

THE CALCULATION OF BORON AND CARBON SOLUBILITY FOR (FeMe)₂BC ALLOY WITH LATTICE IN MODIFIED YUM-ROZERI MODEL

Z.A. Matysina¹, S.Yu. Zaginaichenko², D.V. Schur³, O.V. Karpets², A.L. Chuprina¹

¹ Dnepropetrovsk State University, Dnepropetrovsk, 320000 Ukraine

² Institute for Problems and Materials Science of NAS, Kiev, 03150 Ukraine

³ Institute of Hydrogen and Solar Energy, P.O. Box 195, Kiev-150, 03150 Ukraine

Abstract

In present work the calculation of boron and carbon solubility in alloys (FeMe)₂BC (Me = Fe, Cr, Mn, Al and others) has been performed. The modified Yum-Rozeri model of crystal has been applied. It has been used the configurational method in calculations taking into consideration all kinds of configurations of Fe, Me atoms around B, C atoms.

Authors have received formulae determining the boron and carbon solubility in alloy in dependence on temperature, concentrations of Fe, Me components and energetic constants and also defining the mutual influence of boron and carbon solubility in alloy. The obtained formulae admits the presence of extremum at the temperature dependence of solubility.

It has been found that boron and carbon are favourable for the dissolution each other in alloy at their atoms interaction of attraction type, and vice versa, these impurities inhibit the dissolution each other in the case of repulsion forces between their atoms. The obtained dependences are in agreement with experimental data according to which the boron presence in alloy decrease the carbon solubility.

Introduction

In the last few years the interest in borides grows in connection with their specific properties, like high hardness, refractoriness, creep resistance. The economically-alloyed and boron-contained

compounds are widely used at the preparation of surface coatings, that have high wear resistance and in operating characteristics they are highly competitive with the indexes of scarce and expensive alloys. Investigation of a limiting solubility of impurities in iron boride is of scientific and practical interest because permits the estimation of concentration and temperature areas of existence of continuous solid solutions.

Atoms of metals and non-metals enter into the composition of studied interstitial phases. In these phases of iron boride Fe₂B type the metals atoms can be Fe, Co, Ni, Cr, Mn, Mo, Au, Al, Th, Ta, W, Zr atoms and others, the non-metals atoms – C, B, H, P, Ge, Si, Sn atoms and others. As this takes place, the metals and non-metals atoms can be of several kinds in alloy and the mixed impurity phases, like borocarbides, nitroborides, hydronitrides, carbonitrosilicides of metals and others, are formed.

The solubility of one impurity component depends not only on the concentrations of matrix components and alloy temperature, but on the solubility of another interstitial impurity as well. As an example, Figure 1 illustrates the experimental plots of hydrogen solubility as a function of boron, carbon and silicon concentration respectively in palladium (Fig. 1a), iron (Fig. 1b) and nickel (Fig. 1c) from data [1-5]. As illustrated in Fig. 1, in the presented cases this dependence manifests itself variously, i.e. the interstitial impurities of carbon and silicon (Fig. 1b, c) decrease the solubility

curve, however boron impurity (Fig. 1a) increases the hydrogen solubility.

The theoretical investigation on the mutual influence of the solubility of two interstitial impurities G, S in alloy (RD)₂GS with a lattice of iron boride has been carried out in this work.

According to the data of papers [1-3], in these alloys the non-metallic atoms of relatively small size occupy the centres of antiprismes (twisted cubes) from metallic atoms and each of them has the eight nearest metallic atoms. The elementary cell of iron boride (FeD)₂BS with a structure by Shubert model of C16 type is shown in Fig. 2. The non-metallic atoms form the tetragonal structure with face-centered squares in equatorial planes (perpendicular to the “c” axis) [6-8].

