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CORRELATION PARAMETERS IN THE FCC ALLOYS AB_3 DOPED BY C

Theoretical investigation of ordering in ternary substitutional solid solutions with fcc lattice of type AB_3 doped by component C is carried out. Correlation parameters of ordered alloys are calculated from the minimum free energy in the framework of the quasi-chemical approximation without taking into account the interaction between pairs of atoms C-C. The analysis of the correlation parameters dependence on the alloy composition, temperature, degree of long-range order and energy parameters is carried out by numerical methods. Temperature dependences of the correlation parameters of the binary fcc alloy AB_3 are obtained for different values of atom concentration. It is shown that the correlation parameter values decrease with increasing temperature of the alloy, decreasing energy parameters and increasing impurity C concentration. The degree of long-range order increasing leads to the decrease of the correlation parameters. It is shown that in the case of low concentrations of C atoms at the investigated values of the energy parameters, the tendency to the ordered placement of atoms in the lattice sites of the alloy is maintained.

Keywords: AB_3 alloy fcc structure doped with C, correlation parameters, temperature dependence.

Проведено теоретичне дослідження впорядкування в потрійних твердих розчинах заміщення з ГЦК кристалічною решіткою типу AB_3 з домішкою третього компоненту C. Параметри кореляції сплаву, що впорядковується, розраховані з умови мінімуму вільної енергії в рамках квазіхімічного наближення без врахування взаємодії мажду парами атомів C-C. Аналіз залежності параметрів кореляції від складу сплаву, температури, ступеня далекого порядку і енергетичних параметрів проведено чисельними методами. Отримані температурні залежності параметрів кореляції бінарного ГЦК сплаву AB_3 при різних значеннях концентрацій атомів. Показано, що значення параметрів кореляції зменшуються із збільшенням температури сплаву, зменшенням енергетичних параметрів і збільшенням концентрації домішки C. Збільшення ступеня далекого порядку спричиняє зменшення параметрів кореляції. Показано, що у випадку малих концентрацій атомів C при досліджених значеннях енергетичних параметрів тенденція до впорядкованого розміщення атомів по вузлах кристалічної решітки сплаву зберігається.

Ключові слова: сплав AB_3 ГЦК структури з домішкою C, параметри кореляції, температурна залежність.

Проведено теоретическое исследование упорядочения в тройных твердых растворах замещения с ГЦК кристаллической решеткой типа AB_3 с примесью третьего компонента C. Параметры корреляции упорядочивающегося сплава рассчитаны из условия минимума свободной энергии в рамках квазихимического приближения без учета взаимодействия между парами атомов C-C. Анализ зависимости параметров корреляции от состава сплава, температуры, степени дальнего порядка и энергетических параметров проведен численными методами. Получены температурные зависимости параметров корреляции бинарного ГЦК сплава AB_3 при различных значениях концентраций атомов. Показано, что значения параметров корреляции уменьшаются с увеличением температуры сплава, уменьшением энергетических параметров и увеличением концентрации примеси C. Увеличение степени дальнего порядка приводит к уменьшению параметров корреляции. Показано, что в случае малых концентраций атомов C при исследованных значениях энергетических параметров стремление атомов к упорядоченному размещению по узлам кристаллической решетки сплава сохраняется.

Ключевые слова: сплав AB_3 ГЦК структуры с примесью C, параметры корреляции, температурная зависимость.

1. Introduction

Creation of new materials for the development of modern energy systems of special purposei involves the widespread use of "metal - hydrogen" stuctures.

Simple electronic structure, low weight and dimensions form the uniqueness of the systems "metal–hydrogen" both as for the theoretical study of a number of problems in solid state physics (diffusion, atomic transport during phase transitions, superconductivity, change of magnetic properties), and for applications, such as transition metal hydride storage systems and hydrogen storage for the power supply battery electrodes and similar systems [1-3].

It is well known that different physical properties of alloys significantly affect the appearance of the atomic order [4, 5]. On the basis of experimental evidence the authors of [6, 7] argue that some physical parameters of the alloys are due to the possibility of placing hydrogen atoms onto lattice sites also.

Short-range ordering in body-centred cubic (bcc) and hexagonal close-packed (hcp) crystal lattices in ternary alloys was studied in [6-9]. Effect of substitutional impurities on the short-range order in alloys with face-centred cubic (fcc) lattice has not been investigated with the quasichemical method yet.

