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Analysis of the Grain Boundary Adsorption Activity for Alloying Elements in Binary Fe-Alloys

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Theoretical analysis of the Gibbs isothermal adsorption equation was conducted and impossibility to identify with its help alloying elements on their adsorption activity is shown. Within the frame of quasi-chemical model of solid solutions, using the early obtained cross-correlation dependences between the fundamental elements parameters and electronic structure of their atoms, a methodology for quantitative determination of adsorption activity of alloying elements was worked out for binary Fe-based solid solutions. It is shown that among the investigated elements, the level of grain-boundary adsorption activity decreases twice in transition from Ca to Mn and Si. High level of linear cross-correlation is revealed between the level of adsorption activity and electron concentration on external atomic energy levels.

Keywords: ALLOY, IRON, ALLOYING ELEMENTS, ADSORPTION ACTIVITY, ANALYSIS

Introduction

Grain size is one of the most important characteristics of the structural state of steels, determining levels of the most responsible indicators of mechanical and service properties: yield point, impact hardness in a brittle state as well as temperature of ductile-brittle transition. Therefore, the study of factors affecting the growth of grain is of great interest. Currently, the dominant view [1, 2], according to which the major factors influencing the growth of grains and the defining possibilities of regulation their size, refer

to physical and chemical effects, causing reduction in grain boundary surface energy with the introduction of microalloying additions. Here we consider two possible mechanisms of influence on the grain boundary energy in the alloys: adsorption and, second, call it conditionally, dispersion due to the presence of highly dispersed inclusions of carbide and nitride phases. The possibility of accumulation of atoms of impurity elements at grain boundaries in the solid solution is thermodynamically proved by Gibbs [3] and as applied to steels theoretical issues were developed in the works of V. Arkharov [4].

Results and Discussion

For According to the thermodynamic theory of J. Gibbs, the equilibrium state of two grains separated by the boundary in a solid binary solution with the concentration of the second component x_B at a constant temperature must correspond to the equality of chemical potentials

$$\mu_B^{31} = \mu_B^{32} = \mu_B^{\Gamma}, \text{ with } x_{B1} = x_{B2} \neq x_B^{\Gamma}, \quad (1)$$

where $x_{B1}, x_{B2}, x_B^{\Gamma}$ - molar concentration of the impurity element in grains 1 and 2 and on the boundary of their section, respectively.

According to the Gibbs theory of the state is achieved as a result of redistribution of atoms of the impurity element between the volumes of grains and their boundary layer which separates them, caused by the difference in their energy state, which is characterized by the specific surface energy σ. Since it follows from equilibrium condition (1) that $d\mu_B^{\Gamma} = d\mu_B^3$, then the analysis of changes in the thermodynamic state of the system leads to the relation:

$$\Gamma_B = -\left(\frac{d\sigma}{d\mu}\right)_T, \quad (2)$$

which is called the Gibbs isothermal adsorption equation, where Γ_B is the excess concentration of the impurity element in the boundary layer.

As can be seen from equation (2), the concentration of impurity element in the boundary layer will increase if the increase in its content in solid solution causes a decrease in the specific boundary energy σ while increasing the chemical potential of the dissolved element μB in the grain volume.

Gibbs equation in this form does not allow to identify the impurity elements by their adsorption activity, as the chemical potential of each impurity element, with other conditions being equal, depends, as we know, not only on its concentration, but also on the nature of the interaction with atoms of the solvent and is determined by the expression

$$\mu = \mu^0 + R \cdot T \cdot \ln a, \quad (3)$$

where a – impurity element activity.

In this case, taking into account (3), equation (2) can be written in the form

$$\Gamma_B = -\frac{1}{R \cdot T} \cdot \left(\frac{d\sigma}{d \ln a} \right)_T \quad (4)$$

Given that the activity is connected with the concentration ratio $a = \gamma_B \cdot x_B$, where γ_B is the activity coefficient then acceptable for using equation form (4) will be:

$$\Gamma_B = -\frac{1}{R \cdot T} \cdot \left[\frac{d\sigma}{d \ln(\gamma \cdot x)} \right]_T \quad (5)$$

From this expression it follows that in case of an ideal solution, for which $\gamma_B = 1$, the equation of adsorption can be written as

$$\Gamma_B = -\frac{1}{R \cdot T} \cdot \left(\frac{d\sigma}{d \ln x} \right)_T$$

