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Journal of Alloys and Compounds 330–332 (2002) 81–84

Journal of ALLOYS AND COMPOUNDS

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Theoretical study of interstitial atoms distribution in the bulk and at the surface of crystal. Surface segregation

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Abstract

A theoretical investigation of diffusion, distribution and thermally activated redistribution of impurity interstitial atoms C (hydrogen, carbon) about the volume and surface both of crystalline films and massive crystals AB has been carried out. These crystals have *bcc* lattice and various types of free facets. The dependence of hydrogen and carbon filling of the surface and volume interstitial sites upon the films' temperature and composition have been studied. Changing the temperature or pressure leads to the redistribution of C atoms in the system. The thermally activated processes of C atom redistribution among the volumetric and surface film interstices in AB alloy are investigated. The formulae for the equilibrium concentrations of interstitial atoms and the rate or relaxation time of interstitial atoms redistribution in dependence on concentrations of A, B alloy components, on long range order in A, B atoms distribution at the sites of crystal lattice, on temperature, on interaction energies of atomic pairs AC, BC are determined.

Keywords: Temperature; Crystalline films; Impurity distribution and redistribution; Interstitial atoms concentration; Segregation

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1. Introduction

The presence of the free surface in crystal can lead to a corresponding distribution of interstitial atoms (hydrogen, carbon) about the interstitial sites on the surface and in the crystal's volume. A change of the thermodynamic parameters, such as temperature and pressure, leads to the redistribution of interstitial atoms in the system. Knowledge of these processes' rates can prove to be important, for example, for the selection of heat treatment regimes for alloys. The surface segregation of interstitial atoms is used in practice for the obtaining of certain surface physical characteristics of crystals, for the prediction of material-making techniques of new chemical compositions.

This paper describes a theoretical investigation of the impurity distribution of interstitial C atoms on the surface and in the volume both of the films and massive crystals AB. The thermally activated processes of interstitial atoms redistribution among the volumetric and surface film interstices are investigated theoretically and also results from the calculation of the dependences of the equilibrium concentrations of hydrogen in the film interstitial sites on the alloy composition, temperature, atomic order and energetic parameters of interatomic interaction are listed below.

2. Interstitial atoms at the volumetric and surface interstices

The monomolecular model of the surface and the principle of detailed equilibration are used in calculations. The subject of inquiry is the film of an ordering alloy AB with the body-centred cubic structure that consists of n atomic layers with two free surfaces. It is supposed that interstitial atoms C are located in interstitial sites of one type (e.g. octahedral) with the different coordination on the surface and in the volume, i.e. the film has the volumetric V and the surface S interstitial sites.

The temperature change from the value T_1 to T_2 disturbs the thermodynamic equilibrium and initiates the redistribution of C atoms. This theory includes the premise that the redistribution of slow A, B atoms does not take place at lattice sites. The solution of the kinetic equations for the

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0925-8388/02/$ – see front matter
PII: S0925-8388(01)01511-0

$V \rightleftarrows S$ transitions shows the exponential dependence of ν_V, ν_S concentrations of interstitial atoms on time t

$$\begin{aligned}\nu_V(t) &= \Delta\tilde{\nu}_V \exp\frac{-t}{t_*} + \tilde{\nu}_V\,(T_2),\\ \nu_S(t) &= \Delta\tilde{\nu}_S \exp\frac{-t}{t_*} + \tilde{\nu}_S\,(T_2),\end{aligned} \tag{1}$$

where

$$\tilde{\nu}_V(T) = \left[1 + \frac{1}{n}\exp\frac{\upsilon_S - \upsilon_V}{kT}\right]^{-1},$$
$$\tilde{\nu}_S(T) = \left[1 + n\exp\frac{\upsilon_V - \upsilon_S}{kT}\right]^{-1}$$

are the equilibrium concentrations of interstitial atoms C at the V and S interstices; $\Delta\tilde{\nu}_V = \tilde{\nu}_V(T_1) - \tilde{\nu}_V(T_2)$; $\Delta\tilde{\nu}_S = \tilde{\nu}_S(T_1) - \tilde{\nu}_S(T_2)$ are the changes of equilibrium concentrations $\tilde{\nu}_V$, $\tilde{\nu}_S$ at the $T_1 \rightarrow T_2$ temperature change, υ_V, υ_S are the energies of C atom in the V and S interstices, which are dependent on the alloy structure and composition, atomic order and the υ_{AC} and υ_{BC} energetic parameters of the interatomic interaction of AC and BC pairs, υ_B is the C atom energy in the vertex of potential barrier at the $V \overset{\rightarrow}{\leftarrow} S$ transitions;

