AES in Metallurgy: Materials Design Based on Anisotropy of Grain Boundary Segregation

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Auger electron spectroscopy has been widely used for metallurgical studies of grain boundary properties through measuring interfacial segregation at *in-situ* intergranular fracture surfaces. This application is documented by the study of chemical composition of single grain boundaries in specially prepared bicrystals of an Fe–3.55at.%Si alloy. Thermodynamic analysis enabled us to construct grain boundary segregation diagrams that serve for prediction of segregation enthalpy of any element at a selected grain boundary knowing its solubility in the bulk matrix element. Based on recently disclosed linear dependence between enthalpy and entropy, it is also possible to predict segregation entropy for a selected boundary. In this way, a complete segregation behavior can be estimated. These thermodynamic data on segregation behavior of individual grain boundaries can serve as a database for controlled construction of polycrystals in the framework of the grain boundary design.

1. Introduction

Many metallurgical problems are connected to the behavior of grain and phase boundaries: Internal interfaces represent a weak link of the structure of polycrystalline materials that are used for final products. Thus, they drastically reduce the product lifetime. Brittle fracture, intergranular stress corrosion cracking and creep rupture are classical examples of the degradation effects [1]. Besides their structure, one of the most important effects influencing the behavior of grain boundaries (GBs) is chemical composition: Impurities and solutes segregate at interfaces where frequently thin layers of significantly changed chemical state and composition occur [2].

However, the properties of individual GBs differ from each other. Regarding their behavior, GBs can be divided into two basic groups: There exist limited number of so called *special (singular)* GBs that differ "not much" from the behavior of crystal interior as compared to the vast majority of so called *general* GBs [3]. Different behavior of individual GBs can successfully be employed for production of polycrystals with optimum properties for a chosen purpose: This can be realized by control of the character and distribution of GBs in materials (*grain boundary design*) [4].

In the present paper, the application of Auger electron spectroscopy (AES) to the study of chemical composition of GBs is displayed. Generalization of the results enabling to predict segregation enthalpy and entropy for a chosen GB is discussed from the viewpoint of construction of the database necessary for successful GB design of polycrystals.

2. Metallurgical applications of AES

One way of the study of chemical composition of GBs is to open the boundary by intercrystalline brittle fracture and to apply a suitable method of surface analysis. To avoid contamination of the fresh fracture surface, it is necessary to open the boundary *in-situ* in an ultra-high-vacuum (UHV) chamber of the measuring apparatus. To facilitate brittle intergranular fracture, an impact bending at low temperatures is recommended. During this process, some defects can occur at the fracture surface (deformation twins, cleavage tongues etc.) that affect the measured values of chemical composition [5]. Therefore, good imaging of the fracture surface (usually by secondary electrons), as well as good lateral resolution of the method of surface analysis is needed. Since segregation effects are confined in a thin (often monatomic) layer along the GB, the depth resolution of the method should be in

the monolayer regime. Among numerous methods of surface analysis, AES optimally fulfills the above requirements and therefore, it is the most widely used technique to study chemical composition of interfaces in metallurgy [6]. Although the detection limit is above 0.1at.%, AES possesses relatively good lateral (< 100 nm) as well as depth (several atomic layers) resolutions (Fig. 1).

AES of fracture surfaces was originally applied to the study of average levels of GB segregation in polycrystals [1,2]. A large scatter of the data measured at individual GBs of the fracture surface suggested different segregation levels at individual GBs. However, the determination of a structure/ property relationship is possible only by means of direct measurements of solute segregation at single GBs. Besides the facility with good lateral resolution, large bicrystals of the alloy studied are necessary for this purpose [2].

3. Measurements of interfacial segregation in bicrystals of an Fe–Si base alloy

In the last decade, numerous [100] tilt bicrystals of an Fe–3.55at.%Si base alloy containing 0.0089at.%P and 0.014at.%C were grown by floating zone technique from the seed. The latter consists of two crystals intentionally misoriented and joined together at the planes having the required orientation of the final GB. The conditions for growth of bulk bicrystals (13 mm in diameter and 50 mm long) are given in more detail elsewhere [7]. The samples, 1 mm in diameter and 10 mm long, were annealed in vacuum at different temperatures between 773 K and 1173 K to reach equilibrium segregation at the respective temperature and quenched in water to preserve that equilibrium state in the sample at room temperature. The GB in a given sample was opened by brittle fracture *in-situ* in the UHV ($<10^{-7}$ Pa) chamber of a PHI 600 Multiprobe (Perkin– Elmer), and immediately studied by AES. Suitable localities without defects were selected by means of the secondary electron image. A primary electron beam (10 kV/350 nA) with a diameter of about 1 μm was used for point analysis. The extent of interfacial segregation was checked by depth profiling of individual segregants using Ar^+ ion sputtering (voltage 3 kV, rate of sputtering of about 1 nm/min) [8].