This means that the addition of the impurity element which forms an ideal solution should be accompanied by the accumulation dissolved atoms in the boundary layer. In the case of a real solution $\gamma_B(x) \neq 1$ and expression (5) can be written in such way

$$\Gamma_B = -\left\{ \frac{1}{R \cdot T} \cdot \left[\frac{d\sigma}{d \ln \gamma_B + d \ln x} \right] \right\} \quad (6)$$

The presence of the activity coefficient of the dissolved element γ_B in this expression is important because its value reflects the level and nature of the interaction of atoms of that element in solid solution and, thus, given a value of γ_B, allows to estimate by calculation the adsorption activity of the impurity component in the solid solution of this composition. In this regard, equation (6) should be rewritten as

$$\left(-\frac{d\sigma}{\Gamma_B} \right) = R \cdot T \cdot \left(d \ln \gamma_B + d \ln x_B \right) \quad (7)$$

In this form left side of equation describes the change in the state of grain boundary layer induced by administration of x_B moles of impurity element B into the solution forming a real solution with the activity coefficient $\gamma_B \neq 1$. According to this equation, the equilibrium in the considered systems of equimolar solid solutions of various impurity elements, which differ in γ_B size in the same solvent, will be achieved by changing the characteristics of grain boundary adsorption depending on the numerical value of γ_B.

Equation (7), with the data on the activity coefficient of the impurity elements, makes it possible to obtain a comparative evaluation of the adsorption activity of the elements in solid solution. However, in literature, such data are not available. In this paper, this problem was solved within the quasichemical theory of solid solutions [3] according to which the calculated value of $\ln\gamma$ can be determined by the expression

$$\ln \gamma_B = \left(1 - x_B\right)^2 \cdot \frac{Q}{R \cdot T}, \quad (8)$$

where Q – exchange energy.

According to the model of pair interactions

$$Q = Z \cdot N_0 \cdot \left[h_{AB} - 0{,}5 \cdot \left(h_{AA} + h_{BB} \right) \right], \quad (9)$$

where Z – number of nearest neighbors; N_0 – Avogadro's number; h_{AA}, h_{BB}, h_{AB} – enthalpy of the atom pairs AA, BB and AB, respectively.

Values h_{AA}, h_{BB} are obtained from the data on the heats of sublimation of components A and B. The h_{AB} values for different pairs of elements were determined on the basis of the established linear correlation dependence between the heat of sublimation and the ratio of the number of outer electrons q to the serial number of the element in the Mendeleev's Periodic Table.

$$H_C = -1234 \cdot \left(\frac{q}{N} \right) + 734 \quad (R \cong 0{,}9), \quad (10)$$

where q – the total number of electrons in the unfilled levels; N - total number of electrons in an atom of the element.

The heat of sublimation of a binary solution H_{AB}^P was found using (9) based on average value (q\N)

$$\eta = \left(\frac{q}{N} \right)_{av} = 0{,}5 \cdot \left[\left(\frac{q}{N} \right)_A + \left(\frac{q}{N} \right)_B \right] \quad (11)$$

The results are used to determine the adsorption activity of the second component in binary metallic solid solutions based on iron. As a parameter characterizing the adsorption activity, we use a value of A_D, equal to the ratio $\left(-\frac{1}{R \cdot T} \cdot \frac{d\sigma}{\Gamma} \right)_T$ in the left-hand side of equation (7). After substituting (8) into equation (7) and the corresponding transformations we received the final form of the estimated equation:

$$A_D = \left[2 \cdot \frac{Q}{R \cdot T} \cdot (x-1) + \frac{1}{x} \right], \qquad (12)$$

where $A_D = \left(-\frac{1}{R \cdot T} \cdot \frac{d\sigma}{\Gamma} \right)_T$ – adsorption activity parameter.

Calculations of this parameter were performed for binary alloys based on iron, containing one of the following elements of the group: Mn, Si, Cr, V, Ti, Nb, Mo, Al, Mg and Ca in the amount of xB ≤ 0-0,005 at T = 1100 K. Further data used in the calculations are given in **Table 1**. There are also given results of calculations of the parameter A_D. The Table shows that the maximum value of this parameter $A_D \cong 500$ corresponds to Ca, on the second and third places $A_D = 480$ and 448 are Nb and Mo, V and Ti elements correspond to the values $A_D = 393$ and 345, the minimum values of this parameter 257 and 254 refer to Mn and Si.

Aluminum and chromium have values A_D = 325 and 299. Attention is drawn to a linear correlation (**Figure 1**) between the value of A_D and the relative electron concentration of the outer levels (η = q\N), which is approximated by the equation A_D = -1392·(q\N)+645, (R^2 = 1). This obviously points to the electronic nature of the adsorption processes.