According to Yum-Rozeri model [9] the non-metallic atoms are distributed over the centres of tetrahedrons, the vertex of which are occupied by the metallic atoms, i.e. the non-metallic atoms are interstitial atoms. The structure of iron boride in modified Yum-Rozeri model is shown in Fig. 3. In this case the non-metallic atoms also form the tetragonal lattice, face-centered in equatorial planes. Both in the first and in the second model of lattice the atoms of metals and non-metals are arranged in alternating planes.

Alloy free energy. Equilibrium equations

The solubility of the G and S interstitial impurities is defined by the equilibrium concentration g and s respectively

$$g = \frac{N_G}{N} = \sum_{i=0}^z \frac{N_{Gi}}{N}, \quad s = \frac{N_S}{N} = \sum_{i=0}^z \frac{N_{Si}}{N}, \quad (1)$$

where N_G , N_S are the numbers of G, S atoms respectively, N_{Gi} , N_{Si} are the numbers of G, S atoms with i-configuration of R and D atoms. The sites of third and fourth type corresponding to G and S atoms are named as interstitial sites. The

configuration of R, D atoms about interstitial site is determined by the number of R and D atoms around this interstitial site. For z nearest atoms of i-configuration i is the number of R atoms and (z-i) is the number of D atoms. In formula (1) N is the number of all positions of G, S atoms.

The calculation of the alloy free energy and the investigation of its thermodynamic equilibrium condition have been performed to solve the raised problem. The free energy of the crystal is calculated by the formula

$$F = E - kT \ln W,$$

where E is the internal configuration part of the free energy, determined by the sum of interaction energies of nearest atoms, W is the thermodynamic probability of interstitial site filling by G and S atoms and is determined by the combinatorial rule, k is Boltzmann's constant, T is absolute temperature. The calculation of free energy is carried out using the molecular-kinetic theory by the method of average energies in a model of pair interatomic interactions, ignoring the correlation in substitution of lattice sites and interstitial sites by corresponding atoms. We take into account the interaction of the nearest G and S atoms of non-metals among them and their interaction with metallic atoms. Let us denote these interaction energies of atomic pairs with opposite sign by $v_{\alpha\beta}$, $v_{\alpha\alpha}$ ($\beta = R, D$, $\alpha = G, S$).

The energy $v_{\alpha i}$ ($\alpha = G, S$) of non-metallic atom is determined by the sum of interaction energies $v_{R\alpha}$, $v_{D\alpha}$ with metallic atoms R, D. For i-configuration it is equal to

$$v_{\alpha i} = i v_{R\alpha} + (z - i) v_{D\alpha},$$

where $z=8$ or $z=4$ correspondingly for the first and second model of lattices.

To a such approximation the calculation of the free energy gives the following formula

$$F = - \sum_{i=0}^z \sum_{\alpha=G,S} N_{\alpha i} v_{\alpha i} - \sum_{\alpha\beta=G,S} N_{\alpha\beta} v_{\beta\alpha\beta} - kT \sum_{i=0}^z (Q_i \ln Q_i - N_{Gi} \ln N_{Gi} - N_{Si} \ln N_{Si} - (Q_i - N_{Gi} - N_{Si}) \ln (Q_i - N_{Gi} - N_{Si})),$$

where $N_{\alpha\beta}$ is the number of non-metallic atomic pairs, N_{Gi} , N_{Si} are the numbers of G, S atoms with i -configurations, Q_i is the number of positions with i -configuration that are occupied by G and S atoms or are vacant,

$$Q_i = N \frac{z!}{i!(z-i)!} r^i d^{z-i}.$$

It should be taken into account that each atom G or S of its six nearest neighbouring atoms G or S have two atoms at $c/2$ distance and four atoms at $a/\sqrt{2}$ distance, where a , c are the lattice parameters. Let us denote the energies of their interaction by

$$v_{\alpha\beta} = v_{\alpha\beta}(c/2), \quad v'_{\alpha\beta} = v_{\alpha\beta}(a/\sqrt{2}),$$

