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On the influence of the electron structure of heterogeneity regions of binary solid solutions on the temperature boundary of solubility

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A model is proposed for description of microheterogeneity of solid solutions, taking into account the donor-acceptor interaction of components in the transition layer. Experimental data of temperature boundaries of solubility are the basis for theoretical estimation of the character of the chemical bond of the transition layers of solid solutions for the Al—Si, Al—Fe, and Al—Ni systems.

Key words: solid solutions, electron structure, chemical bond, solubility.

The nature of heterogeneity is one of the most complicated problems in the theory of solutions. There are several models that consider solid solutions either as homogenous systems in which atoms of the second component are chaotically distributed as atoms of insertion or substitution,[1] or as microheterogeneous systems including atoms of the second component in the form of formations similar to the Guinier—Preston zones.[2] Although there is considerable experimental material suggesting the heterogeneity of solid solutions, the nature of this phenomenon is still unclear. The role of the transition layer between the areas formed by atoms of a solvent and a solute is especially obscure. Experimental studies of the valence zone of the Al—Si solid solution have been the basis for establishing[3] that the heterogeneity of the solid solution is related to the formation of areas with the Al^dSi^a chemical bond (d is the element-donor, a is the element-acceptor). Therefore, it is interesting to develop a physical model of the electronic structure of the microheterogeneity of binary solid solutions based on the configuration model.

The model we propose is based on the following statements. 1. Properties of a solid solution are determined by the electronic structures of atoms of a solvent and a solute and by the electronic structure of transition layers of a solid solution. 2. It is assumed that the interaction of atoms of a solvent and a solute in the transition layer is described in terms of the donor-acceptor bond according to Mulliken[4] with the charge transfer (the ionic component). 3. In a solid solution, new electronic states can exist in the transition layer between the areas of the main components of the system. The properties of the transition layer can be described, using parameters of atoms whose electronic configurations are analogous to the configurations formed as a result of the donor-acceptor interaction of atoms of a solvent and a solute.[5]

The functional dependence of the temperature boundary of solubility[6] is used in the work. Unlike the work,[6] for calculations of the temperature boundary of solubility for the systems described previously, all parameters entering the formulas are taken for atoms whose con-

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figurations are formed as a result of the donor-acceptor bond formation in the transition layers of solid solution. The functional dependence of solubility is presented by the system of equations (1).

In the determination of the boundary of solubility, the problem of the determination of $R_A{}^{d(a)}$, $R_B{}^{a(d)}$, $\alpha_A{}^{d(a)}$, and $\alpha_B{}^{a(d)}$ arises. The configuration model of eutectic alloys allows one to assume[5] that properties of areas with the $A^{(d)a}B^{a(d)}$ chemical bond are determined by the superposition of atoms, which are closest in Z (atomic number) and whose configurations are analogous to those formed in the interaction of components. For example, when the chemical bond of the Al^dSi^a type in the Al—Si system is taken into account, atomic radii and thermal-expansion coefficients of Mg and P were used, whose electronic configurations are analogous to those formed in the charge transfer from Al to Si. The value of K in model (1) was determined from the data of the state diagram using the temperature of the eutectic transformation and the corresponding point of lyotectics (limit of solubility).

Dependence (1) was used for the calculation of the temperature boundary of solubility in the Al—Si system. It can be seen from Fig. 1 that the assumption about the absence of the charge transfer between Al and Si results in an increase in solubility of Si as the temperature decreases, which does not agree with the experimental data. At the same time, the assumption about the formation of the Al^dSi^a chemical bond in transition layers makes it possible to obtain good agreement of calculated and experimental data. It can be seen from the comparison of the calculated data of the boundary of solubility for the Al—Si system, obtained for two types of transition layers (Al^dSi^a and $Al^{2d}Si^{2a}$), that the best accordance with the experiment is observed for the layer with the Al^dSi^a chemical bond. Assuming that the value of the transition layer of interacting Al and Si atoms changes with temperature according to the law

