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SEGREGATION TO SURFACES AND INTERFACES

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Abstract

The thermodynamics of segregation to surfaces and interfaces establish a framework of solute enrichment behaviour at equilibrium, depending on temperature and bulk concentration. It is represented by the Langmuir-McLean adsorption theory and its modifications. Solute-solute interactions in binary and multi-component systems allow a description of the occurrence of two-dimensional phases, of site competition of segregants and of cosegregation. The kinetics of segregation are mainly governed by the bulk diffusivity of the solute. Calculations of the segregation free energy based on surface energy differences of the components and on strain relief energy serve as a guideline for predictions of enrichment in binary systems and for the influence of surface orientation. Results of computer modelling of the atomistics of grain boundary segregation show the occurrence of specific interface sites corresponding to a spectrum of segregation energies, which help to understand the experimental evidence of segregation anisotropy. Similar conclusions are obtained from molecular orbital cluster calculations which disclose the chemical bond strength and its dependence on the segregant and the structural configuration. The importance of segregation to materials properties is explained for grain boundary cohesion and diffusion.

KEY WORDS: Segregation Surfaces, Interfaces, Grain Boundaries, Surface Energy, Strain Energy, Orientation Dependence, Solute-Solute Interactions, Site Competition, Cosegregation, Grain Boundary Cohesion, Grain Boundary Diffusion.

Introduction

The chemical composition of surfaces and interfaces is responsible for a large number of materials properties. To name only a few, the free surface composition affects adhesion, oxidation, catalysis, sintering etc. whereas grain boundary composition is decisive for temper embrittlement, intergranular corrosion and stress corrosion cracking, creep rupture, hydrogen embrittlement, recrystallization behaviour etc. The interfacial composition generally differs from the bulk composition, a phenomenon, which is commonly called segregation. Whereas concentration gradients may build up by a variety of mechanisms, we will restrict our consideration here to thermodynamic equilibrium. This implies its reversibility and its distinction from non-equilibrium segregation as encountered in casting of alloys and in the dragging of solutes by vacancies to interfaces during quenching and other kinetic processes.

Equilibrium segregation to surfaces and interfaces describes a redistribution of solutes governed by the minimization of the total free energy of the systems bulk+surface or bulk+interface. With the availability of powerful surface- and microanalysis techniques such as Auger and photoelectron spectroscopy (AES, UPS and XPS), field ion microscopy with time-of-flight mass spectrometry (FIM-atom probe) and scanning transmission electron microscopy (STEM) with X-ray analysis, to mention the most important ones, the direct analysis of surface and interface composition has become accessible, which is reflected in the increase in experimental work during the past decade (Seah 1980a, 1983a, b). Today, the fundamentals of equilibrium segregation are well understood and can be rationalized by a general theoretical framework.

A number of excellent reviews on the subject have appeared in recent years (see, e.g., Abraham and Brundle 1981, Johnson and Blakely 1979, Seah 1980 a,b, Hondros and Seah 1983). The attempt here is not to reiterate the details of experiment and theoretical work, but to summarize the main results under generalized aspects and to emphasize current research activities and prospects for further research on hitherto unsolved problems. After a brief introduction to basic

phenomena and their theoretical understanding, some predictions are discussed in the light of recent experimental and theoretical studies.

Thermodynamic Description of Equilibrium Segregation

The common fundamental aspect of segregation is the attainment of thermodynamic equilibrium between the bulk of a solid and a planar structural defect such as a free surface, grain boundary, stacking fault or interphase boundary (we will not consider here solute-vacancy and solute-dislocation interactions which can be treated by similar formalisms).

The difference of the free energy (or chemical potential) of foreign atoms at the planar structural inhomogeneity and in the homogeneous medium adjacent to it is the driving force of segregation. Thus, surface adsorption and segregation differ only with respect to the reference reservoir of the segregant and can be treated formally in a similar manner using well established adsorption theories. (Hondros and Seah 1977a, Lea and Seah 1977). This is also valid for grain boundary segregation taking into account the physical differences between surfaces and internal interfaces (Seah and Hondros 1973). Therefore we may use the same equations for a phenomenological description of adsorption, surface and interface segregation. However, as we will see, the specific parameters, segregation enthalpy and -entropy can only be derived by atomistic models of the structure and the type of interactions present in the respective case.

Many efforts have been made to establish theories of segregation. Conventional or statistical thermodynamics have been applied treating the system as ideal, regular or real solution. Only a brief outline of the most important of these approaches will be given here. For a more extended treatment, the reader is referred to recent reviews (e. g., Wynblatt and Ku 1979, Hondros and Seah 1983).

Gibbs' Equation

The first approach connecting surface free energy with the chemical composition was given by W. Gibbs and modified by Guggenheim (1950). A solute which lowers the surface free energy γ will be enriched at the surface according to the relation:

$$\Gamma_i = - \frac{1}{RT} \cdot \left(\frac{d\gamma}{d \ln X_i} \right)_T \quad (1)$$

where X_i is the molar fraction of the solute in the bulk and Γ_i (in mole/area) is the "surface excess" of the solute with respect to its bulk concentration. Equation (1) is the appropriate form of Gibbs adsorption equation for a dilute binary system, which is applicable to all types of interfaces. However, due to the difficulty in measuring the surface energy as a function of composition and temperature, only a few results have been reported applying the Gibbs approach. Stimulated by the development of modern surface analysis techniques which are able to measure the

surface concentration of a solute directly related to the surface excess quantity in eq. (1) (Hondros and Seah 1983), there have been many attempts to develop alternative descriptions of segregation by adoption of adsorption isotherms and by statistical thermodynamic models. In general, all types of adsorption analogue theories can be used, as shown by Hondros and Seah (1977a), e. g., Langmuir, Tempkin, Freundlich, Brunauer-Emmett-Teller (BET). Conceptually, the partition of solute atoms between two states (bulk and interface) of different free energies may be thought to follow a Boltzmann distribution. However, due to the assumed fixed number of sites in both states, a Fermi-like distribution equilibrium is obtained, which is expressed in the so-called Langmuir-McLean segregation isotherm.

The Langmuir-McLean Equation

The most simple model of monolayer adsorption has been proposed by Langmuir assuming a fixed number of adsorption sites, which are energetically identical, and no interaction between the adsorbed atoms. The adsorption rate is then proportional to the partial pressure P , the number of unoccupied sites $n \cdot (1-\theta)$ at the surface, and the desorption rate is proportional to the occupied sites $n \cdot \theta$ with θ the coverage in fractions of a monolayer. In equilibrium, $P \cdot (1-\theta) = K \cdot \theta$ where K is the equilibrium constant, which gives:

$$\frac{\theta}{1-\theta} = K \cdot P \quad (2)$$

With P replaced by the bulk concentration X_c (for ideal solution) and θ by the relative coverage X_b/X_b^0 , eq. (2) corresponds to the dilute approximation of the equation of McLean (1957) which was originally derived for grain boundary segregation but is also valid for surface segregation. Adopting the notations of Seah (1980a), the Langmuir-McLean equation can be written:

$$\frac{X_b}{X_b^0 - X_b} = \frac{X_c}{1 - X_c} \cdot \exp\left(-\frac{\Delta G}{RT}\right) \quad (3)$$

where X_b^0 is the fraction of the surface or interface layer covered with the segregant at saturation, X_b is the fraction actually covered, X_c is the bulk molar fraction and ΔG is the free (molar) energy of segregation which is negative if enrichment occurs. $\Delta G = \Delta H - T \cdot \Delta S$ with ΔH the segregation enthalpy and ΔS the segregation entropy. The latter does not contain the configuration entropy but includes vibrational and anharmonic terms.

Eq. (3) is the basis of many extensions, modifications and analogous treatments, which differ mainly in the functional dependencies of ΔG on interaction parameters between the segregated atoms.

Eq. (3) allows the determination of the segregation enthalpy ΔH and -entropy ΔS by measuring the surface concentration as a function of temperature for different bulk concentrations.

Ideal Langmuir-McLean behaviour has been frequently observed, for example for surface segregation of C on Fe (100) (Grabke et al. 1977), O on Nb (Joshi and Strongin 1974, Hofmann et al. 1976), S on Cu (Frech and Hofmann 1985) and for grain boundary segregation of S in Cu (Moya and Moya-Gontier 1975) and P in Fe (Erhart and Grabke 1981, see Fig. 2).