and the numbers of these pairs are equal correspondingly

$$N_{GG} = g^2 / N, \quad N'_{GG} = 2g^2 / N,$$

$$N_{SS} = s^2 / N, \quad N'_{SS} = 2s^2 / N,$$

$$N_{GS} = 2gs / N, \quad N'_{GS} = 4gs / N.$$

The equilibrium concentrations g , s of G and S atoms can be found by the minimization of free energy with respect to g and s in the case of $N_{Gi} \ll Q_i$, $N_{Si} \ll Q_i$

$$g = \gamma_1 \left(r \exp \frac{v_{AG}}{kT} + d \exp \frac{v_{DG}}{kT} \right)^z \exp \frac{2[g(v_{GG} + 2v'_{GG}) + s(v_{GS} + 2v'_{GS})]}{kT}, \quad (2)$$

$$s = \gamma_2 \left(r \exp \frac{v_{AS}}{kT} + d \exp \frac{v_{DS}}{kT} \right)^z \exp \frac{2[g(v_{GS} + 2v'_{GS}) + s(v_{SS} + 2v'_{SS})]}{kT},$$

where r and d are the atomic concentrations of R and D components in alloy, γ_1 , γ_2 are the coefficients independent of atoms concentrations.

For structures with relationship between lattice parameters c , a satisfied equation $c = a\sqrt{2}$, when $v_{\alpha\beta} = v'_{\alpha\beta}$, the equations (2) become:

$$g = \gamma_1 \left(r \exp \frac{v_{AG}}{kT} + d \exp \frac{v_{DG}}{kT} \right)^z \exp \frac{6(gv_{GG} + sv_{GS})}{kT}, \quad (3)$$

$$s = \gamma_2 \left(r \exp \frac{v_{AS}}{kT} + d \exp \frac{v_{DS}}{kT} \right)^z \exp \frac{6(gv_{GS} + sv_{SS})}{kT}.$$

Equations (2), (3) allow one to define the solubility of the G and S interstitial impurities in the disordered alloy $(RD)_2GS$, their dependence on temperature, r and d concentrations, energetic parameters, and also to ascertain the mutual influence of G and S component solubility. As is evident from equations (2), (3) the nature of dependences $g = g(T, r, d, s)$, $s = s(T, r, d, g)$ is identical for both models of $(RD)_2GS$ alloys structures.

As this takes place, the $g = g(r, d)$ and $s = s(r, d)$ are monotonic functions and plots of these dependences are more flat for $z=4$ in comparison with the slope of these curves for $z=8$. The studied dependences $g = g(s)$ and $s = s(g)$ show that their mutual effect is defined to a large extent by the numerical value and sign of v_{GS} energy of G and S atoms interaction.

Solubility of interstitial impurities in iron boride

Investigation of the solubility of aluminium, carbon impurities in iron boride Fe_2B has been performed by the method of computer simulation. In line of accepted designations and nomenclature the Al atoms is D impurity, the B atoms is G impurity and the C atoms is S impurity.

For iron boride contained these impurities the sign and numerical value of v_{GS} energy define the effect of solubility of one of B, C elements on another. For $v_{GS} > 0$ we have $\exp(6s v_{GS}/kT) > 1$ and carbon impurity favour the boron solubility (Fig. 4) and vice versa, for $v_{GS} < 0$ we have $\exp(6s v_{GS}/kT) < 1$,

carbon impurity inhibits the boron solubility (Fig.5). The second result is in agreement with experimental data on definition of carbon solubility in iron boride Fe_2B [12].

Curve 1 of Fig. 5 has been received on the assumption that interaction energies of atomic pairs B-C, C-C, C-Fe, C-D depend on carbon concentration in iron boride and undergoes a rise with increasing concentration of carbon. In this case the curve of $s = s(g)$ dependence become more flat as the boron concentration increases in iron boride in comparison with calculation result that uses the constant values of interaction energies of these atoms (curve 2 of Fig. 5). The form of $s = s(g)$ curves is independent of a means of interaction energies choosing.