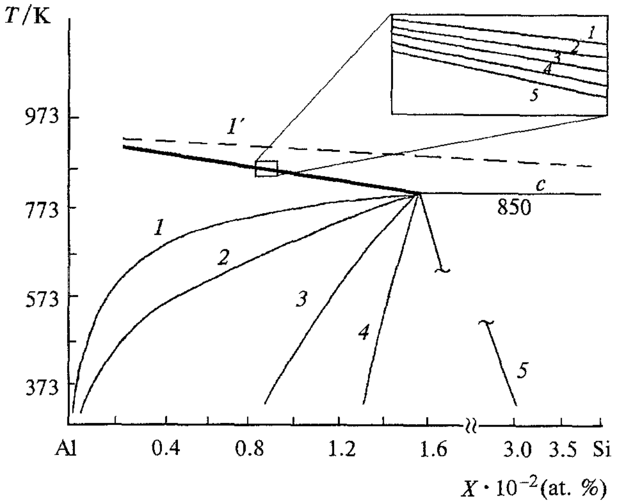

Fig. 1. Calculated data for the dolyotectic area of the state diagram for Al—Si obtained with inclusion of different types of chemical bonds in the transition layers of the solid solutions: *1,1'*, experiment;[9] *2*, Al^dSi^a ($n = 3.4 \cdot 10^{-2}T - 9$); *3*, Al^dSi^a; *4*, $Al^{2d}Si^{2a}$; and *5*, AlSi. *1'*, experimental liquidus; *c*, theoretical liquidus.

$$n = 3.4 \cdot 10^{-2}T - 9,$$

one can obtain the best agreement of experimental and calculated data on the temperature boundary of solubility (Fig. 1, curve *2*).

Thus, the calculations show that in the solid and liquid-solid states the Al—Si alloys of dolyotectic concen-

$$\begin{cases} X(T) = \dfrac{100KR_A{}^{d(a)}\,(1 + \alpha_A{}^{d(a)}(T)T)\,A_1(T)n}{\left(\dfrac{\varphi_A{}^{d(a)}}{1+2\alpha_A{}^{d(a)}(T)T} - \dfrac{\varphi_B{}^{a(d)}}{1+2\alpha_B{}^{a(d)}(T)T}\right)^2 R^3_{B^{a(d)}}(1 + \alpha_{B^{a(d)}}(T)T)^3 + A_2(T)} \\ A_1(T) = R_A{}^{d(a)}\,(1 + \alpha_A{}^{d(a)}(T)T) + R_B{}^{a(d)}\,(1 + \alpha_B{}^{a(d)}(T)T) \\ A_2(T) = \mathrm{K}\left[R_A{}^{d(a)}\,(1 + \alpha_A{}^{d(a)}(T)T) + R_B{}^{a(d)}\,(1 + \alpha_B{}^{a(d)}(T)T)\right] n\; R^3_{A^{d(a)}}(1 + \alpha_{A^{d(a)}}(T)T)^3 \\ \mathrm{K} = \mathrm{K}_0,\ T < T_{\mathrm{eut}}, \\ \mathrm{K} = \mathrm{K}_0(T^A_m - T)/(T^A_m - T_{\mathrm{eut}}),\ T_{\mathrm{eut}} < T < T^A_m \end{cases} \qquad (1)$$

where $X(T)$ is the concentration of component **B**; $R_A{}^{d(a)}$, $R_B{}^{a(d)}$, $\alpha_{Ad(a)}$, $\alpha_B{}^{a(d)}$, $\varphi_A{}^{d(a)}$, $\varphi_B{}^{a(d)}$ are atomic radii, thermal-expansion coefficient (taken from the Ref. 7), and potentials ($\varphi = E_F/e$, where E_F is the Fermi energy of electrons in the valence zone determined in the free-gas approximation) of elements whose configurations are formed as a result of the formation of the chemical bond between atoms A and B in the transition layer, respectively; n is the parameter that characterizes the fraction of atoms A and B bonded chemically in the transition layer; $T^A{}_m$ is the melting point of the A component; T_{eut} is the temperature of the eutectic transformation. Formulas (1) at $R_A{}^{a(d)} \to R_A$, $R_B{}^{a(d)} \to R_B$, $\varphi_A{}^{a(d)} \to \varphi_A$, $\varphi_B{}^{a(d)} \to \varphi_B$ transform to the formulas that describe the boundary solubility of the two-component system.[6] It is assumed in equation system (1) that the properties of the interacting atoms change in the transition layer, while this fact was not taken into account in Ref. 6.