The Langmuir-McLean model in its original form assumes constant ΔG over the interface independent of the interface coverage below one monolayer. Therefore it is strictly valid only for single crystalline surfaces. If several sites are requested for the adsorption of a solute, appropriate modifications have been developed (Hondros and Seah 1977a, Hofmann and Erlewein 1978). For the description of multilayer segregation, the BET adsorption analogue has been used (Seah and Hondros 1973).

The BET Adsorption Equation

By applying the multilayer gas adsorption theory of Brunauer, Emmett and Teller (BET), Seah and Hondros (1973) were able to explain their results of surface and grain boundary segregation of Sn in Fe. The solid state analogue of the truncated BET theory may be written as (Seah and Hondros 1973):

$$\frac{X_b}{X_b^0 - X_b} = \frac{X_c}{X_c^0} \cdot \exp\left(\frac{-\Delta G}{RT}\right) \quad (4)$$

where X_c^0 is the solubility limit in the bulk. Compared with the Langmuir-McLean equation (3) for $X_c \ll 1$ and with $X_c^0 = \exp(\Delta G_{sol}/RT)$, where ΔG_{sol} is the free energy of precipitation, it is

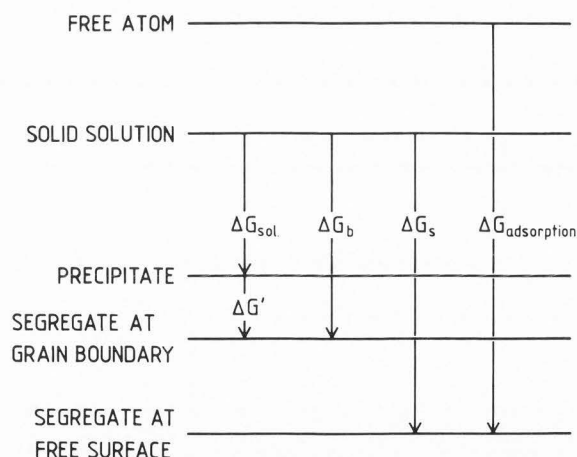


Fig. 1

Schematic diagram showing the relation between free energy of adsorption (ΔG_{ad}), surface (ΔG_s) and grain boundary (ΔG_b) segregation and solubility (ΔG_{sol}), after Hondros and Seah (1983).

seen that $\Delta G = \Delta G' + \Delta G_{sol}$. The relations between the different free energies of adsorption, surface and grain boundary segregation and solution are schematically shown in Fig. 1. The main advantage of the BET equation (4) is that, in the dilute limit, an enrichment factor $X_b/X_c = \beta = \exp(-\Delta G/RT)/X_c^0$ can be defined which relates β to X_c^0 . Since empirically, $\Delta G'$ is about 10 ± 6 kcal/mole, eq. (4) allows a prediction of enrichment ratios (within an order of magnitude) for surfaces and grain boundaries with the solubility taken from binary phase diagrams (Seah and Hondros 1973). An interesting feature of the BET analogue is that it tentatively implies the alteration of the enrichment level by changing the solubility limit, for example by addition of a third species, as discussed by Guttman and McLean (1979). Recent studies of Sn segregation on Fe (100) surfaces by Zhou (1983) and by Hennessen et al. (1984) show that a two dimensional phase at 1.5 monolayers of Sn is formed, pointing out the importance of structural features not covered by the BET model.

The Fowler Isotherm

Interaction of segregating atoms often is the cause of strong deviations from the ideal Langmuir-McLean behaviour at higher segregation levels. This is described by the analogue to the Fowler and Guggenheim (1939) adsorption equation. It can be obtained by introducing an interaction term ω which is proportional to the amount of the segregation X_b , i. e., by replacing in eq. (3) $\Delta G = \Delta G^0 + 2Z_1\omega \cdot X_b/X_b^0$ which gives for $X_c \ll 1$:

$$\frac{X_b}{X_b^0 - X_b} = X_c^0 \cdot \exp\left(\frac{-\Delta G^0 - 2Z_1\omega(X_b/X_b^0)}{RT}\right) \quad (5)$$

where ΔG^0 does not depend on the segregation level, Z_1 is the number of nearest neighbours in the segregation layer (lateral coordination number) and ω is the interaction energy. (For free surfaces, $2\omega = -\epsilon_{AA}$, the pair bonding interaction energy of A atoms). Eq. (5) is identical to the McLean equation (3) for $\omega = 0$ (no mutual interaction). $\omega < 0$ means attractive interaction and increases the apparent segregation free energy (note that ΔG^0 is negative) with the segregation level. This steepens the isotherms with respect to the ideal McLean behaviour, with a discontinuous behaviour obtained for $-2Z_1\omega/RT > 4$. A plot of X_b as a function of $X_c \cdot \exp(-\Delta G^0/RT)$ according to Hondros and Seah (1977a) is shown in Fig. 2, which includes the results of Pichard et al. (1975) of grain boundary segregation as a function of the bulk concentration of Te and of Se in pure Fe at 1073 K with $2Z_1\omega/RT = -2.5$ and -4 , respectively, if analyzed by eq. (5). It can easily be shown, that at constant X_c , the temperature dependence of X_b after eq. (5) also leads to a discontinuity for a large interaction term. For surface segregation of C on Ni (111), such a behaviour has been obtained by Shelton et al. (1974), which is consistent with the establishment of new two-dimensional surface phases, as dis-

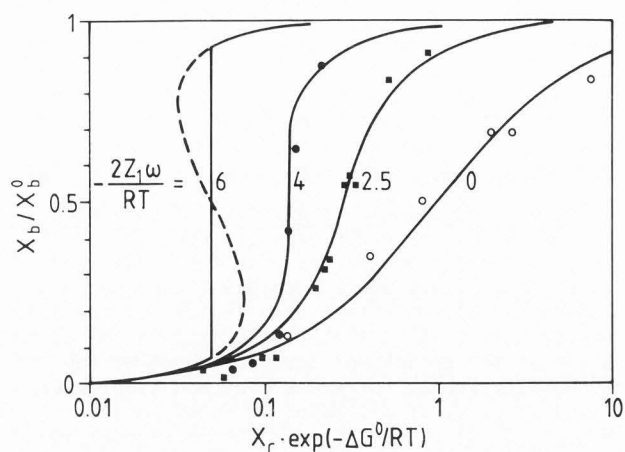


Fig. 2

Fowler isotherm plot for grain boundary segregation after Hondros and Seah (1977a) with the interaction term $-2Z_1\omega/RT$ as a parameter. Experimental data are for Se (●) and Te (■) in iron from Pichard et al. (1975), and for P (○) in iron from Erhart and Grabke (1981), the latter showing ideal Langmuir-McLean behaviour ($-2Z_1\omega/RT=0$).

cussed by Guttman (1977) and by Blakely and Thapliyal (1979). On the other hand, ideal McLean behaviour for vanishing segregant interaction has been found in many surface and grain boundary segregation studies. For example, the results of grain boundary segregation of P in pure Fe by Erhart and Grabke (1981) plotted in Fig. 2 correspond to $\omega = 0$.