$$t^* = \frac{\tau}{4}\left[\exp\frac{-(\upsilon_V - \upsilon_B)}{kT} + n\exp\frac{-(\upsilon_S - \upsilon_B)}{kT}\right]^{-1},$$
$$\tau \approx 10^{-3}\ \mathrm{s} \tag{2}$$

is the relaxation time of the redistribution process of the interstitial atoms that escape the potential barrier υ_B at the $V \rightleftarrows S$ transitions.

The $\nu_V(t)$, $\nu_S(t)$ dependences are monotonic functions in accordance with Eq. (1). The investigation of Eq. (1) show that plots (Fig. 1) of $\nu_V(t)$ and $\nu_S(t)$ dependences have a greater rate of change if $\upsilon_V < \upsilon_S$ in comparison with the same if $\upsilon_V > \upsilon_S$. Therefore, from the curve slope one might suppose the value and the sign of energetic parameters υ_V, υ_S and the kind of this dependence (strong or weak) dictates the interaction character of AC, BC pairs.

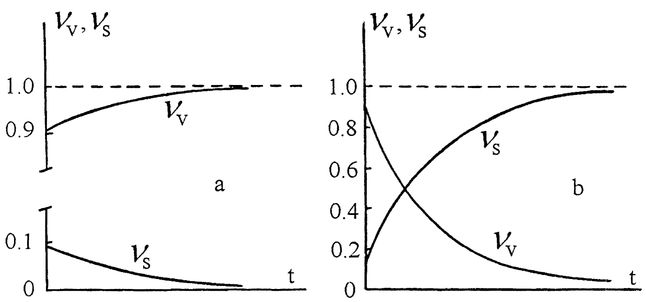

Fig. 1. Time dependence of concentrations of interstitial atoms in interstices of two types V, S in response to a sharp temperature decrease of metal thin film ($n=10$). (a) Attraction character of interacting forces of atomic pairs AC ($\upsilon_V > \upsilon_S$). (b) Repulsion character of interacting forces of atomic pairs AC ($\upsilon_V < \upsilon_S$).

3. Distribution of interstitial atoms at the interstices of three types

In certain cases, i.e. when the nodal plane (*111*) is the free face, the potential surface of the crystal lattice provides two types of surface interstitial sites S_1, S_2 with a different depth of the potential well (Fig. 2). Kinetic equations permit the establishing of the time dependence of the ν_V, ν_{S_1}, ν_{S_2} concentrations for the $V \rightleftarrows S_1$, $V \rightleftarrows S_2$, $S_1 \rightleftarrows S_2$ transitions and the extremal dependence of interstitial atoms concentrations $\nu_S(t)$ on time may be shown for interstitial sites with average depth of potential well (Fig. 3).

The extremal dependence of concentrations (Fig. 1) on time do not take place with a distribution of interstitial atoms only in interstitial sites of two types. Therefore, as a result of experiments the presence of a maximum at the dependence $\nu_S(t)$ suggests the distribution of interstitial atoms in interstitial sites of three types.

The equilibrium concentrations of interstitial atoms C, the rate or time of relaxation Eq. (2) of interstitial atoms redistribution are dependent on the a, b concentrations of A, B alloy components, on the long range order η in the A, B atoms distribution at the sites of crystal lattice and on the temperature T. These dependences may be elucidated if the dependences of υ_V, υ_S, υ_B energies on a, b, η, T can be determined.

In the particular cases: (1) $b=0$; (2) $b \ll 1$; (3) $\eta=0$;

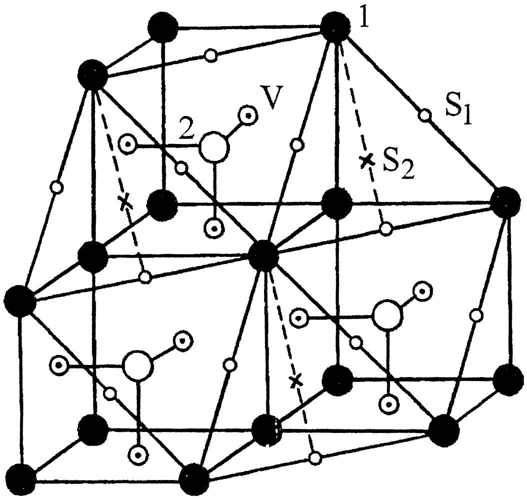

Fig. 2. Face (*111*) of crystal with b.c.c. structure and upper surface layer. ●, sites of first type; ○, sites of second type; ⊙, volume interstices *V*; ∘, ×, surface interstices S_1, S_2.

