OUTLINE OF THE MTCIP-1A THEORY OF INTERFACE SEGREGATION**

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Abstract

Large and increasing interest is shown for the description of the surface chemical composition, surface free energy and other surface characteristics of solids in view of their large practical importance. The problem, however, has not been solved so far even on a qualitative level. The new MTCIP-1A (Modern Thermodynamic Calculation of Interface Properties — First Approximation) method is shortly outlined and illustrated by results for an AuPd alloy.

1. Introduction

It is widely known now that the surface chemical composition of a phase in general differs from its bulk one. This difference was established experimentally first for liquids (Bain, 1939) and then for solids (Sachtler and Dorgelo, 1965). Since the surface composition as well as the surface free energy and other surface characteristics of solids are connected with important effects in catalysis, corrosion, microelectronic device performance etc., a large and ever increasing interest is shown for the theoretical and experimental investigations of these quantities.

As for the theoretical calculations: "the basic thermodynamic concept was derived more than a century ago by Gibbs . . . the major inconvenience of Gibbs' theory is that it cannot be correlated to experimental data, since it involves the surface energy of solids, which is largely unknown. Later theoretical or semiempirical approaches were generally focused on other aspects of this problem . . . in spite of considerable theoretical improvements during the last five years *the problem of quantitative description of segregation phenomena at a free surface has not been* solved so far" (de Rugy and Viefhaus, 1986).

The problem is not solved even on a qualitative level and not even for the dilute alloys. As it was shown (Lundberg, 1987) no prediction of the enriching component worked in all the 40 binary alloy free surface segregation problems investigated. The subject becomes even more problematic for not free surfaces with surface chemical bonds which differ from the bulk ones in important aspects (see e.g. in Pashutski et al., 1989).

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** Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

2. Basic problems connected with the thermodynamic calculation of solid surface properties

An attempt is made by the present authors for the solution of this problem. This approach is based on the solution of the following "sub-problems", which, in our opinion are the basic ones, hindering so far the theoretical description of solid surface composition:

1. *Present lack of a general thermodynamic theory of interfaces* as three-dimensional and vertically very strongly inhomogeneous objects (such a theory may be deduced only in relation with recent results in basic thermodynamics (Mezey, 1986; Mezey and Giber, 1989a).

2. The surface energy (more exactly: *the surface free energy*) *of solids is not adequately known* even for the polycrystalline solid chemical elements. This holds even more in regard to its temperature and orientational dependence (anisotropy).

3. The problem of *the description of the surface chemical bonds is* just under investigation and *not solved so far.*

4. *The quantitative description of real mixture (excess) properties is not solved for even the bulk case*, especially for the "strongly real" mixtures exhibiting phase transitions as a result of compositional changes (mixibility gaps).

5. In solids an *anomalously strong (or weak) diffusion* perpendicular to the surface, is observed, which e.g. may proceed 10^6—10^{10} times more quickly as in the bulk phase. This strongly nonlinear transport process has not been described so far either.

3. A short outline of the MTCIP-1A theory

Our attempt is leading now to a new, basically thermodynamic theory and method of calculation of the interface properties, termed as the MTCIP-1A (Modern Thermodynamic Calculation of Interface Properties, First Approximation). Its basic relation is given here for binary alloys:

$$\overline{\beta^1} = \frac{\overline{X^1}}{\overline{X^{(1)}}} = \overline{C}_m \overline{C}_n \overline{C}_b \overline{C}_r \tag{1}$$

Here X is the mole fraction of one of the two components, "1" refers to the topmost surface layer and (1) to the solid bulk phase; the bar is the sign of the thermodynamic equilibrium state (TES). The quantities $\overline{C}_j$ are the equilibrium factors of surface segregation:

$$\bar{C}_m(\text{mixing}) = \left(\frac{1-\overline{X^1}}{1-\overline{X^{(1)}}}\right)^{\bar{q}_2} \tag{2}$$

$$C_\mathrm{n}\,(\text{non-bonding}) = \exp\left[\frac{[(1-\bar{b}_1)\overline{\gamma_1^0} - (1-\bar{b}_2)\overline{\gamma_2^0}]\overline{\Phi_2^0}}{RT}\right] \tag{3}$$

$$C_\mathrm{b}\,(\text{bonding}) = \exp\left[\frac{q_2\bar{b}_1\overline{\alpha_1^0}G_1^\mathrm{e} - \bar{b}_2\overline{\alpha_2^0}G_2^\mathrm{e}}{RT}\right] \tag{4}$$

$$C_\mathrm{r}\,(\text{real mixture}) = \exp\left[\frac{\bar{q}_2\overline{\Delta\mu_1^\mathrm{e}(l)} - \overline{\Delta\mu_2^\mathrm{e}(l)}}{RT}\right] \tag{5}$$