The subject of interest of the present paper is the theoretical research of the ordering process and calculation of the correlation parameters in ternary substitutional solid solutions AB_3 with fcc lattice type doped by a third component C, which can be hydrogen atoms.

2. Theory. Correlation parameters

Let us consider an ordered AB_3 alloy doped with a third component C. We assume that the geometrically perfect crystal lattice of the alloy contains $N = 8N_0$ ($2N_0$ – number of unit cells) units; $N^{(1)} = 2N_0$ of them are nodes of the first type and $N^{(2)} = 6N_0$ are nodes of the second type. Nodes of the first type, "legitimate" for the atoms of type A, are located at the vertices of the cubic cells, and nodes of the second type, "legitimate" for the atoms of type B – in the centres of their faces. Atoms of the third component C may be located at nodes of both types. Pair interaction of atoms is central and considered to be in the first coordination sphere.

Calculations will be carried out within the framework of the quasi-chemical approximation [5, 10, 11], except for a couple of neighbouring atoms of independent "molecules". Interaction between pairs of atoms C-C will not be taken into account.

We denote the number of atoms in the alloy grade as N_α, $N_\alpha^{(i)}$ – the number of atoms of type α for node types i, $N_{\alpha\beta}^{(ij)}$ – the number of pairs of atoms of type α, β (α, β = A, B, C) of the following type of node i, j (i, j = 1, 2). $P_\alpha^{(i)}$ – the aprior probability of substitution of atoms α node i, $P_{\alpha\beta}^{(ij)}$ – the posterior probability of the location of atoms α, β in the nearest-neighbour sites i, j, $\nu_{\alpha\beta}$ – minus the energy of interaction between pairs of atoms of type α, β.

Short-range order in the arrangement of the atoms can be characterized by correlation parameters

$$\varepsilon_{\alpha\beta}^{(ij)} = P_{\alpha\beta}^{(ij)} - P_\alpha^{(i)} P_\beta^{(j)} . \qquad (1)$$

In a disordered alloy, the correlation parameters $\varepsilon = \varepsilon_{\alpha\beta}^{(ij)}$ can be easily expressed through the short-range order parameters γ, introduced by Cowley [10, 11] and often used in experimental studies.

Constraint equation for a binary alloy is

$$\varepsilon = -\gamma ab . \tag{2}$$

Free energy F of the alloy in the configuration approximation is calculated by the formula

$$F = E - kT \ln W \tag{3}$$

where E - the configuration part of the internal energy of the alloy, W - the number of different configurations of atoms on the lattice sites, k - Boltzmann constant, T - absolute temperature.

Taking into account the number of pairs and number of different configurations W in the quasi-chemical approximation, the expression for the free energy takes the form

$$\begin{aligned} F = &-24N_0\left[\sum_{\alpha}(P_{\alpha\alpha}^{(12)} + P_{\alpha\alpha}^{(22)})\nu_{\alpha\alpha} + \sum_{\alpha\neq\beta}(P_{\alpha\beta}^{(12)} + P_{\beta\alpha}^{(12)} + 2P_{\alpha\beta}^{(22)})\nu_{\alpha\beta}\right] + \\ &+ 24N_0kT\sum_{\alpha,\beta}\sum_{i,j}P_{\alpha\beta}^{(ij)}\ln P_{\alpha\beta}^{(ij)} - 22N_0kT\sum_{\alpha}(P_{\alpha}^{(1)}\ln P_{\alpha}^{(1)} + 3P_{\alpha}^{(2)}\ln P_{\alpha}^{(2)}) \\ &\alpha = A, B; \quad \beta = A, B, C; \quad i, j = 1, 2. \end{aligned} \tag{4}$$

From the minimum free energy condition, one can determine the equilibrium values of the probabilities $P_{\alpha}^{(i)}$, $P_{\alpha\beta}^{(ij)}$, knowledge of which gives us possibility to investigate the correlation parameters of ordered alloys, depending on its composition, temperature, degree of long-range order and energy parameters $\nu_{\alpha\beta}$.