Segregation in Multicomponent Systems

In systems with two or more solutes the latter will compete for the available interface sites, and, depending on the type and magnitude of interactions, rather complex segregation behaviour may result as extensively discussed by Guttman and McLean (1979). If there is no interaction between the segregants, the Langmuir-McLean equation can simply be modified to include the site competition (Gupta and Peraillon 1981). For a ternary system with solutes 1 and 2, the McLean analogue are the pair of equations:

$$\frac{X_{b1}}{X_b^0 - X_{b1} - X_{b2}} = \frac{X_{c1}}{1 - X_{c1} - X_{c2}} \cdot \exp\left(-\frac{\Delta G_1}{RT}\right) \quad (6a)$$

$$\frac{X_{b2}}{X_b^0 - X_{b1} - X_{b2}} = \frac{X_{c2}}{1 - X_{c1} - X_{c2}} \cdot \exp\left(-\frac{\Delta G_2}{RT}\right) \quad (6b)$$

For a fixed number of segregation sites, the amount of possible segregation of species 1 is reduced by the segregation of species 2 and vice versa. Thus, a strong segregant - even a low bulk concentration - can completely expel a weaker segregation solute from the interface. This has

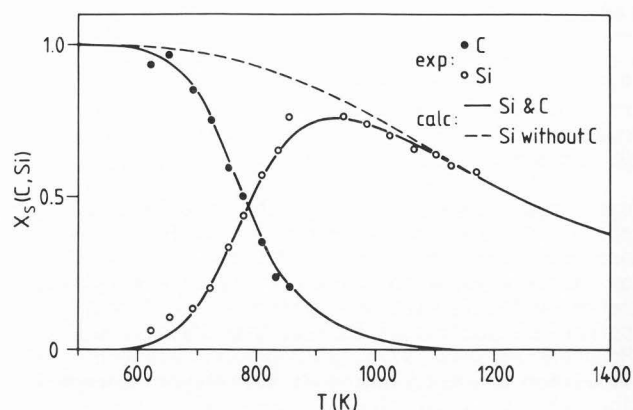


Fig. 3

Site competition of C and Si during surface segregation at (100) Fe-3% Si, after de Rugy (1982). Calculations according to eqns. (6a,b).

been shown recently by de Rugy (1982) for the segregation of C and Si at the (100) surface of an Fe-3% Si alloy. The general behaviour is depicted in Fig. 3. The dashed line is for the ideal McLean type segregation of Si if no C is present. Due to the higher segregation enthalpy of carbon (~ -141 kJ/mole as compared to Si (~ -48 kJ/mole)), even for a C bulk concentration below 20 ppm the segregation of C completely impedes that of Si at lower temperatures.

Site competition in grain boundary segregation has been reported by Tauber and Grabke (1978) for S and N in Fe, by Erhart and Grabke (1981) for C and P in Fe and recently by Hofmann and Hofmann (1984) for C and P in W (Ni, Fe). Simple site competition behaviour is easily recognized from the relation:

$$X_{b1} = X_{b1}^* \cdot (1 - X_{b2}) \quad (7)$$

where X_b and X_b^* denote the interfacial concentration with and without enrichment of the other solute, respectively. In Fig. 4, results of observed site competitive segregation are plotted according to relation (7).

The importance of site competition in practice is that in equilibrium the segregation level of one solute is strongly dependent on that of the other with higher segregation energy. As shown by Erhart and Grabke (1981), addition of Cr to an Fe-P-C alloy reduces the active C bulk concentration by formation of carbides and consequently enhances the P segregation.

If an interaction between two cosegregating species occurs, the free segregation energies ΔG_1 , ΔG_2 in eq. (6) will depend on X_b . Guttman (1975) has developed an extension of the Fowler isotherm by introducing an additional interaction term. In the dilute limit ($X_c \ll X_b$), ΔG_1 and ΔG_2 in the coupled equations (6a,b) are given by:

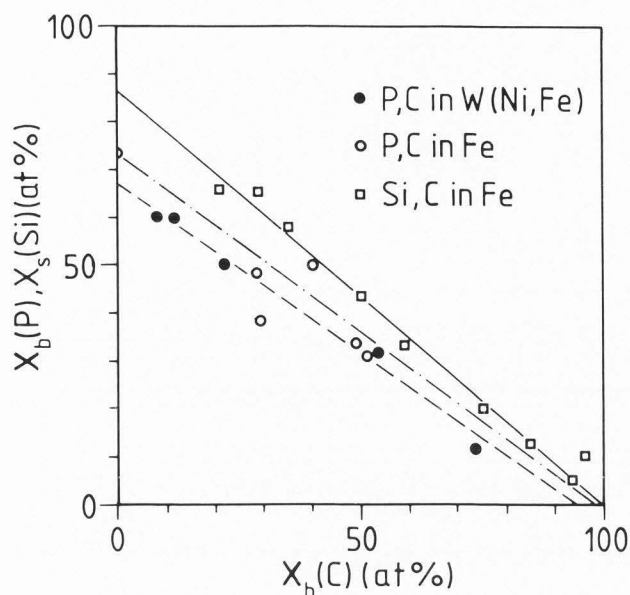


Fig. 4

Site competition for grain boundary segregation of P and C in W(Ni,Fe) (Hofmann and Hofmann 1984) and in pure Fe (Erhart and Grabke 1981) and for surface segregation of Si and C on (100) Fe-3 % Si (de Rugy 1982).

$$\Delta G_1 = \Delta G_1^0 + \alpha_{12}' \cdot X_{b2} \quad (8a)$$

$$\Delta G_2 = \Delta G_2^0 + \alpha_{12}' \cdot X_{b1} \quad (8b)$$

where ΔG_1^0 , ΔG_2^0 are the segregation free energies of each solute without interaction. The relative binary pair interaction coefficients α_{12}' are proportional to the net reduction in energy when a pair of the interacting solutes (1,2) forms with respect to their bonding to the matrix (3):

$\alpha_{12}' = \alpha_{12} - \alpha_{13} - \alpha_{23}$. The coefficients α_{ij} are taken from the standard molar enthalpies of formation of the respective binary compounds or from solid solubility data (Guttman 1976).

From eqns. (6) - (8) it is obvious that negative values of α_{12}' , that means - according to the notation used here - attractive interaction of the segregating species, lead to a synergistic cosegregation in terms of mutual enhancement. Indeed the general behaviour resembles that shown in Fig. 2 for the Fowler relation of self-attraction of one solute. Again here, for sufficiently high attraction, S shaped curves may be obtained resulting in a discontinuous increase of the segregation level when the bulk content is continuously increased, indicating the formation of two dimensional phases. As pointed out by Seah (1980b), the site competition in the denominator of eqns. (6a,b) may be removed if for example interstitial and substitutional solutes cosegregate which are bound to different sites. More complex extensions of the interactive segregation theory have been given by Guttman and McLean (1979).

Evidence for synergistic cosegregation at surfaces of α -Fe was reported by Dumoulin and Guttman (1980), and the Guttman theory has been successfully applied in the description of grain boundary segregation in alloy steels (McMahon 1980, Gas et al. 1982). Recently its validity was also demonstrated for grain boundary segregation in Ni, Fe activated sintered W with P, O, C as impurities (Hofmann and Hofmann 1984).

In the case of very strong interaction of solutes, a scavenging effect may result by bulk compound formation, i.e., a lowering of the bulk activity (X_C in eq. 6) which decreases enrichment. Erhart and Grabke (1981) have shown for Fe-Ni-P alloys that increasing Ni contents lower the amount of P segregation, which can be explained by a reduced P bulk activity through the scavenging of P by Ni in the bulk. Well known examples of this effect are also the impediment of S segregation by Mn in steels and also by La, Zr and Hf in Ni (Johnson et al. 1974).

For Fe-P-C alloys, Erhart and Grabke (1981) have shown that enhanced P segregation by addition of Cr cannot be explained with a Cr-P interaction after Guttman, but rather with site competition of P with C which is influenced by scavenging of C in chromium carbides. It should be noted here, that Guttman's theory refers to interaction terms which are deduced from bulk properties of binary systems, but it is questionable whether interaction at interfaces occurs in a similar manner as in the bulk.

For $\alpha_{12}' = 0$, the Guttman equation reduces to the simple site competition of segregants. For repulsive interaction ($\alpha_{12}' > 0$), the segregation level of both species may be reduced. Depending further on the bulk concentrations and the values of ΔG^0 , total desegregation of one species may occur. In general, site competition, bulk and interface interaction has to be considered which may lead to a rather complicated segregation pattern in multicomponent systems (McMahon and Marchut 1978, Guttman and McLean 1979).

Although the thermodynamic approaches give a framework of the generally expected behaviour of a system in terms of concentration and temperature, it is obvious that a detailed description of real systems should include atomistic aspects of bonding with respect to structural factors and two dimensional phase formation (Blakely and Thapliyal (1979).