The solubility of boron and carbon in iron boride depends upon the interaction energy of these atoms with atoms of metallic impurity. The carbon solubility rises in iron boride as the concentration of metallic impurity atoms increases, if the interaction energy of boron atoms with metallic impurity atoms is greater than the interaction energy of carbon atoms with iron atoms, i.e. when $\nu_{DS} > \nu_{RS}$ (Fig. 6).

As shown in Fig. 7, with a temperature increase, in a case of predominance of repulsive forces between atoms of boron and carbon (when $\nu_{GS} < 0$) the boron solubility in iron boride decreases, but the carbon solubility increases.

In an analogous way it can be investigated the solubility of hydrogen and another impurities in the interstitial alloys of $(RD)_2GS$ type.

Conclusions

Hence the carried out theoretical investigation shows the possible essential dependence of the mutual influence of the solubilities of interstitial

impurities in alloys with studied structure. It has been found that the solubility of one interstitial impurity can promote as well as inhibit the dissolution of another depending on the sign of interaction energy of atomic pairs. These dependences become more essential, if interaction energies depend on the atomic concentrations of these impurities in alloy. The solubility of interstitial impurity is dependent also on the composition of matrix elements of alloy. It has been elucidated that the temperature dependence of the solubility of interstitial impurity can be extremal.

The obtained theoretical formulae on mutual influence of one interstitial impurity solubility on another are in agreement with experimental results of effect of silicon, boron, carbon on hydrogen solubility.

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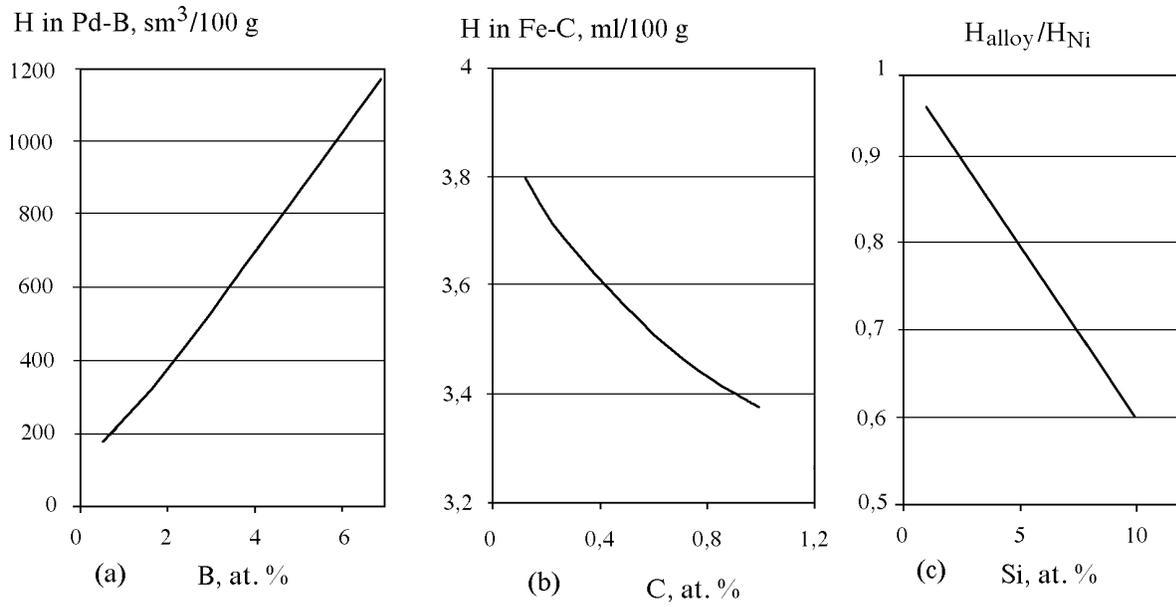


Fig. 1. Experimental concentration dependences of hydrogen solubility in alloys [1-5]