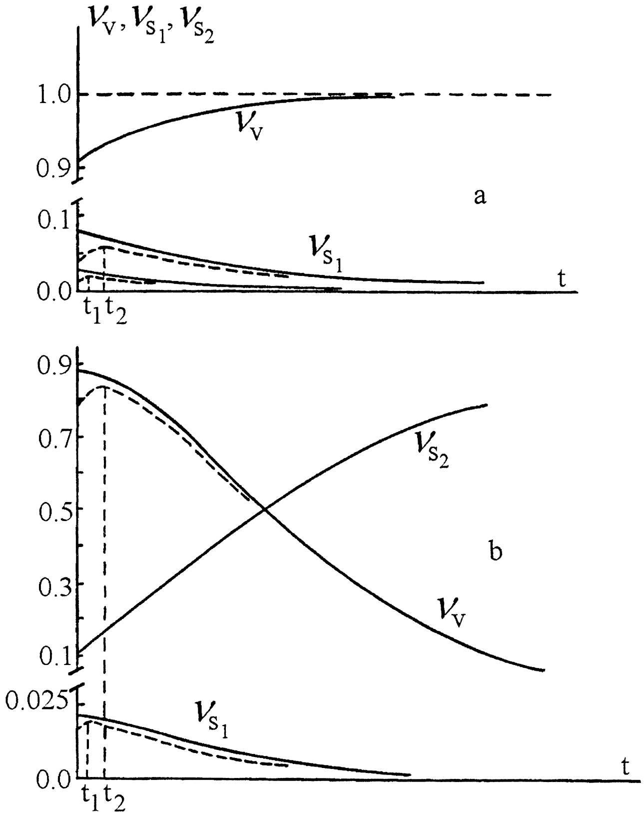

Fig. 3. Possible view of time dependences of interstitial atoms concentrations in interstices of three types V, S_1, S_2 in response to a sharp temperature decrease of metal thin film ($n = 10$). Dotted lines show these dependences in presence of maximum. (a) Interacting forces of atomic pairs AC have attraction nature ($v_V > v_{S_1} > v_{S_2}$). (b) Interacting forces of atomic pairs AC have repulsion nature ($v_V < v_{S_1} < v_{S_2}$).

(4) $\eta \ll 1$ the formulae for the relaxation time assume the forms

$$t^*_A = \frac{\tau}{4}\left(n \exp\frac{v_{AC}}{kT} + \exp\frac{v'_{AC}}{kT}\right)^{-1} \quad \text{if } b = 0, \tag{3}$$

$$t^* = t^*_A \left(1 + b\frac{n\alpha \exp\dfrac{v_{AC} + v'_{AC}}{kT} - \beta}{n \exp\dfrac{v_{AC} + v'_{AC}}{kT}}\right) \quad \text{if } b \ll 1, \tag{4}$$

$$t^*_o = \frac{\tau}{4}\left(n \exp\frac{av_{AC} + bv_{BC}}{kT} + \exp\frac{-av'_{AC} - bv'_{BC}}{kT}\right) \quad \text{if } \eta = 0, \tag{5}$$

$$t^* = t^*_o\left[1 - \frac{1}{2}\eta \frac{3n(\alpha - 2\beta)\exp\dfrac{av_{AC} + bv_{BC}}{kT} + (3\alpha - 7\beta)\exp\dfrac{-av'_{AC} - bv'_{BC}}{kT}}{n \exp\dfrac{av_{AC} + bv_{BC}}{kT} + \exp\dfrac{-av'_{AC} - bv'_{BC}}{kT}}\right] \quad \text{if } \eta \ll 1 \tag{6}$$

where

$$\alpha = (v_{AC} - v_{AC})/kT, \quad \beta = (v'_{AC} - v'_{BC})/kT \tag{7}$$

and the v_{AC}, v_{BC}, v'_{AC}, v'_{BC} are the interaction energies of atomic pairs AC, BC being correspondingly at the 0,5d and 0,7d distances, where d is the lattice parameter.

