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On impurity segregation on dislocations in metals

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Abstract. — Thermodynamic and crystallo-chemistry considerations are given about the possibility of existing linear distribution laws for some impurities in metals between bulk solution and near-dislocation segregation regions (NDSR) with composition and structure close to the corresponding intermetallic compound. The solutions of Fe in Al are considered. NDSR composition can be close to FeAl₁₃. The experimental data on the solubilities are treated within the model developed to determine the effective binding enthalpy which is close to the dissolution enthalpy of the FeAl₁₃ compound in Al. The effective distribution law differs from true adsorption forms. It is valid for limited concentration range and connected to the phase diagram change for the NDSR. The known diffusion anomalies for transition impurities in Al are satisfactorily explained with using this distribution law.

According to previous works [1-5], the known anomalies of diffusion and solubility of transition metal impurities in aluminium and some interstitial impurities (C, H, N) in metals (Fe, Ni, etc.) at elevated temperatures are explained by the effect of dislocations. A phenomenological consideration was done [1-4] of the influence of the near-dislocation segregation regions (NDSR) on diffusion and solubility of the impurities in the mentioned metals. The approximation of the local equilibrium and impurity distribution linear law was used. The characteristics of the NDSR in the considered systems were determined: the effective binding enthalpy (close to the dissolution enthalpy of the corresponding compound), the diameter of the NDSR cross-section (about several nm), diffusion coefficients and activation energies of impurity diffusion in NDSR. As was shown [1-5], the NDSR structure and composition could be close to the corresponding intermetallic compound. These results were confirmed by the results of gamma-ray spectroscopy, electron microscopy, electrical resistance studies [6-11], and the results of the crystallo-chemistry and thermodynamic analyses [5-7] of the systems in question. Some experimental results were discussed on the NDSR influence on the processes of phase formation, recrystallisation and diffusion during decomposition of supersaturated solution of iron and vacancies in aluminum [5-12]. In the present work a thermodynamic consideration is presented of the possibility of the impurity distribution linear law for the case of NDSR with compound-like structure. Solutions of Fe in
Al are herein considered where NDSR can be close to FeAl₃ (or FeAl₆) compound with respect to composition and structure [3, 5-7]. According to the analysis [5-7], the structure FeAl₃ may be regarded as quasi-isomorphous to the structure of Al, if we take into account the presence of structural vacancies (D). The stoichiometric formula of FeAl₃ can be rendered as Fe□₁₂Al₃ [5-7]. It can be also assumed [5-7] that surface energy in the coherent interphase boundary (Fe□₁₂Al₃/Al) has a relatively small value (as for coherent twin boundaries). The structure Fe□₁₂Al₃ is more compact than Al [5-7]. Therefore NDSR with such a structure (Fe□₁₂Al₃) must be located preferably in the compressing strain areas near the dislocation edge components. « Reactions » of dissolution of such a structure of NDSR in an aluminum bulk solution can be presented in the following form [6, 7]:

$$(\text{Fe}_{1,2}\text{Al}_3)_\perp + (2.2 + n) \text{Al} = \text{Fe} + 1.2\Box + 5.2(\text{Al})_\perp + n\text{Al}$$

(1)

where index « ⊥ » indicates the localisation of the « agent » in the area near dislocations with the volumetric compression $P_\perp$ and $n \gg 1$.

From the thermodynamic equilibrium conditions, we obtain the expression for the concentration of Fe-atoms (in atomic fractions) in a bulk aluminium solution, saturated at the temperature $T$ with respect to NDSR of the structure Fe□₁₂Al₃ [6, 7]:

$$C = \frac{(a_{\text{Al}})^{2.2}}{(a_{\Box})^{1,2} (a_{\text{Al}})_\perp^{5.2}} = \exp \left\{ \left( \Delta G^0_c + P_\perp \Delta V - \Delta \tilde{G}_{\text{Fe}} + (\sigma V_c/r)/(RT) \right) \right\}$$

$$= \exp \left( \left( \Delta H^0_c - \Delta \tilde{H}_{\text{Fe}} + P_\perp (V_c - 5.2V_{\text{Al}}) + (\sigma V_c/r) + T \Delta \tilde{S}_{\text{Fe}} - T \Delta S^0_c/(RT) \right) \right)$$