Kinetics of Segregation

Transport of a solute to a surface or interface is governed by bulk diffusion. The kinetics of grain boundary segregation have first been described by McLean (1957) applying Fick's laws for diffusion of the solute from two half crystals to the boundary. Assuming a constant enrichment ratio β of the interface concentration X_b to that of the bulk layer adjacent to it, X_C (which is independent of the actual X_C and $X_b(t)$ values) this model gives:

$$\frac{X_b(t) - X_b(0)}{X_b(\infty) - X_b(0)} = 1 - \exp(p^2) \cdot [1 - \text{erf}(p)] \quad (9)$$

where $X_b(0)$ is the interface concentration at the

start ($t = 0$), $X_b(\infty)$ the final (equilibrium) and $X_b(t)$ the actual one at time t . The parameter p is defined by

$$p = \frac{1}{\beta \cdot d} \cdot (f \cdot D \cdot t)^{1/2} \quad (10)$$

where D is the bulk diffusivity and d the thickness of the boundary. The factor $f = 2$ for free surfaces and $f = 4$ for grain boundaries, since for the latter the solute flux comes from both sides.

Within the concept of eq. (9), $\beta \cdot d$ is given by the ratio of the number of solutes per unit area of the interface to the number of solutes per unit volume in the bulk. According to Seah (1980a) $d = a$ should be better replaced by a^3/b^2 where a and b are the matrix and solute atomic sizes, respectively.

For short times (i. e., small $X_b(t)$), the series development of eq. (9) shows that, together with eq. (10) the solution is approximated by:

$$\frac{X_b(t) - X_b(0)}{X_b(\infty) - X_b(0)} = \frac{2}{\pi^{1/2}} \cdot p = \frac{2}{d \cdot \beta} \cdot \left(\frac{f \cdot D \cdot t}{\pi} \right)^{1/2} \quad (11)$$

This corresponds to an ideal sink behaviour of the interface for the solutes. The McLean segregation kinetics model was modified by Lea and Seah (1977) considering the change in β during segregation and a detailed analysis was given by Rowlands and Woodruff (1979). With these modifications for the final level near saturation, it is concluded that eq. (11) may be valid up to saturation ($X_b(\infty)$), as shown in the surface segregation kinetics of Sn on Cu (110) by Hofmann and Erlewein (1976, 1978). In general, McLean's equation (9) and the ideal sink solution (11) establish the limiting cases with real binary systems lying in between. This is shown in Fig. 5, where eqns. (11) and (9) are plotted together with experimental results of surface segregation kinetics of S on Cu (Frech and Hofmann 1985). The use of eq. (11) for the determination of bulk diffusivity from surface segregation kinetics was shown for Sn on Cu by Hofmann and Erlewein (1976), for O in Nb by Kirchheim and Hofmann (1979) and recently for Sn on Fe by Hennessen et al. (1984). In the dilute limit with $X_b(0) \approx 0$ and $X_b(\infty)/\beta = X_C$, eq. (11) can be used for trace analysis of X_C in the ppm range as shown for S in Cu (Hofmann and Frech, 1985). An extension of segregation to ternary systems was given by Tyson (1978) incorporating Guttman's theory of solute interaction. His numerical calculations show that considerable deviations from eqns. (8) and (11) may occur, depending mainly on the ratio D/β^2 of the two segregants. Applications of the segregation kinetics allows a conclusive analysis of temper embrittlement in steels (Seah 1977). Surface segregation kinetics are altered if evaporation of the segregant occurs (Lea and Seah 1977, Seah and Lea 1975).

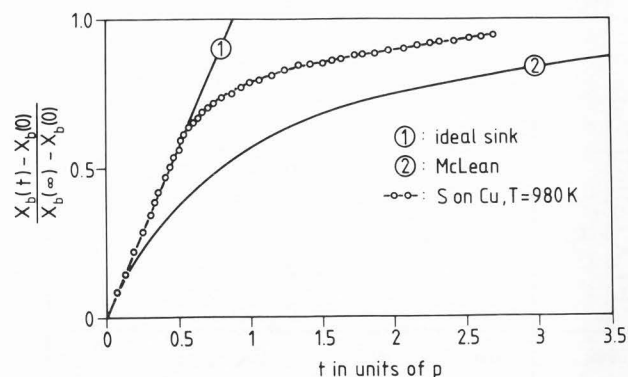


Fig. 5

Plot of segregation kinetics after eq. (11) (ideal sink behaviour) and eq. (9) (McLean equation). Data are for surface segregation of S on Cu (Frech, 1983).

Model Predictions of Segregation Parameters

Segregation Enthalpy

There have been many attempts to predict interfacial segregation enthalpies ΔH on the basis of empirical and semi-empirical models which have often shown remarkable agreement with experimental data.

The first approach of McLean (1957) predicted ΔH by taking it as a measure of the relief of strain energy associated with a substitutional solute atom in a solid solution, due to the difference in atomic volume between solute A and solvent B. Using continuum elastic theory, he derived

$$\Delta H = E_{el} = - \frac{24\pi \cdot K \cdot G \cdot r_B \cdot r_A (r_A - r_B)^2}{3Kr_A + 4Gr_B} \quad (12)$$

where K is the bulk modulus of the solute, G is the shear modulus of the solvent, and r_B and r_A are the appropriate radii of solvent and solute, respectively. Predictions were generally correct within a factor of two, indicating that other terms are also important for ΔH .

An empirical approach to derive segregation parameters from binary alloy data was introduced by Lücke and Stüwe (1963). Regarding the grain boundary as having a liquid-like distorted structure, they proposed to take the liquid/solid distribution coefficient $k = (dX_{liq}/dT)/(dX_{sol}/dT)$ at the melting temperature T_m in a dilute binary system. At low solute contents, k as determined from binary phase diagrams can be taken as the analogue for the interface enrichment term X_b/X_C , which in the dilute approximation of the McLean equation (3) (and neglecting the entropy term) gives

$$\Delta H = RT_m \cdot \ln k \quad (13)$$

Stüwe and Jäger (1976) and Burton and Machlin (1976) have shown that predictions from eq. (13) for surface segregation are at least qualitatively

in agreement with the majority of experimental data. However, the exact determination of k in the limit $X_C \rightarrow 0$ is difficult because k varies strongly with X_C .

Using the BET analogue of gas adsorption, Seah and Hondros (1973) showed for grain boundary segregation the proportionality between the inverse of the solubility limit X_C^0 and the enrichment factor β , from which ΔH can be deduced (cf. eq. (4) and Fig. 1). Other predictive models for surface segregation in binary alloys are based on the difference in surface energy of pure solute and solvent (Somorjai and Overbury 1975), as evident from the Gibbs formalism. Miedema (1978) describes ΔH in terms of surface energy differences, heat of solution and elastic size mismatch energy. Electronic theories of surface segregation in binary alloys as developed in recent years are physically preferable, but are still in a rather limited stage with respect to generalized quantitative predictions (Balseiro et al. 1980, Barnett et al. 1983, Kirschner 1985). The broken-bond model of Williams and Nason (1974) as modified by Wynblatt and Ku (1977, 1979) has been shown rather successful in predicting surface segregation free energies and will be briefly outlined below.

In this model, the two main factors contributing to the driving force for segregation are interface bond alteration and elastic strain energy relief, which may be modified by an electron density relaxation term. The segregation enthalpy is then expressed as a sum of a "chemical" and an "elastic" term:

$$\Delta H = \Delta H_{\text{chem.}} + \Delta H_{\text{el.}} \quad (14)$$

The current theoretical approaches differ mainly in the details of the derivation of the two factors in terms of accessible thermodynamic and elastic parameters and the used approximations (e.g., ideal or regular solution, dilute or non-dilute case). More recently, models based on computer simulation of grain boundary structure and of quantum mechanics treatment of the alteration of the electronic local density of states have been developed to predict the propensity of segregation and bonding modification for different solutes in grain boundaries, which will be briefly discussed below.