Assume that the posterior probabilities $P_{\alpha c}^{(ij)}$ ($\alpha = A, C$) and the correlation parameters $\varepsilon_{\alpha c}^{(ij)}$ differ little from the values $P_{\alpha c}$ and $\varepsilon_{\alpha c}$ corresponding to the disordered state of the alloy, C atoms are randomly distributed over alloy lattice sites and $P_{CC}^{(ij)} = 0$ [5, 8]. Then for the ternary alloy A-B-C with an fcc lattice, in which the degree of long-range order is zero, and the posterior probabilities P_{AC} and P_{BC} in the linear "c" approach in the case of equal concentrations of A atoms $a = 0.25$ can be determined as follows

$$P_{AC} = c\left[1 + \left(\frac{(1-3\theta)^{1/2} + (1+3\theta)}{(1+3\theta) + (1-\theta)^{1/2}}\right)^{1/2}\exp(\sigma)\right]^{-1} \tag{5}$$

$$P_{BC} = c\left[1 + \left(\frac{(1+3\theta)^{1/2} - (1-\theta)}{(1-3\theta) + (1+3\theta)^{1/2}}\right)^{1/2}\exp(-\sigma)\right]^{-1} \tag{6}$$

where $\theta = \exp(\omega_{AB}/kT)$, $\sigma = (\omega_{BC} - \omega_{AC})/2kT$, $\omega_{\alpha\beta} = 2\nu_{\alpha\beta} - \nu_{\alpha\alpha} - \nu_{\beta\beta}$ – mixing energy of atoms of type α, β.

In a disordered binary alloy correlation parameters are equal $\varepsilon^{(12)} = \varepsilon^{(22)} = \varepsilon$

$$\varepsilon = \frac{2a^2b^2(\exp\frac{\omega_{AB}}{kT} - 1)}{\left[(a-b)^2 \exp\frac{2\omega_{AB}}{kT} + 4ab\exp\frac{\omega_{AB}}{kT}\right]^{1/2} + (a^2+b^2)\exp\frac{\omega_{AB}}{kT} + 2ab} \qquad (7)$$

The obtained formulas (5-7) allow us to investigate the change of short range order in the alloy with the addition of a third component of the impurity.

3. Results and discussions

The results of numerical analysis methods concerning the temperature dependence of the correlation parameters $\varepsilon^{(ij)}$ of binary disordered alloy *A*-*B* at ω_{AB}= 0.0125 eV and different values of the concentration of atoms in the alloy show that the correlation parameters for pairs of atoms *AB* take positive values, thus demonstrating the *A* and *B* atoms tendency to the ordered distribution over the lattice sites of the alloy (Fig. 1). Increasing the temperature of the alloy reduces the values of the correlation parameters.

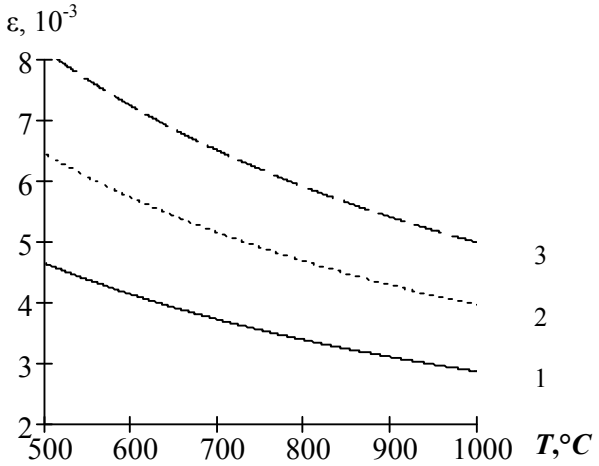

Fig.1. Graphs of the temperature dependence of the correlation parameters of the disordered fcc binary alloy AB_3 constructed by formula (7) with ω_{AB}=0,0125 eV and concentration *a,* equal to 0.2, 0.25, 0.3 (curves 1, 2, 3)

The calculations also show that the addition of the impurity *C* to a disordered alloy AB_3 reduces the correlation parameters $\varepsilon^{(12)}, \varepsilon^{(22)}$. The parameter σ increase slows disordering which occurs while adding impurity *C*. For example, for an alloy with the stoichiometric composition of the AB_3, with (ω_{AB}/kT) = 1.22 and σ = –1.1, the impurity concentration change from 0 to 0.1 reduces the correlation parameters value from 0.035 to 0.027, and for σ = 0.8 the correlation parameters decrease from 0.035 to 0.026. Characteristically, that in the case of low concentration of *C* atoms and the indicated values of the energy parameters (ω_{AB}/kT) and σ, the tendency to the ordered placement of atoms in the lattice sites of the alloy is maintained.

Our investigations show that the appearance of long-range order in the alloy has different effects on the correlation parameters. Increasing the degree of long-range order reduces the correlation parameters. Correlation parameters decrease with decreasing energy parameters σ and (ω_{AB}/kT), but increase with the impurity concentration C.