(2)

where $\Delta G^0_c$, $\Delta H^0_c$, $\Delta S^0_c$ are the standard Gibbs energy, enthalpy, and entropy of formation of one mole Fe□₁₂Al₃ from pure components at T and atmospheric pressure; $V_c$ and $V_{\text{Al}}$ are the molar volumes of Fe□₁₂Al₃ and Al for T and $P_\perp$; $\Delta \tilde{G}_{\text{Fe}}$ is the excess partial molar Gibbs energy for Fe in a bulk Al-solution ($\Delta \tilde{G}_{\text{Fe}} = \Delta \tilde{H}_{\text{Fe}} - T \Delta \tilde{S}_{\text{Fe}}$); $r$-lateral cross-section radius for NDSR with the structure Fe□₁₂Al₃; $a_{\text{Al}}$ and $a_{\text{Al}}_\perp$ thermodynamic activities of Al at T in a bulk Al-solution and in the areas near dislocations; $a_{\Box}$ is the thermodynamic activity of vacancies at T in a bulk Al-solution (at the equilibrium with the surface of crystal $a_{\Box} = 1$).

The overall positive pressure (compression) in the areas near dislocations can be described by the known expression:

$$P_\perp = \frac{\mu b (1 + \nu)}{6 \pi (1 - \nu) r} = \frac{A}{r}$$

(3)

where $\mu$ is the shear modulus value for Al; $\nu$, the Poisson coefficient for Al; $b$ is the minimum Burgers vector value for Al.

In the approximation of relation (3), the surfaces of equal pressure ($P_\perp$) are cylinders with the radius $r$, tangent to the gliding plane of the dislocation lines. The form of the lateral cross-section of NDSR with the structure Fe□₁₂Al₃ can be approximated by a contour with the pressure $P_\perp$.

With the change of the iron content in Al-samples (at a given T) the equilibrium concentration in solution in the bulk (expressions (2) and (3)) may be reached, due to the change of the lateral cross-section radius of NDSR ($r$), [11], and due to the change in composition and structure of these regions from FeAl₆ (Fe□₁₅Al₆) to FeAl₃ (Fe□₁₂Al₃) and more « concentrated » compounds [6, 7].

The diffusion of the Fe-atoms in NDSR, running with the characteristics $D_\perp$ and
\( Q \perp \) [3], is, evidently, conditioned by the existence of a chemical potential gradient of the Fe-atoms along NDSR (due to the change in the structure and composition of NDSR during the change of the Fe-content in the bulk Al-solution). Therefore it is rational to examine the distribution law in a simplified model, that supposes the change in the NDSR composition (in a certain interval near Fe\( _{1.2} \)Al\(_3\)) when the NDSR lateral cross-section diameter is constant \((d_c = \text{Const.). In such an approximation the } \Delta G_c^0 \text{ in the expression (2) is described as:}

\[
\Delta G_c^0 = \Delta G_c^0' + RT \ln \left( \frac{a_{(Fe)}^i}{a_{(Fe)}^{i'}} \right) + 1.2 RT \ln \left( \frac{a_{(Fe)}^{i'}}{a_{(Fe)}^{i''}} \right) + 3 RT \ln \left( \frac{a_{(Al)}^{i'}}{a_{(Al)}^{i''}} \right)
\]

where \( \Delta G_c^0' \) and the thermodynamic activities \( a_{(Fe)}^i, a_{(Al)}^i, a_{\text{c}}^i \) correspond to the NDSR stoichiometric composition, i.e. Fe\( _{1.2} \)Al\(_3\); \( \Delta G_c^0 \) and \( a_{(Fe)}^i, a_{(Al)}^i, a_{\text{c}}^i \) correspond to the NDSR non-stoichiometric composition; at the equilibrium with the crystal surface, the ratio of the NDSR vacancy activities is equal to 1. In the model of the ideal solutions, in place of the Fe and Al activities in NDSR, one may use the atomic fractions in the expression (4). In such an approximation from (2)-(4) one may obtain the distribution law in the following form:

\[
\frac{(C_r - C)}{C} = B \exp \left( \frac{\Delta H}{RT} \right)
\]

where

\[
C_r - C = C_{(Fe)} \eta
\]

\[
\eta = d_c^2 \rho_r
\]

\[
B = \eta C_{(Fe)} \left( \frac{C_{(Al)}^i}{C_{(Al)}^{i''}} \right)^3 \exp(\Delta S_c^0' - \Delta S_{Fe})/R
\]

\[
\Delta H = \Delta H_{Fe}^0 - \Delta H_{c}^0 + P \Delta V - \frac{2 \sigma V_c}{d_c}
\]

\[
\Delta G_c^0 = \Delta G_{c}^0 - T \Delta S_c^0
\]

\[
\Delta V = V_c - 5.2 V_{Al}
\]

\[
C_{(Fe)} = 0.2, \quad C_{(Al)} = 0.6
\]