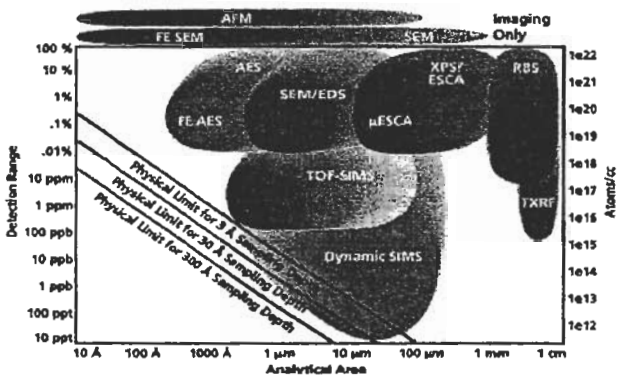

Figure 1. Detection ranges and analytical areas of individual methods of surface analysis. FE AES (Field Emission AES), SEM/EDS (Scanning Electron Microscopy with Energy Dispersive X–Ray Spectroscopy), XPS/ESCA (X–Ray Photoelectron Spectroscopy or Electron Spectroscopy for Chemical Analysis), TXRF (Total Reflection X–Ray Fluorescence), RBS (Rutherford Backscattering Spectroscopy), TOF–SIMS (Time-Of-Flight Secondary Ion Mass Spectroscopy). AFM (Atomic Force Microscopy) and FE SEM are methods used for imaging only. With permission of Charles Evans & Associates.

Derivative Auger spectra of the fracture surfaces were transformed into chemical composition of GBs X^{Φ}_I by [8]

$$X^{\Phi}_I = \Lambda^{\Phi}_I \Big/ \sum_{J=1}^{N} \Lambda^{\Phi}_J \qquad (1)$$

where

$$\Lambda^{\Phi}_I = F_I \frac{2\Omega^{FS}_I - \Omega^{B}_I\{1+\exp[-d/\lambda(E_I,\phi)]\}}{1-\exp[-d/\lambda(E_I,\phi)]} \qquad (2)$$

$F_I = \Lambda^s_I \lambda^s(E_I,\phi) R^s(E_I,\alpha)/[\Omega^s_I \lambda(E_I,\phi) R(E_I,\alpha)]$, Ω^{FS}_I and Ω^{B}_I are the peak-to-peak heights of element I at fracture surface FS and in the bulk B, respectively, d is the width of the segregated layer, $\lambda(E_I,\phi)$ is the product of the attenuation length $\lambda(E_I)$ of Auger electrons with the energy E_I in the matrix N and the cosϕ. ϕ is the angle of emission of Auger electrons to the surface normal. Λ^s_I is the atomic density of pure solid

standard I, $R(E_I,\alpha)$ is the backscattering term which depends on both matrix N and E_I, α is the angle of the incident electron beam to the surface normal. The superscript s relates the value of each parameter to the pure elemental standard. Ω^s_I is the relative sensitivity factor for the Auger peak with the energy E_I.

Table 1. Enthalpy ΔH^0_P (in kJ.mol^{-1}) and entropy ΔS^0_P (in J.mol^{-1}.K^{-1}) of P segregation at various [100] symmetrical and asymmetrical tilt GBs in α-Fe [2,10].