It should be noted that the addition of impurity C decreased correlation values $\varepsilon^{(12)}$ are larger than $\varepsilon^{(22)}$. This is apparently due to the fact that C atoms are getting into the alloy at $\sigma < 0$ and eager to surround themselves with atoms A, which mainly occupy sites of the first type. This decreases the number of pairs of A-B holding units of the first and the second types and the degree of short range order in the alloy decreases.

Such results are consistent with investigations of soluble component C in the binary hcp alloy that show the following: the property of impurities to change the physical parameters of the alloys is largely determined by both the crystal structure and the presence of long-range ordering as well as by energy parameters of interatomic interaction [12]. The latter may be such that the impurity atoms C are placed mainly in the ordered state of the alloy on the nodes of a certain type. In this case, the extremity may occur in the temperature dependence of occupation probabilities of C atoms from these positions, the experimental identification which can be used to establish a presence in the alloy superstructure [5].

4. Conclusions

The investigation of parameter correlations in ternary substitutional solid solutions with fcc lattice showed that the addition of a third component to the alloy with a low concentration can significantly affect the degree of short-range order in the arrangement of atoms of the alloy, and hence lead to changes in its physical properties. The resulting independent experiments values of the energy parameters of atom interaction in the alloy may allow using the derived formulas (5-7) to calculate the required amount of a certain type of impurity needed to produce an alloy with a given degree of near- and long-range order.

When comparing the calculated and experimental results, they should be considered as concerning the given composition of the ternary alloy. The development of the theory of correlation effects for the ternary alloys of any composition is a promising step in the research field under consideration.

References

1. **Chotard, J. N.** Hydrogen induced site depopulation in the $LaMgNi_4$ hydrogen system [Text] / J. N. Chotard, D. Sheptyakov, K. Yvon // Z. Kristallogr. – 2008. – V. 223. – P.690 – 696.

2. **Denys, R. V.** New Mg-M-Ni (M = Mn, Ti, Al) alloys as efficient hydrogen storage materials [Text] / R. V. Denys, I. Yu. Zavaliy et al. // Hydrogen materials science and chemistry of carbon nanomaterials. – 2007. – P. 332 – 335.

3. **Denis, R. V.** Struktura i vodorodosorbtsionnyye svoystva novykh soyedineniy i splavov na osnove magniya [Text] / R. V. Denis, V. V. Berezovets, I. V. Koval'chuk i dr. // Vodorodnoye materialovedeniye i khimiya uglerodnykh nanomaterialov. – K., 2009. – P. 40 – 43/

4. **Smirnov, A. A**. Molekulyarno-kineticheskaya teoriya metallov [Text] / A. A. Smirnov – M., 1966. – 488 p.

5. **Matysina, Z. A.** Rastvorimost' primesey v metallakh, splavakh, intermetallidakh, fulleritakh [Text] / Z. A. Matysina, S. Yu. Zaginaychenko, D. V. Shchur. – D., 2006. – 514 p.

6. **Masharov, S. I.** Korrelyatsionnyye effekty i pogloshcheniye gazov binarnymi uporyadochivayushchimisya splavami [Text] / S. I. Masharov, N. M. Rybalko // Izv. vuzov. Fizika. – 1979. – No. 2. – P. 75 – 81.

7. **Masharov, S. I.** Korrelyatsionnyye effekty v uporyadochenii troynykh splavov [Text] / S. I. Masharov, A. I. Rybalko. // FMM. – 1979. – Vol. 47, No. 4. – P. 702 – 710.

8. **Matysina, Z. A.** Molekulyarno-kineticheskaya teoriya uporyadochivayushchikhsya tverdykh rastvorov [Text] / Z. A. Matysina. – D., 1978. – 119 p.

9. **Matysina, Z. A.** Atomnyy poryadok i svoystva splavov [Text] / Z. A. Matysina. – D., 1981. – 112 p.

10. **Cowley, J. M.** Short– and long-range parameters in disorder solid solutions [Text] / J. M. Cowley // Phys. Rev. – 1960. – Vol. 120, No. 5. – P. 1648 – 1657.

11. **Cowley, J. M**. Short-range and long-range order parameters [Text] / J. M. Cowley // Phys. Rev. – 1965. – Vol. 138, No. 5. – P. 1384 – 1389.

12. **Matysina, Z. A.** The solubility of substitutional impurity [Text] / Z. A. Matysina // Phys. Met. Metallograph. – 1992. – Vol. 74, No. 4. – P. 322 – 327.

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