Here $\bar{q}_2 = \overline{\Phi_2}/\overline{\Phi_1}$ is the quotient of the $\overline{\Phi_\mathrm{i}}$ partial molar surface areas of the components. The latter are taken to be equal to the pure component values $\overline{\Phi_\mathrm{i}^0}$, the $\bar{b}_\mathrm{i}$-s are the bonding parts of the component atoms in the surface (with e.g. the oxygen atoms of the gaseous phase). Presently these are estimated from the sign of the G_i^e-s (see below) with $\bar{b}_\mathrm{i} = 0$ if $G_\mathrm{i}^\mathrm{e} > 0$ and $\bar{b}_\mathrm{i} = 1$ if $G_\mathrm{i}^\mathrm{e} < 0$. The $\overline{\gamma_\mathrm{i}^0}$-s are the surface free energies of the components [8]. The $\overline{\alpha_\mathrm{i}^0}$-s are the so-called "surface coupling factors" (Mezey, 1986) which may be estimated (Mezey and Giber, 1989b) e.g. from the knowledge of the quotient of the nearest neighbours missing above the surface (in comparison with the bulk situation). The G_i^e-s are calculated from the molar free enthalpies of the chemical reactions at the surface (Mezey and Giber, 1989b). Finally, the $\Delta\mu_\mathrm{i}^\mathrm{e}(l)$-s account for the change of the lateral neighbours in the surface in comparison with the bulk situation.

While the first three equilibrium factors are already described now, the fourth one ($\overline{C_\mathrm{r}}$) is just planned to be described in the near future. Consequently, at present the description is limited to ideal binary mixtures, with, however, account for surface anisotropy influence on surface segregation.

4. Example: results for AuPd alloys

Recently calculations have been made for AuPd alloy (100) surfaces, with $X^{(1)}$ (Au) = 24.9 at %. For this alloy ISS (Ion Scattering Spectroscopy) experiments were made. It was found (Hetzendorf, 1987), that at $T = 773.2$ K and P_{O_2} (oxygen partial pressure) $= 5 \cdot 10^{-10}$ Pa, after 15 min of equilibration the surface Au content was 75 at %, with a starting value (after sputtering to $t = 0$) 29 at %. On the other hand, at $T = 298.2$ K and $P_{\mathrm{O}_2} = 5 \cdot 10^{-5}$ Pa the surface Au content was just 26 at % (with the same starting value). In *the first case*, then, *Au enrichment* while *in the second Au impoverishment* was found. Furthermore, experiments have shown no surface bonding with O_2 in the first case for Pd and Au, while in the second one the surface Pd was found mostly bonded with O_2 (while the Au was bonded at most in a small part).

The theoretical calculations (Mezey et al., 1989a, b) led to 66 at% Au in the 773.2 K case while to 0 at% Au in the 298.2 K case for the TES. The difference is explained by the calculations showing no oxidizing effect for Au and Pd in the first, while a strong oxidizing effect for Pd and no such effect for Au in the second case. The factors $\bar{C}_m$ and $\bar{C}_n$, acting alone would lead to strong Au enrichment in both cases (with 95 at% Au in the first and 99 at% Au in the second case). The inclusion of the factor $\bar{C}_b$ in the description leads to the compositions mentioned before.

As far as we know it, the present calculation is the first attempt to describe surface segregation anisotropy together with the surface chemical bonding effect.

5. Discussion

The qualitative agreement between the experiment and theory (surface Au enrichment in the first and surface Pd enrichment in the second case) may be improved by considering also *the C_r term* and *the effect of diffusion*, perpendicular to the surface.

The real mixture effect leads to an increased Au segregation in both cases, since Au is solved in Pd only to a limited extent, the Pd lattice is driving out the Au. This effect would lead to larger TES Au contents in both cases, however, in the second one it is totally counteracted by the oxidational effect.

The diffusional problem is best treated in a first approximation by the use of Fick's Law, and then, in a much better second one by the use of the Governing Principle of Dissipative Processes (GPDP) (Gyarmati, 1970; Verhás 1985) finally, in a third one by also considering the Thermodynamic Wave Theory TWT (Gyarmati, 1970; Verhás 1985) of Gyarmati. The GPDP gives a general theoretical possibility of description of (even very strongly) non-linear Transport processes (Verhás 1985) while the TWT further helps for more concrete characterizations. Such a work is planned to be done in the near future.

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