Grain boundary	ΔH^0_P	ΔS^0_P
18.9°[100] {016}	−31	+17
22.6°[100] {015}	−16	+38
28.1°[100] {014}	−35	+19
36.9°[100] {013}	−13.3	+45.2
45°[100] {0kl}	−37	+18
50.0°[100] {0 7 15}	−31	+25
53.1°[100] {012}	−10.9	+42.5
58.1°[100] {012}	−34	+20
64.0°[100] {058}	−37	+16
36.9°[100] (018)/(047)	−32	+19
36.9°[100] (001)/(034)	−25	+29
36.9°[100] (017)/(011)	−14.5	+39.3
36.9°[100] (0 3 11)/(097)	−32	+21
11.3°[100] (001)/(015)	−22	+32
18.4°[100] (001)/(013)	−19	+35
26.5°[100] (001)/(012)	−26	+28
45°[100] (001)/(011)	−19	+38
56.3°[100] (011)/(015)	−18	+37
63.4°[100] (011)/(013)	−17	+37
71.6°[100] (011)/(012)	−17	+36

From the temperature dependence of the chemical composition of individual GBs, the standard molar enthalpy ΔH^0_I and entropy ΔS^0_I of GB segregation in dilute binary alloys Fe–I (I = Si, P, C) were determined according to the quasichemical Guttmann model of segregation in multicomponent systems [9]

$$\frac{X^{\Phi}_I}{X^0-\sum_{J\neq N}X^{\Phi}_J}=\frac{X^B_I}{1-\sum_{J\neq N}X^B_J}\exp\left[-\frac{\Delta G_I}{RT}\right] \qquad (3)$$

where X^0 is the saturation level of the boundary and X^B_I is the bulk concentration of I. The free energy of segregation, ΔG_I can be expressed as

$$\Delta G_I=\Delta H^0_I-T\Delta S^0_I-2\alpha\left(X^{\Phi}_I-X^B_I\right)+\sum_{J\neq I,N}\alpha'_{IJ}\left(X^{\Phi}_J-X^B_J\right) \qquad (4)$$

In equation (4), α_{NI} and α'_{IJ} are the coefficients of binary interaction of I atoms in matrix N and of ternary interaction of I and J atoms in matrix N, respectively.

For example, the values of the enthalpy and entropy of P segregation at various [100] tilt GBs in α-Fe are given in Table 1. Orientation dependences of the enthalpy of Si, P and C segregation at [100] symmetrical tilt GBs is shown in Fig. 2.

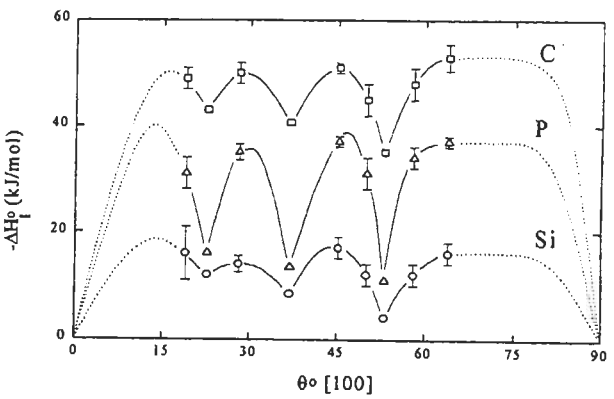

Figure 2. Orientation dependence of enthalpy of Si, P and C segregation at [100] symmetrical GBs of α-Fe [2].

4. Anisotropy of interfacial segregation

It is clearly seen from Table 1 that there are large differences in the values of particular segregation parameters for different GBs suggesting a pronounced anisotropy of GB segregation. The orientation dependence of ΔH^0_I is qualitatively similar for all three segregants (Fig. 2): Three minima of absolute value of ΔH^0_I are apparent on this orientation dependence at 22.6°[100] {015}, 36.9°[100], {013} and 53.1°[100] {012} symmetrical tilt GBs. The low absolute values of ΔH^0_I suggest a low tendency of these GBs to segregation. From this point of view, these GBs can be considered as *special* [2,8]. Similarly, the 18.4°[100] (001)/(013) and all θ°[100] (011)/(0kl) asymmetrical GBs are *special* [10].

5. Grain boundary segregation diagram

As found by Hondros and Seah, there exists a simple correlation between the GB enrichment ratio, $\beta_I \equiv X^{\Phi}_I/X^{B}_I$, and the reciprocal solid solubility limit, X^*_I: $\beta_I = K/X^*_I$ [11]. Using this simple relationship, it is possible to estimate – within one order of magnitude – the level of segregation of any element at GBs in polycrystalline matrix knowing only bulk solid solubility data. In 1980, Watanabe et al. extended this relationship by considering orientation of individual GBs and proposed to construct so called *grain boundary segregation diagram* as a three-dimensional dependence of β_I on both the X^*_I and the boundary orientation [12]. However, at that time there were no suitable quantitative data on segregation of different solutes at individual GBs that could be used to construct such a diagram. The first GB segregation diagram was constructed only recently using the data on Si, P and C segregation at various [100] tilt GBs in α-Fe [13]. For this purpose, β_I was replaced by ΔH^0_I as an independent thermodynamic parameter since β_I depends strongly on many factors such as temperature and bulk composition.