Table 1. The values of the exchange energy Q, the electron concentration η and grain boundary adsorption parameter A_D for the investigated Fe-Me systems

Metal	Q, kJ/mol	η	A_D
Mn	-3.2	0.28	257
Si	0.66	0.28	254
Cr	-22.7	0.25	299
V	-44.1	0.21	345
Ti	-66.8	0.18	393
Nb	-105.8	0.12	477
Mo	-92.2	0.14	448
Ca	-120.1	0.1	508
Mg	-74.7	0.17	411
Al	-35	0.23	325

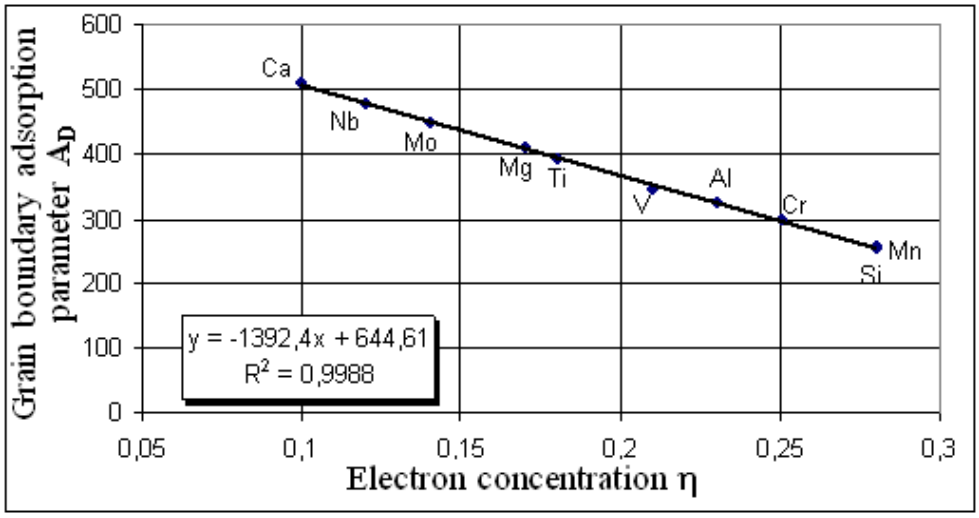

Figure 1. Dependence of the grain boundary adsorption parameter A_D on the electron concentration η of dissolved elements in binary alloys based on iron

Thus, the results of the calculations show that the adsorption activity of elements of the studied group decreases from the maximum value of Ca, A_D = 508 to a minimum value A_D of Si = 254 in the following order: Ca, Nb, Mo, Mg, Ti, V, Al, Cr, Mn and Si. In the same order, in accordance with the linear law, increases the electron concentration of the outer electron levels.

In conclusion we note that the results obtained, characterizing the level of adsorption activity for most of the investigated elements are in agreement with the experimental data [4].

Conclusions

1. Within basic notions of the Gibbs thermodynamic theory of grain boundary adsorption and the quasichemical model of solid

solutions, using the established correlations between the fundamental characteristics of the elements and the electronic structure of atoms, the methodology of calculation of the adsorption activity of the impurity elements in binary solid solutions based on iron was developed.

2. It is shown that in a number of the investigated elements Ca, Nb, Mo, Mg, Ti, V, Al, Cr, Mn and Si the A_D parameter, characterizing the intergrain adsorption activity is reduced two times during the transition from Ca to Mn and Si.

3. High linear correlation dependence ($R^2 = 1$) between the parameter of the adsorption activity A_D and electron concentration ($\eta = q/N$) of the external energy levels was established.

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Анализ зернограничной адсорбционной активности легирующих элементов в двойных сплавах на основе железа

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Выполнен теоретический анализ уравнения изотермической адсорбции Гиббса и показана невозможность идентифицировать с его помощью примесные элементы по их адсорбционной активности. В рамках квазихимической модели твердых растворов, с использованием установленных корреляционных зависимостей между фундаментальными характеристиками элементов и электронным строением их атомов, разработана методика расчетного определения адсорбционной активности примесных элементов в бинарных твердых растворах на основе железа. Показано, что в ряду исследованных элементов уровень межзеренной адсорбционной активности снижается в два раза при переходе от Ca к Mn и Si. Установлен высокий уровень линейной корреляционной зависимости между уровнем адсорбционной активности и концентрацией электронов внешних энергетических уровней.