\( C_r \) is the effective solubility (atomic fraction) of impurity atoms (Fe) in a crystal (Al) with high density of dislocations \( (\rho_r) \); \( C_r \), the solubility of impurity atoms (Fe) in the normal lattice; \( C_{(Fe)} \), \( C_{(Al)} \), the local atomic fraction of Fe and Al, respectively, in the non-stoichiometric NDSR; \( C_{(Fe)}', C_{(Al)}' \), in stoichiometric NDSR. The average value of the local atomic fraction of Al in the non-stoichiometric NDSR may be used in (8) within the approximation of \( B = \text{Const.} \).

The data [6] on the solubilities \( C_r \) and \( C \) at various temperatures (Tab. 4 in [3]) and the diffusion data (Tab. 3 in [3]) are satisfactory described with the help of (5-12). By using the data [6] and the results of the treatments [3] one can evaluate the average value of \( C_{(Al)} = (\eta + C - C_r)/\eta \), where for the specimens [6] \( C_r = 2.2 \times 10^{-4}, C = 6 \times 10^{-5} \) and \( \eta = 4.5 \times 10^{-4} \). Hence, the factor of \( B \) in (5) is close to \( \eta \) within the approximation of [1-4].

The values of the other parameters (including \( V_c, \Delta V, \sigma, \Delta \bar{H}_{Fe}, \Delta \bar{H}_{c}^0 \), etc.) are presented in [6, 7, 13, 14].

The conducted consideration shows that the effective law of distribution of Fe-atoms between NDSR with the intermetallic-like structure and Al-solution may correspond to the linear concentration dependence (in the limited range of concentration). Effective binding
enthalpy $\Delta H$ can be close to that of dissolution of FeAl$_3$ in Al, that is $(\Delta H_{Fe} - \Delta H_{c}^0)$ or slightly exceed the value mainly due to the $P_{\perp} \Delta V$ term ($\Delta V < 0$) [6, 7, 13, 14].

It is appropriate to note that the $\Delta H$ value obtained in [3] by the modified treatment of the anomalous diffusion data ($\Delta H = 65 \pm 4$ kJ/mol) is less than the value obtained in [1] by the more simplified treatment of the diffusion data ($\Delta H = 86 \pm 9$ kJ/mol). The differences in the $\Delta H$ values are obviously connected both with the experimental errors and the used approximations.

The further corrections of the $\Delta H$-value are reasonable. Nevertheless the results show quite satisfactory applicability of the model developed. The distribution law obtained in the present work differs from a true adsorption law (the Henry, Langmuir, Gibbs or Fowler-Guggenheim forms, etc.) and can be used within limited concentration range (as was mentioned above). This effective law is mainly grounded by the change of the constitution diagram for NDSR discussed in [6, 13, 14].

In physico-chemical sense the obtained distribution law could be compared with the Fowler-Guggenheim adsorption isotherm for the concentrations exceeding the critical one of the phase transition.

The consideration above allows to conclude that in solid solutions of transition metals in aluminium, which are characterized by a relatively low solubility and formation of intermetallic compounds, the impurity distribution law for dislocations can exhibit a linear concentration dependence, the structure and composition of the near-dislocation segregation regions (with the diameter of 20-30 angströms) can be close to the corresponding intermetallic compounds of variable composition and possess low diffusion conductivity, high binding enthalpy and high trapping ability (in comparison to the Cottrell «clouds»). Such NDSR can condition the anomalies and the specific features of decomposition, recrystallisation, and phase formation processes in aluminium alloys. Similar situation may take place in a number of technologically significant systems, for example, in solid solutions of carbon and hydrogen in iron [2-5].

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