{0A}}{\partial a} + \theta X_A \frac{1}{2k_A}\frac{\partial k_A}{\partial a}\right) + \\ +c_B\left(\frac{1}{6}\frac{\partial u_{0B}}{\partial a} + \theta X_B \frac{1}{2k_B}\frac{\partial k_B}{\partial a}\right) + \frac{kTc_Ac_B}{4}\frac{\partial}{\partial a}\frac{(k_B-k_A)^2}{k_Ak_B}, \tag{8}$$

where $V = Nv, v$ is the volume of unit cell for crystal lattice, a is the nearest neighbour distance between two atoms in alloy and k is the Boltzmann constant. At temperature $0K$, the equation (8) has the form:

$$-\frac{Pv_0}{a_0} = c_A\left(\frac{1}{6}\frac{\partial u_{0A}}{\partial a} + \frac{\hbar\omega_{0A}}{4k_{0A}}\frac{\partial k_{0A}}{\partial a}\right) + \\ +c_B\left(\frac{1}{6}\frac{\partial u_{0B}}{\partial a} + \frac{\hbar\omega_{0B}}{4k_{0B}}\frac{\partial k_{0B}}{\partial a}\right) + \frac{kTc_Ac_B}{4}\frac{\partial}{\partial a}\frac{(k_B-k_A)^2}{k_Ak_B}. \tag{9}$$

The lattice parameter of disordered binary alloy is derived from the formula:

$$a = a_0 + c_Ay_A + c_By_B, \tag{10}$$

where y_α is the mean displacement of atoms α from lattice knot and is calculated from the following relation in [10]:

$$y_\alpha^2 = \frac{2\gamma_{0\alpha}\theta^2}{3k_{0\alpha}^3}\left[1 + \frac{X_\alpha}{2} + \frac{\gamma_{0\alpha}^2\theta^2}{k_{0\alpha}^4}\left(\frac{13}{3} + \frac{47}{6}X_\alpha + \Delta_1\right)\right], \tag{11}$$

where Δ_1 is the additional part and $\Delta_1 \ll 1$.

Applying the modified Lennard Jones potential $(n-m)$ to the interaction between atoms in metal [13]:

$$\varphi_{(a)} = \frac{D}{n-m}\left[m\left(\frac{r_0}{a}\right)^n - n\left(\frac{r_0}{a}\right)^m\right], \tag{12}$$

where the potential parameters for metals Cu, Al and Ni are given in Table 1.

Table 1. Parameters D, r_0, n and m in metals Cu, Al and Ni

Metals	$D/k(K)$	$r_0(A^0)$	n	m
Cu	3401.0	2.5487	9.0	5.5
Al	2995.6	2.8541	12.5	4.5
Ni	4782.0	2.4780	8.5	5.5

Applying the general formulae $u_{0\alpha}, k_\alpha, y_\alpha$ in [9] and the potential (12), from (9),(10), (11) we derive the expression in order to calculate the lattice parameter, thermal expansion coefficient and the equation of state in simple analytic form for alloys $CuAl$ and $CuNi$.

The lattice parameter and thermal expansion coefficient of disordered binary alloy $CuAl$ with 8% atoms Al is determined by:

$$a = a_0 + 0.322 \times 10^{-9} T(5.34a_0^{10} + 0.15a_0^{13.5} + 7.7 \times 10^{-7} a_0^{21.5})[1 + (1.27a_0^{18} + \\ +0.076a_0^{21.5} - 2.53 \times 10^{-3} a_0^{25} + 1.42 \times 10^{-8} a_0^{33} - 2.68 \times 10^{-11} a_0^{39})0.57 \times 10^{-14} T^2], \quad (13)$$

where a_0 is found from the equation of state:

$$5.124 \times 10^{-6} P a_0^{15.5} - 0.9 \times 10^{-9} a_0^{21.25} - 0.89 \times 10^{-4} a_0^{14} + 5.58 \times 10^{-5} a_0^{13.5} + \\ +0.015a_0^{10.5} + 0.42a_0^8 + 15.7a_0^7 - 0.84a_0^{5.25} - 410.5a_0^{3.5} - 1674.3 = 0. \quad (14)$$