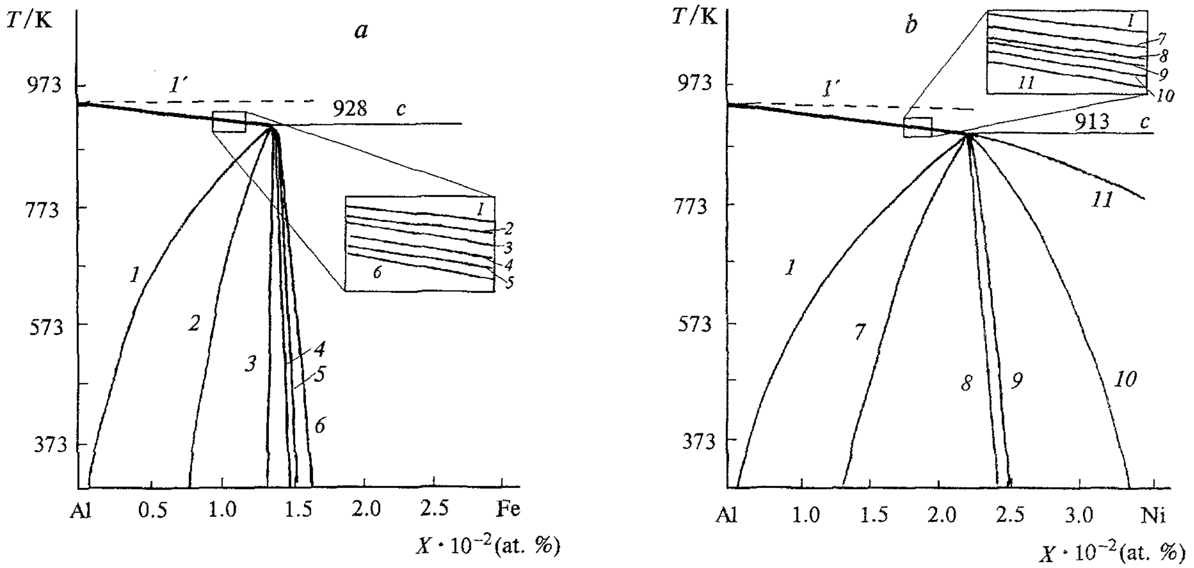

Fig. 2. Calculated data for the dolyotectic area of the state diagrams for Al—Fe (*a*) and Al—Ni (*b*) obtained for different types of the chemical bond in the transition area of atoms of a solvent and a solute: *1*, experimental data;[9] *2*, $Fe^{d}Al^{a}$; *3*, $Fe^{3d}Al_3{}^{a}$; *4*, $Fe^{a}Al^{d}$; *5*, $Fe^{3a}Al_3{}^{d}$; *6*, AlFe; *7*, $Ni^{3d}Al_3{}^{a}$; *8*, $Ni^{a}Al^{d}$; *9*, $Ni^{3a}Al_3{}^{d}$; *10*, $Ni^{d}Al^{a}$; and *11*, AlNi. *1'*, experimental liquidus; *c*, theoretical liquidus.

trations contain a heterogeneity, whose surface comprises the areas with a chemical bond of the $Al^{d}Si^{a}$ type with the charge transition from Al atoms to Si atoms. This agrees well with the experimental data on the studies of the framework spectra (chemical shifts) and valence zones of the Al—Si alloys and their components.[8]

The data suggest a model to explain the decrease in the melting temperature of solid solutions (the effect of the liquidus decrease) of aluminum containing silicon. The difficulties in explaining the decrease in liquidus are related to the fact that Si is a high-melting element and its "appearance" in Al should result at first glance in an increase in liquidus ($T_m{}^{Si}$ = 1423 K, $T_m{}^{Al}$ = 933 K). In fact this does not occur. The decrease in liquidus can be explained by assuming that the areas with a chemical bond of the $Al^{d}Si^{a}$ type appear in the Al—Si solid solution. From the viewpoint of the configuration model, this results in the appearance of areas with $s^2p^0(Al^d)$ and $s^2p^3(Si^a)$ configurations in addition to s^2p^1 of aluminum and s^2p^2 of silicon. These configurations are similar to configurations of Mg and P, and it is known that the latter have very low melting points. Thus, the decrease in liquidus in the Al—Si system can be accounted for by the appearance in the Al—Si solid solution of electronic states characteristic of low-melting elements (P and Mg).

At the next stage, the limits of applicability of the suggested model to other systems were evaluated. We have chosen the Al—Fe and Al—Ni systems with a strong interaction between components, which is indicated by melting points of intermetallides $FeAl_3$ (T_m = 1420 K) and $NiAl_3$ (T_m = 1120 K). The results of the calculations are presented in Fig. 2, and it can be seen that for the Al—Fe and Al—Ni systems the best agreement of the experimental and calculated data for the temperature boundary of solubility is obtained with the assumption that donor-acceptor bonds of the $Fe^{d}Al^{a}$ and $Ni^{3d}Al_3{}^{a}$ type are formed in the transition layers of the solid solution (Fig. 2). Unsatisfactory agreement of the calculated and experimental data is obtained with the assumption that there is no charge transfer in the transition layers (Fig. 2, curves *6*, *11*). Other variants of the charge transfer between components in the Al—Fe and Al—Ni system also give a great difference between the experimental and calculated data for the temperature dependence of the boundary of solubility (Fig. 2).

Thus, the suggested model makes it possible to elucidate the character of the chemical bond in the transition layers of the solid solutions and to discover the electronic mechanism of the formation of heterogeneity in the solid solutions. This provides additional opportunities for calculations of the state diagrams.

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