A derivation of the quasicheical interaction enthalpy ΔH_{chem} can be derived by the broken bond approach of Williams and Nason (1974) for surface segregation using the common pair interaction terms of nearest neighbours ϵ_{AA} , ϵ_{BB} and ϵ_{AB} in an A-B alloy. Wynblatt and Ku (1977, 1979) have extended this approach to rationalize segregation enthalpy and -entropy in terms of thermodynamic parameters of the pure constituents and its compounds for the surface segregation of alloys. According to them, the total energy of the system surface and bulk can be calculated considering the pair bond energies and taking into account the molar fractions X_A , $X_B = 1 - X_A$ and the number of bonds in the respective structural configuration. Segregation then consists in the exchange of A and B atoms in the surface layer with respect

to the bulk (for substitutional alloys). An atom in a bulk cubic structure has Z bonds to nearest neighbours (i. e. the coordination number), which can be divided into lateral bonds Z_l in a plane parallel to the surface and $2 \cdot Z_v$ in the both remaining directions with components in directions perpendicular to the surface. Bringing an A atom to the surface (i. e. segregation of A) means cutting off the Z_v bonds with respect to a bulk site and changing the lateral bonds from the bulk (X_A) to the surface (X_A^S). Replacing the pair interaction by the surface energy of the components i , $Z_v \cdot \epsilon_{ii}/2 = \gamma_i \sigma$ with σ the surface area per atom for the alloy, the chemical term in eq. (14) is given by

$$\Delta H_{\text{chem}} = (\gamma_A - \gamma_B) \cdot \sigma + 2 \cdot \Omega \cdot [Z_l (X_A - X_A^S) - Z_v \cdot (X_A - \frac{1}{2})] \quad (15)$$

where the second term contains the regular solution parameter $\Omega = \Delta H_m / (Z \cdot X_A \cdot X_B)$ with ΔH_m the enthalpy of mixing (Hultgren et al. 1973) and γ_A , γ_B are the surface energies of the pure components. They can be expressed by (Williams and Nason 1974):

$$\gamma_i \cdot \sigma = \frac{Z_v}{Z} \cdot H_i^{\text{sub}} \quad (16)$$

where H_i^{sub} is the sublimation enthalpy of i . The factor Z_v/Z , the ratio of the broken bonds at the surface to the total bonds in the bulk, contains the orientation dependence. According to Wynblatt and Ku, for an average surface orientation the surface energy term can be approximated by the empirically confirmed relation

$$(\gamma_A - \gamma_B) \cdot \sigma_B = 0.75 (H_A^{\text{sub}} \cdot \sigma_B / \sigma_A - H_B^{\text{sub}}) \quad (17)$$

Adding the strain energy term of eq. (12) gives for the total segregation enthalpy:

$$\Delta H = (\gamma_A - \gamma_B) \cdot \sigma + \frac{2\Delta H_m}{Z \cdot X_A (1 - X_A)} \cdot Z_l (X_A - X_A^S) + Z_v (X_A - \frac{1}{2}) - \frac{29 \cdot \pi \cdot K \cdot G \cdot r_B \cdot r_A (r_A - r_B)^2}{3 \cdot K \cdot r_A + 4 \cdot G \cdot r_B} \quad (18)$$

On the basis of eqns. (17) and (18), Wynblatt and Ku (1979) have calculated the segregation enthalpies for 20 substitutional alloys showing reasonable agreement with available data. With the argument that the strain energy is zero for $r_A \leq r_B$, Seah (1979) obtained a semiempirical relation of the form of eq. (18), which represents ΔH for 32 dilute binary systems with a standard deviation of less than 9 kJ/mol for a range of ΔH from - 80 to 20 kJ/mol.

It should be noted that the approach of eq. (18) as described by the three terms: surface energy difference of the components, their enthalpy of mixing and strain release energy contains many simplifications. For example, pure component data for the surface energies or interaction terms based on bulk data are used which may be prone to alteration by solute surface bonding, and the

atomic sizes refer to pure element values which are generally different from those in a solid solution (Zhou 1983).

In view of the above mentioned approximations, the at least semi-quantitatively correct predictions for surface segregation in substitutional alloys show that the basic physical parameters are reasonably well understood. Similar arguments for interstitial solutes, that means for most nonmetal/metal systems are more difficult to derive, mainly because of the more complex bonding states involved (Egert and Panzner 1982).

The general picture of surface segregation in alloys by the bond breaking model cannot be easily transferred to segregation to grain boundaries. Obviously, the change in binding energy is less than that at the free surface given by Z_V and the strain energy term must also be considerably smaller since no complete relaxation will take place if an atom is transferred from the bulk into the boundary. While the latter quantity can be estimated by molecular statics calculation using appropriate pair interaction potentials (Sutton and Vitek 1982), the surface energy term may be estimated by introducing the empirical rule $\gamma_b \approx 1/3 \gamma_s$. (Seah and Lea 1975). Therefore there should be close analog between surface and grain boundary segregation, and generally the segregation enthalpy is expected to be lower for the latter case. However, there may be exceptions, particularly for interstitial solutes which may considerably reduce the existing strain in the boundary of the pure matrix and lead to improved boundary cohesion (Seah 1980c).

The Segregation Entropy

For a real solid solution, the entropy term ΔS in the free energy relation $\Delta G = \Delta H - T\Delta S$ must be evaluated. It should consist of three contributions associated with changes in vibrational (ΔS_V), anharmonic (ΔS_A) and site multiplicity (ΔS_m) behaviour of segregation. As shown by Seah and Lea (1975), ΔS_A and ΔS_m can generally be neglected as compared to ΔS_V , which is approximately given by

$$\Delta S_V = 3R \cdot \ln(\theta_D/\theta_D^*) \quad (19)$$

where θ_D and θ_D^* are the Debye temperature for the solute atom in the matrix and at the distorted site on the free surface or at the grain boundary. Seah and Lea find $\Delta S_V = 3.5 R$ for surface and $S_V = 3.3 R$ for grain boundary segregation of Sn in Fe. Other authors (Abraham and Brundle 1981) argue that the vibrational term should include the coordination numbers which counteract the difference in the Debye temperatures so that $\Delta S_V \approx 0$ is obtained. Wynblatt and Ku (1977, 1979) derive an expression for the segregation entropy taking into account the entropy terms for surface free energy, the excess entropy of mixing (which should be zero in a simple regular solution), and the temperature dependent parts of the elastic moduli K and G in analogy to eq. (18). In the system Ni-Au they calculate $\Delta S = -3R$ for the Ni rich and $\Delta S = 0.55$ for the gold rich alloy, but with high uncertainty. It appears that entropy

terms outside $-3R < \Delta S < 3R$ are rather unlikely. Experimentally, ΔS is recognized in a shift of the segregation isotherm on the bulk concentration scale. Therefore, particularly in very dilute systems where often the exact concentration of the solute is not precisely known, ΔS values are difficult to separate accurately. On the other hand, high entropy values obtained in the evaluation after the McLean formalism (eq. (3)) may be a hint that the latter has to be modified by interaction or site dependent terms (e.g. Erlewein and Hofmann 1977).

Structural Dependence of Segregation

The general assumption of equivalent segregation sites is strictly only valid for surfaces of well defined low index orientation. For a randomly oriented surface, as well as for a grain boundary, we would expect a variation of the driving force for segregation related to the free energy of the surface. This is immediately seen from the bond breaking model through variations of the relative energy difference with the orientation dependence of the parameters Z_V/Z and Z_I/Z (see eqns. (15,16)). However, such a straightforward prediction may be modified by surface phase transition (Blakely and Thapliyal 1979). Grain boundaries are even more complex to describe with respect to orientation dependence of segregation.

Surface Segregation Anisotropy

There is consistent experimental evidence that surface segregation depends on orientation. For Au segregation on Ni, Johnson et al. (1978) found a wide scatter of the amount of segregation within the orientation triangle, with the highest level around (100). Similar results of Zhou and McMahon (1981) for C, Sn and Si segregation on Fe-Si-Sn-C alloys indicate high amounts of enrichment for the high index orientations. Recently, King and Donnelly (1985) studied the orientation dependence of surface enrichment in Ag-Au alloys. Increased segregation levels of Cu on (100) with respect to (111) in a CuNi alloy were reported by Brundle and Wandelt (1981). That the more open surface structures favor the segregation is confirmed by electronic theories (Barnett et al. 1983). Erlewein and Hofmann (1977) and Frech and Hofmann (1985) obtained reasonable agreement between the Z_V/Z terms in the broken bond model and the respective relative segregation enthalpies for Sn and for S on (100), (110) and (111) surfaces (Table 1). As expected, $-\Delta H$ is low for (111) and (100) and highest for the least densely packed plane (110). Their results showed also, that a mean (Cu-S) and even a considerably lower Cu-Sn segregation enthalpy was determined for high index surfaces. According to the terrace-ledge-kink model, it is likely that there are generally more sites available for segregation on randomly oriented surfaces, but with different segregation enthalpies. Therefore the temperature dependence of surface enrichment will be broadened over a wider temperature region than that compared to low index surfaces. If analyzed by the McLean equation, an apparent segregation enthalpy is obtained with a tendency to lower

Table 1

Measured segregation enthalpies ΔH for different surface orientations as compared to broken bond model predictions for Sn on Cu (Erlewein and Hofmann 1977) and S on Cu (Frech and Hofmann 1985). Z_V/Z is the relative number of broken bonds

Orient.	Z_V/Z		ΔH in kJ/mole	
	(nearest neighb.)	(+2nd near. neighb.)	Cu-Sn	Cu-S
(111)	0.25	0.3	51	120
(100)	0.33	0.3	50	140
(110)	0.42	0.4	68	150
random	-	-	33	135

values than the low index average (Erlewein 1977). This has been shown by calculations of White and Coghlan (1977) for a distribution of segregation enthalpies. For systems with surface phase transitions occurring (Blakely and Thapliyal 1979, Zhou 1983) the Langmuir-McLean equation cannot adequately describe the segregation behaviour.