Thermal expansion coefficient:

$$\alpha = \frac{1}{a_0}\frac{da}{dT} = 0.322 \times 10^{-9}(5.34a_0^9 + 0.15a_0^{12.5} + 7.7 \times .10^{-7} a_0^{20.5})[1 + (1.27a_0^{18} + \\ +0.076a_0^{21.5} - 2.53 \times 10^{-3} a_0^{25} + 1.42 \times 10^{-8} a_0^{33} - 2.68 \times 10^{-11} a_0^{39})1.7 \times 10^{-14} T^2]. \quad (15)$$

The lattice parameter and thermal expansion coefficient of disordered binary alloy $CuNi$ with 35% atoms Ni is determined by:

$$a = a_0 + 0.625 \times 10^{-9} T(0.28a_0^{9.5} + 3.77a_0^{10} + 0.013a_0^{12.5} + 0.1a_0^{13.5})[1 + (0.805a_0^{17} + \\ +0.897a_0^{18} + 0.09a_0^{20} + 0.054a_0^{21.5} - 1.83 \times 10^{-3} a_0^{25})0.43 \times 10^{-14} T^2], \quad (16)$$

where a_0 is found from the equation of state:

$$5.124 \times 10^{-6} P a_0^{12} - 0.63.10^{-4} a_0^{7.5} - 6.34 \times 10^{-4} a_0^{7.75} + 0.01a_0^7 + 0.06a_0^{3.75} + \\ +19.36a_0^{3.5} - 1.14a_0^{1.75} - 119.8a_0^{0.5} - 290 = 0. \quad (17)$$

Thermal expansion coefficient:

$$\alpha = \frac{1}{a_0}\frac{da}{dT} = 0.625 \times 10^{-9}(0.28a_0^{8.5} + 3.77a_0^9 + 0.013a_0^{11.5} + 0.1a_0^{12.5})[1 + (0.805a_0^{17} + \\ +0.897a_0^{18} + 0.09a_0^{20} + 0.054a_0^{21.5} - 1.83 \times .10^{-3} a_0^{25})1.3 \times 10^{-14} T^2]. \quad (18)$$

III. NUMERICAL CALCULATIONS AND DISCUSSION

The calculated results of lattice parameter and thermal expansion coefficient for alloys $CuAl$ and $CuNi$ at pressure $P = 0$ are summarized in Table 2 and are represented in Figure 1.

In the range of temperature from 200 to $800K$, our numerical results of thermal expansion coefficient are in good agreement with experiments. In addition, our obtained results have simple analytic and easy to calculate numerically form in comparison with that from other statistical methods.

Table 2. Values of lattice parameter and thermal expansion coefficient for alloys $CuAl$ and $CuNi$ at different temperatures and pressure $P = 0$

Alloy	$T(K)$	200	300	400	500	600	700	800
$CuAl-$	$a(A^0)$	2.5951	2.6012	2.6078	2.6148	2.6224	2.6308	2.6400
$8\%at.Al$	$\alpha \times 10^5(K^{-1})$	1.6123	1.6629	1.7338	1.8249	1.9363	2.0679	2.2198
	exp[12]		1.66	1.74	1.82			
$CuNi$ -	$a(A^0)$	2.5057	2.5097	2.5137	2.5179	2.5222	2.5268	2.5315
$35\%at.Ni$	$\alpha \times 10^5(K^{-1})$	1.5704	1.5992	1.6396	1.6915	1.7550	1.8300	1.9165
	exp [11]		1.60	1.64	1.75	1.82	1.88	1.92

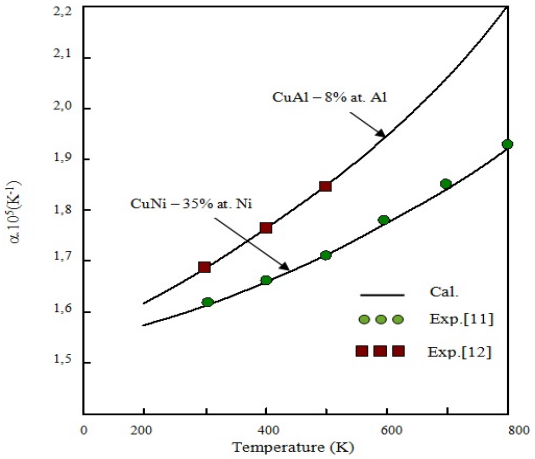

Fig. 1. Dependence of thermal expansion coefficient on temperature for alloys CuAl and CuNi

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