Formula (3) represents the relaxation time for the pure metal A. Formula (4) permits to ascertain the exerted influence of an impurity B to the metal A on the relaxation time and it follows from this dependence that the B impurity increases the time of relaxation and reduces the rate of redistribution of H atoms among the interstitial sites in the case of

$$n\alpha \exp\frac{v_{AC} + v'_{AC}}{kT} > \beta. \tag{8}$$

As appears from the above, doping and suitable selection of B component can change the relaxation time in the necessary direction.

Formula (5) defines the relaxation time of a disordered alloy AB of any composition. It follows from that formula that the dependence $t^*_o(a)$ can have a maximum at the composition

$$a^* = \frac{\left[\ln\dfrac{v'_{AC} - v'_{BC}}{n(v_{AC} - v_{BC})} - 1\right]}{\left(\dfrac{v_{AC} + v'_{AC}}{v_{BC} + v'_{BC}} - 1\right)}. \tag{9}$$

The knowledge of the energetic parameters for each specific disordered alloy gives the possibility of selecting the interval of concentrations with the most suitable value of the relaxation time that can permit either the acceleration or the slowing down of the redistribution process of the interstitial atoms C along the film interstices.

Formula (6) permits the obtaining of more specific information about the influence of the long range order on the redistribution process of interstitial atoms C. It follows from (6) that atomic order η decreases the relaxation time and, consequently, speeds up the process of redistribution of interstitial atoms C under the conditions

$$3n(\alpha - 2\beta)\exp\frac{a(v_{AC} + v'_{AC}) + b\,(v_{BC} + v'_{BC})}{kT} > 4\alpha - 7\beta. \tag{10}$$

Knowledge of the energy parameters and the temperature (that must be below the Kurnakov temperature) permits the estimation of the influence of order on the relaxation time.

Thus, if the values of energetic parameters for each alloy are known from independent experiments, for example, by the estimated values of the diffusion activation energies, then by means of formulae (3)–(6) one can predetermine the influence of composition, atomic order and temperature on the value of the equilibrium concentration of interstitial atoms and the relaxation time for the process of temperature redistribution of C atoms among the interstices in AB alloy. By suitable selection of alloy composition and specific atomic order in it (by means of thermal annealing), one can purposefully change the t^* value with a view to attain equilibrium quickly or, on the contrary, to freeze a definite non-equilibrium state. And that in turn will exert an influence equally upon the forming of one or another physical and chemical properties of the alloy. Theoretical results for equilibrium concentrations of interstitial atoms, for the kinetic curves (1) and for the relaxation time (3)–(6) have been compared with experimental data concerning the surface enrichment by hydrogen of Pd–H, Ti–H alloys and these alloys with impurity levels of Ag, Au, In, Mo, Co, Pt [1–7] and for the graphitization of Fe–C, Co–C, Ni–C alloys and an Fe–C alloy with the addition of Cr, V, Co, Ni, Ti metals [8]. The agreement of theory and experimental data has been satisfactory.

4. Conclusions

The comparison of theoretical and experimental plots for the volume concentration of carbon in Co–C, Fe–C, Ni–C demonstrate that the relationship between activation energies corresponds to data of independent experiments, i.e. $Q_{Ni} > Q_{Co} > Q_{Fe}$. In this case the values of activation energies are low in comparison with experiments [5–7], but our Q values are closer to experiment than in the paper [8].

Furthermore, as $Q_V < Q_{Cr} < Q_{Fe} < Q_{Ti} < Q_{Co} < Q_{Ni}$, then by our calculations V or Cr addition to Fe must decrease the surface concentration of carbon, but Ti, Co or Ni impurity must increase it. This conclusion is in complete agreement with experimental results: it is well known that addition of V or Cr to Fe inhibit and of Ti, Co or Ni to Fe accelerate the graphitization of FeMe–C alloys, where Me = H, Cr, Ti, Co, Ni [4].

The presented dependences for the equilibrium concentrations of impurity and the relaxation on time of redistribution of impurity atoms can be used for creation of polycrystalline films with resistant surface properties conserved in a wide temperature range.

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