Orientation Dependence of Grain Boundary Segregation

The main reason why the orientation dependence of grain boundary segregation is expected to be more complex than that of surface segregation is the completely different atomic structure of an internal interface with respect to the bulk lattice. Experimental and theoretical determinations of the energy of tilt boundaries in Al by Hasson and Goux (1971) have shown that for coherent twin orientations with the close packed (111) plane the interfacial energy will almost approach zero. This indicates that the relative variation in interfacial energy is larger than that of free surface energies. The occurrence of pointed minima, so called cusps, in energy versus misorientation diagrams has been elucidated by the sphere sintering experiments on a plate of Gleiter and coworkers which show the establishment of preferred orientations with minimum energy. Adding a solute changes the grain boundary energy. Intuitively, one would expect a situation as schematically shown in Fig. 6 after Sautter et al. (1977). If, in analogy to surface segregation, the driving force for grain boundary segregation is a decrease in interfacial energy, general boundaries with orientations between cusps would be more prone to segregation as compared to shallow cusps (B'), which may even disappear (C) and the lowest influence should occur for the deep cusps (A,A') in accordance with the results of Gleiter (1982) and Roy et al. (1982) for Bi in Cu. It seems that the chemical interaction term in eq. (18) with the surface energies replaced by the grain boundary energies is the essential factor for the orientation dependence of the segregation enthalpy. The structural variation is associated with the difference in the coordination number across and parallel to the boundary with respect to the bulk, introduced instead of Z_V , Z_I in eq. (18). Contrary to free surfaces, a strong influence on orientation is expected from the strain energy term, since the stress relief

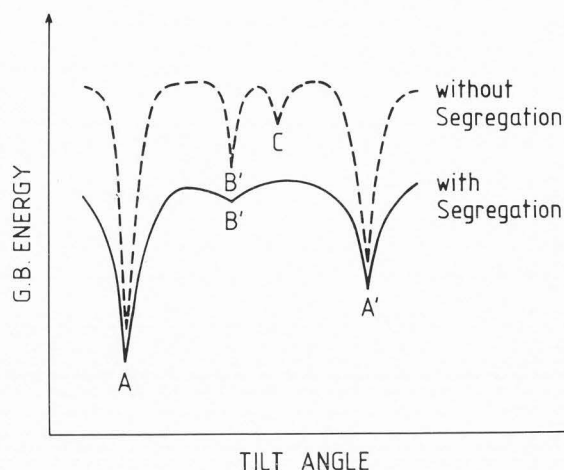


Fig. 6

Schematic diagram of the grain boundary energy as a function of the tilt angle for a solid solution with low energy orientations (cusps) at A, B', C, A', adapted from Sautter, et al. (1977). Due to preferred solute segregation at random orientations between the cusps, the deep ones A,A' remain virtually unchanged, B' becomes rather shallow and C vanishes.

cannot be complete. As shown by molecular statics calculation (Sutton and Vitek 1982), hydrostatic pressure can even be positive on certain sites in a grain boundary.

From many experimental studies of grain boundary segregation with AES, there is general evidence of the influence of orientation (Mulford et al. 1980). Studies on polycrystalline fracture surfaces in Fe-Sn (Seah and Hondros 1973), Cu-Bi (Powell and Woodruff 1976) and Fe-P (Briant 1983) have shown variations of the amount of segregation at different grain boundaries. In Fig. 7, the ratio of the Auger peak to peak heights of P to that of W at the fracture surfaces of two matching sides are plotted for various grain boundaries of a sintered W (Ni,Fe) material with P as the main segregant. In agreement with the results of Briant (1983) for Fe-P, the scatter is small between both sides of the same boundary. However, the variations of individual boundaries show qualitatively that a strong orientation influence exists. Studies on oriented bicrystals with segregation of Sn in Fe (Watanabe et al. 1980) have shown that above a tilt angle of 15° the segregation level is high with about $\pm 20\%$ variation for different orientations. A distinct influence of bicrystal orientation was detected for segregation of Sb in Cu by Chuang et al. (1982). Suzuki et al. (1981) reported variations of P grain boundary segregation in Fe which they correlate with the orientation index of the fracture surface with segregation being lowest for low index surfaces. Recent results of Fraczkiwicz and Biscondi (1985) on grain boundary segregation of Bi in

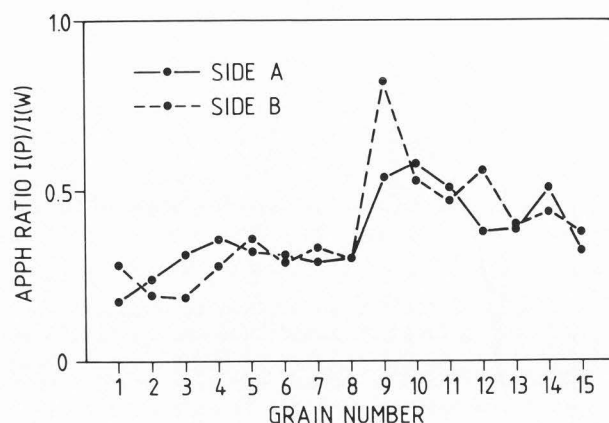


Fig. 7

AES results for two sides of an intergranular fractured sample of polycrystalline W (Ni,Fe) with P as the main impurity. The Auger peak to peak height ratios of the P and W intensities are plotted for 15 matching grains showing reasonable correlation but a marked scatter for different grains.

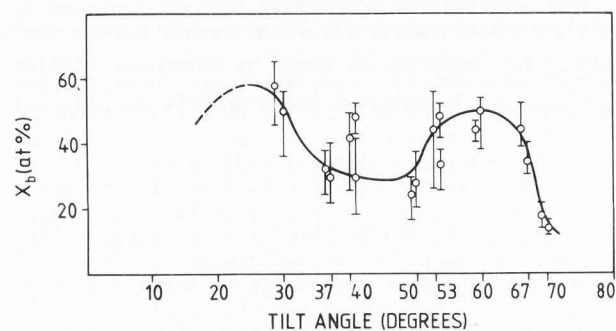


Fig. 8

Grain boundary segregation results of Bi in copper from Fraczkiewicz and Biscondi (1985). The Bi concentration determined by AES is plotted against the misorientation angle of Cu <100> tilt bicrystals. (Bulk concentration of Bi = 120 µg/g, heat treatment 773 K for 24 h).

oriented Cu bicrystals show a distinct dependence on orientation (Fig. 8). For Cu-Bi, Roy et al. (1982) have demonstrated by their ball rotation sintering technique combined with rupture by ultrasonic treatment that low energy boundaries exhibit less segregation and are therefore more resistant to fracture. Pierantoni et al. (1985) have found three times more sulfur at 40° [110] than at 20° [110] tilt boundaries in Ni-S. Although there is still a lack of accurate quantitative experiments relating grain boundary orientation to segregation enthalpies, the general conclusion is that there is a definite influence and that high index, general grain boundaries

exhibit more segregation than special boundaries with low energies.

The relation between segregation and orientation is based on the actual structure of grain boundaries. Recent reviews (e. g., Balluffi 1979, Gleiter 1982, Fischmeister 1985) summarize the main results of the large number of calculations of grain boundary structures in recent years and their relation to segregation. At present, there is general agreement that special grain boundaries as defined by the coincidence site lattice model by their inverse density of coincidence sites, Σ , can be described by a periodic sequence of structural units. The atomic structure of general boundaries is regarded as composed of two types of units at least one of which corresponds to the unit cell of a stable, short period boundary (Vitek and Wang 1982). The structural units correspond to regular atomic arrangements which are distorted versions of the Bernal polyhedra being building blocks of amorphous structures (Ashby et al. 1978).

Two main types of theoretical approaches to understand grain boundary segregation in terms of grain boundary structure have shown reasonable results. One is based on atomic pair interaction potentials used in both molecular statics (Sutton and Vitek 1982) and in molecular dynamics calculations (Nichols 1981, Hashimoto et al. 1982). The other approach is based on molecular orbital models of bonding in the structural units of grain boundaries (Messmer and Briant 1982, Hashimoto et al. 1984). Whereas the latter aspect is closely related to the simple chemical bonding approach in Wynblatt and Ku's model (see above), the pair potential approach emphasizes the strain term contribution.

Using molecular statics computer calculations, Sutton and Vitek (1982) have studied the behaviour of Bi and Ag in Cu (and of Ag in Au) at two kinds of symmetric tilt boundaries ($\Sigma = 5(210) 36.87^\circ$ and $\Sigma = 17(530) 28.07^\circ$). Whereas they found no substantial difference in the segregation energy E_s between both boundary types, its variation for the seven different boundary sites studied is particularly high for the strong segregant Bi and ranges from $-1.1 \text{ eV} < E_s < +2.3 \text{ eV}$. Segregation is only favorable to sites with negative E_s associated with hydrostatic tension. Therefore it is suggested that the segregation of Bi in Cu is governed by the size effect (the atomic volume of Bi is three times larger than that of Cu) in accordance with the early model predictions of McLean (1957). However, the atomistic model of Sutton and Vitek predicts a significant effect of boundary structure on segregation with a pronounced selectivity of segregation sites.

The chemical bonding aspect in grain boundary segregation as outlined by Losch (1979) was worked out by Messmer and Briant (1982). They used the molecular orbital method to calculate the chemical bonding characteristics for clusters which have atomic arrangements representative for the polyhedral structure elements in a grain boundary. Considering tetrahedron structure (Me_4I cluster) for Ni-S, Ni-B, Fe-S, Fe-P and Fe-C they conclude from the calculated valence electron charge density distribution that an electronegative element

(such as S) draws charge from the metal atom to the impurity and consequently weakens the adjacent metal-metal bonds. Therefore the boundary cohesion is reduced with explains the embrittlement effect of S found experimentally. On the other hand, the least electronegative element, B, forms a covalent like bond with the metal and will enhance boundary cohesion. Qualitatively, the conclusions are in accordance with the pair interaction bonding model of Seah (1980c). More complex cases showing the influence of additional metallic elements (Ni, Cr, Mn) in Fe related to their respective electronegativity difference with the impurity have also been treated by Briant and Messmer (1982).

The role of P and B segregation in Fe was studied by Hashimoto et al. (1982, 1984) and by Wakayama et al. (1984) using molecular dynamics calculation and by evaluating the local density of electronic states as well as the vibrational states for impurity and host atoms at different sites in two ($\Sigma = 5$ (013), $\Sigma = 9$ (114)) different symmetric tilt boundaries. These boundaries contain a stack of capped trigonal prisms and pentagonal bipyramids as structural units. Their results show conclusively that electronic and strain energy arguments are both responsible that P decreases and B strengthens grain boundary cohesion in iron. Particularly the strain energy argument favours interstitial impurities such as B, C, N as cohesion enhancers which reduce embrittlement (Seah 1980c).

Facetting of grain boundaries has been frequently observed as a result of increased segregation (Pichard et al. 1973, Donald 1976). In recent TEM studies of S doped Ni, Beaunier et al. (1985) found a relative increase in the occurrence of general boundaries in Ni with 16 ppm S as compared to pure Ni, and increased faceting of the special boundaries of $\Sigma = 3$ type. Whereas maximum and continuous segregation was reported for general boundaries, the special boundaries show none or low segregation depending on the orientation of the boundary plane. The general behaviour appears to be in accordance with the model of Sautter et al. (Fig. 6), and with the atomistic calculations of Hashimoto et al. (1982). These authors show for a $\Sigma = 5$ (013) symmetrical tilt boundary in iron, that low amounts of P (i.e., single impurity atoms placed at specific boundary sites) do not change the boundary structure. If a monolayer of P atoms is involved, a new structure is generated with considerably higher segregation energies. The structure is built up of F_3P clusters with a local atomic environment similar to amorphous Fe-P alloys. It is evident that the grain boundary will change to a more stable structure by strong impurity segregation. If selection of new structures leads to new boundary orientation faceting should be promoted.

The similarity of bulk phase and interface phase formation in segregation has been shown by Guttman (1977). In analogy to the often observed occurrence of two-dimensional structures in surface segregation studies, he points out that interaction of the segregating species may lead to two-dimensional (and even three-dimensional) phase formation at a boundary. The first direct experimental evidence of two dimensional segregation structure at an internal interface was recently

reported by Herschitz and Seidmann (1985), who detected a periodic arrangement of Nb atoms in the case of Nb segregation to stacking faults in a Co-0.96 at.% Nb alloy using atom probe field ion microscopy. They explain their results with a solute interactive term of the Fowler type.

This aspect could be revealed by including segregant-segregant interaction terms in computer simulation approaches. Recently Eberhart et al. (1984) have introduced sulfur-sulfur interactions in molecular orbital cluster calculations in order to explain the generally observed effect of grain boundary decohesion on the amount of S segregation.

In summary, our present understanding of grain boundary segregation is characterized by a strong coupling of local structure with a specific segregant. This means that for a well defined boundary, different sites (which vary for different segregants) with various segregation energies are predicted, and the structure may be altered for higher concentration. Furthermore, due to the dependence of grain boundary structure on orientation, segregation should also vary with the latter. This is obvious from the current picture of a general grain boundary being composed of different structural units, the above mentioned polyhedral clusters. Depending on the local structure, the chemical bonding will change and therefore lead to different segregation energies. An illustration of this situation after Briant (1983) is shown in Fig. 9, where schematically the hypothetical energy for a solute at a boundary in a certain configuration is depicted. If the energy is lower than that for the bulk configuration, the respective boundary site will be a trap for the solute which will segregate to this site. For configuration with higher energies with respect to the bulk, no segregation (in fact "desegregation") will occur, and segregation will be strongest for the lowest energy configuration.

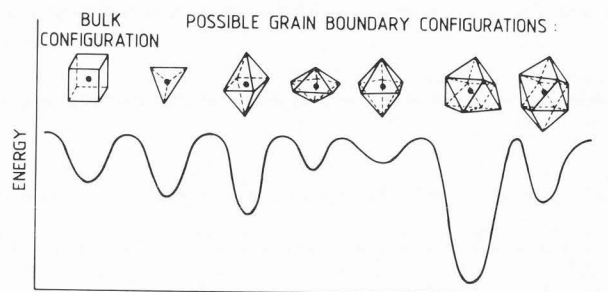


Fig. 9

Diagram showing schematically the variations of the energy for solute segregation if the segregant is in different possible grain boundary configurations according to the structural units consisting of various polyhedra. The respective cluster will become a segregation site if the hypothetical energy minimum is below the bulk configuration value. Adapted from Briant (1983).

The general picture is that we have a) sites with different segregation enthalpies for one boundary and b) boundaries which differ with respect to number and segregation enthalpy of the different sites. Boundaries, for which the prevalent configuration is associated with a strong bonding for solutes will be the one with high segregation level. Thus we envisage a spectrum of different segregation enthalpies not only for polycrystalline material, but also for a single boundary.

The distribution of the segregants will depend on both the number and the characteristic energy of each site, since a large number of shallow traps may result (at a given temperature) in the same segregation level as a few deep traps.

A spectrum of sites with different segregation energies means that we have different segregation isotherms operating simultaneously, as suggested by White and Coghlan (1977). Therefore, experiments interpreted in one segregation enthalpy would only give a mean value with the tendency to lower apparent values. Theoretical predictions of structural dependence of segregation are now in a stage where accurate experiments are needed to test them. However, quantitative experiments on grain boundary segregation are extremely difficult and laborious. They require in first instance high purity, well characterized materials, preferably in the form of synthetic bicrystals.

Segregation and Materials Properties

Surface segregation has a direct impact on any type of reaction on surfaces. These reactions superpose chemical driving forces on segregation which can mask the effects depending on segregation alone. On the contrary, the microchemistry of internal interfaces develops in a closed system and it is here where segregation has its most direct effect on properties.

It is obvious that all those materials properties are influenced by segregation which involve interfacial energetics and kinetics. For example, temper embrittlement, grain boundary diffusional creep and creep cavitation, creep embrittlement, intergranular stress corrosion cracking, hydrogen embrittlement and sintering behaviour are among the most important mechanisms. (For comprehensive reviews, see Hondros and Seah 1977b and 1983). The basic physical parameters governing these properties are grain boundary cohesion and diffusion.

Grain Boundary Cohesion

The effect of solute segregation on grain boundary cohesion is the basic mechanism for temper brittleness in low alloy steels and is caused by residual impurity elements such as P, Sn, Sb, As, with the coupling to alloying elements Ni, Cr, Mo, Mn etc. being of importance (Guttman 1975, Seah 1977, Fischmeister and Olefjord 1978). A measure of the loss in grain boundary cohesion is the observed shift of the ductile-brittle transition temperature to higher temperatures as a function of the segregation level. Time-temperature-transition contour calculations based on Guttman's theory have shown excellent agreement

with the behaviour of commercial steels (Seah 1977, Tyson 1978).

Seah has proposed a model of grain boundary cohesion which explains the influence of segregants on the fracture strength across the boundary using a simple pair bonding model in close analogy to Wynblatt and Ku's segregation model (see above). The basic result is that the boundary cohesion is proportional to the "broken bond" energy of the elemental material at the boundary determined by the molar sublimation enthalpy H_{sub} per unit area. The change in boundary cohesion energy ΔFE by a segregant A is then roughly given by the difference of its sublimation enthalpy to that of the matrix B, and proportional to its amount at the grain boundary X_B , i. e., in the ideal solution approximation:

$$\Delta FE = \frac{Z_g}{N_0 \cdot Z} \left(\frac{H_A^{\text{sub}}}{a_A^2} - \frac{H_B^{\text{sub}}}{a_B^2} \right) \cdot X_B \quad (20)$$

with N_0 = Avogadro's number, Z_g and Z the coordination number in the boundary and in the pure element, respectively, a_A and a_B the atomic diameters of solute A and matrix B. The lower the value H_{sub}/a_A^2 , the more will the segregant embrittle. This is consistent with experimental findings that P, S, Sn, Sb, Cu embrittle iron, whereas Mo and C improve boundary cohesion (Seah 1980b). Recent results on segregation dependent fracture strength in sintered W (Ni,Fe) (Hofmann and Hofmann 1984 and 1985) support the model of Seah, which is in general agreement with the molecular orbital approach of Briant and Messmer (1982) to grain boundary cohesion. However, their model can predict the fracture path along the weakened bonds introduced by embrittling species.

Grain Boundary Diffusion

Solute segregation generally results in the preferred occupation of boundary sites with a high degree of disorder, leaving a more dense structure and less favourable sites for diffusion. Consequently, the transport of matter along the boundary should be reduced as compared to the pure boundary. This effect has been demonstrated experimentally and theoretically by Bernardini et al. (1982) for the influence of Sn segregation on the grain boundary self diffusion of Fe.

With respect to solute heterodiffusion in the boundary, two opposite effects can be expected: Due to the increased solute concentration, the transport of matter is enhanced. On the other hand, the selective filling of favourable sites will decrease the jump frequency. Therefore, the net effect is difficult to predict. For example, Bernardini and Cabané (1985) have shown in Fe (Ni,Sb) alloys that the Sb diffusion parameter is increased in the presence of Ni due to Ni-Sb cosegregation and prevalence of the concentration effect.

It is felt that molecular dynamics calculations (as performed by Kwok et al. (1981) for self diffusion), which allow one to follow the jump path in the boundary structure, could be applied to solute diffusion to enable the determination of the atomistics of heterodiffusion in the

boundary. This should also help to clarify its dependence on orientation as observed experimentally (Pierantoni et al. (1985), and lead to a better understanding of the atomistics of the interaction of solutes with moving grain boundaries, as in recrystallization.

Conclusions

The physicochemical principles of segregation at surfaces and internal interfaces are well understood in metallic materials. They can also be applied to the more complicated cases of heterophase boundaries and of interfaces in ceramics (Johnson 1977, Wynblatt and McCune 1981), where research is much less advanced. Equilibrium surface segregation in substitutional alloys is most advanced in both experimental data and theoretical understanding, and predictions can be made from bulk data with good accuracy. The same applies to the kinetics of both surface and interface segregation. For interstitial, non-metallic solutes predictions appear less reliable due to the more complex bonding mechanisms. The principles of the orientation dependence of surface segregation are sufficiently well understood, with current progress in rationalizing the occurrence of two-dimensional segregation structures.

Segregation to grain boundaries in metallic materials can be adequately described by a well established framework of segregation isotherms on a semi-empirical level, and the effect of segregation on embrittlement can be rather well predicted. However, on an atomistic level there are still a number of open questions concerning mainly the relation between grain boundary structure and segregation. It is felt that recently, based on computer calculations of structure and bonding in grain boundaries, the theoretical modelling of segregation is rapidly advancing, widening the gap between theoretical predictions and experimental evidence. Specific experiments are urgently needed which can unambiguously answer, for example, questions concerning

- segregation site distribution in different boundaries
- dependence of boundary structure on the segregation level
- occurrence of two dimensional segregant structures
- faceting of boundaries dependent on solute segregation
- chemical bonding states of the segregants

Experiments of such a kind require a high standard of control-structurally and chemically- in all different steps, based on ultra high purity materials, preparation of synthetic bicrystals, processing and analysis in ultrahigh vacuum. Future progress will mainly depend on the degree of attainment of these prerequisites, together with the application of advanced surface and micro-local analysis techniques.

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Discussion with Reviewers

M.P. Seah: You state "It is questionable whether interaction at interfaces occurs in a similar manner as in the bulk". In Guttman's theory the regular solution approximation is used and while the bond terms are deduced from the bulk they are re-written into an expression for the 2-D behaviour. Exactly the same approach is used for calculating both the free surface energies and the free energy of surface segregation, with considerable success. Thus, I do not believe Guttman's approach to be questionable or that there is no coupling occurring in Erhart and Grabke's study. Rather it would appear that any coupling effect is simply dominated by a much stronger site competition effect which causes the major effect in that work. Do you have any comment?

Author: I do not question the consistency of Guttman's theory. The critical remark refers to the simplifications implied in the direct deduction of interface interaction terms from bulk interactions, neglecting the generally unknown details of atomistic structure and bonding. Dumoulin and Guttman (1980) conclude that "the surface interactions appear to be much smaller than the bulk interactions". In this respect I agree to your comment on Erhart and Grabke's work.

C.J. McMahon, Jr.: The assumption of a fixed number of segregation sites at surfaces or grain boundaries of systems undergoing segregation from bulk solid solution is, in my opinion, a critical weakness of many existing thermodynamic treatments. Other treatments exist which contemplate sites in layers below that which constitutes the surface.

Author: The assumption of a fixed number of segregation sites is a reasonable first order approximation which is supported by experimental evidence for segregation on single crystal surfaces in many systems (e.g. Fe-C, Fe-N, Cu-S etc.). Complications may arise due to sites with different segregation energies, which may be altered at higher enrichment levels and may even lead to structural transformations as described e.g., by molecular dynamics calculations for grain boundaries (Hashimoto et al. 1982).

C.J. McMahon, Jr.: For repulsive interaction, if one of the two solutes is surface active, e.g. C in Fe-Si-C, the segregation of that solute can be enhanced by the presence of the other.

Author: Repulsive interaction at the surface will generally strengthen the site competition behaviour. Enhanced segregation of the more surface active solute is expected for repulsive interaction in the bulk which in turn increases its bulk activity.