An analysis showed that the dependence of ΔH^0_I on both X^*_I and GB orientation can be expressed as [14]

$$\Delta H^0\left(\Phi, X^*_I\right) = \Delta H^*(\Phi) + \nu R\left[T \ln X^*_I\right] \qquad (5)$$

where $\Delta H^*(\Phi)$ is the enthalpy of segregation of an element with unlimited solubility ($X^*_I = 1$) at selected GB in the chosen matrix, and ν is the parameter relating the activity a^*_I and concentration X^*_I of I in this matrix at the bulk solid solubility limit, $a^*_I = (X^*_I)^{\nu}$. Such dependence was found to exist for numerous solutes in α-Fe [14]. An example of the GB segregation diagram is shown in Fig. 3. Using the GB segregation diagram, segregation enthalpy of any element at any GB in a given matrix can be predicted knowing the data on its bulk solid solubility (T and X^*_I). The reliability of the GB segregation diagram was tested by comparing the estimate of the segregation enthalpy for general interfaces with experimental data on segregation of Si, P, C, S and Sn in polycrystalline Fe found in the literature. The differences between predicted and experimental data were found to be less than ± 5 kJ.mol^{-1}: Such differences are comparable with the error of determination of the segregation enthalpy [14].

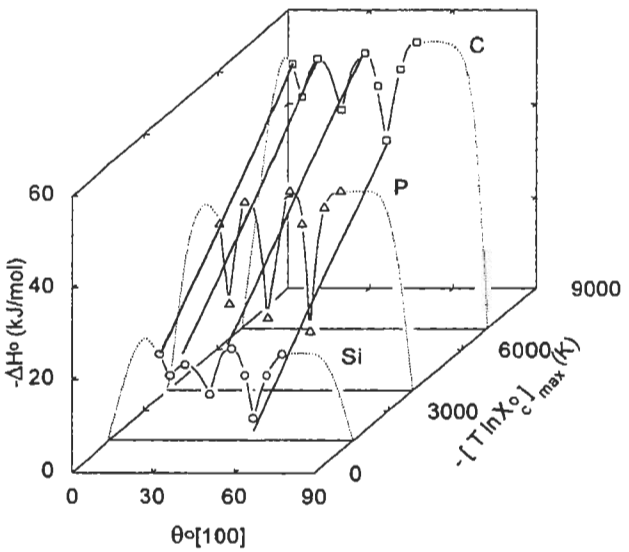

Figure 3. Segregation diagram for the [100] symmetrical tilt GBs [2].

6. Relation between segregation enthalpy and entropy

To predict the whole segregation behavior of an element at a GB, it is also necessary to consider the entropy term (cf. Eqs. (3) and (4)). This parameter has been often neglected [2] but its importance for segregation behavior was proved recently by disclosing a simple linear dependence between enthalpy and entropy of segregation for individual interfaces as well as for different sites in GB core [15]. The relationship is documented in Fig. 4 for the data on Si, P and C segregation at different GBs of α-Fe.

The dependence between enthalpy and entropy of segregation can be expressed as [16]

$$\Delta S^0_I = \frac{\Delta H^0_I}{\tau_I} + \sigma_I \qquad (6)$$

where $\tau_I = (d\Delta H^0_I/d\Phi)/(\Delta S^0_I/d\Phi)$ quantifies the change of segregation enthalpy with the change of segregation entropy due to changes of GB structure Φ, and σ_I is the entropy of segregation for an interface with $\Delta H^0_I = 0$. In fact, τ_I is the temperature at which the free energy of

segregation is constant for all GBs. The values of parameters τ_I and σ_I are given for Si, P and C segregation in α-Fe in Table 2.

Table 2. Values of parameters τ_I (in K) and σ_I (in $J.mol^{-1}.K^{-1}$) of Eq. (6) for Si, P, C and P+C [16].

Parameter	Si	P	C	P+C
τ_I	940	930	1260	920
σ_I	5	56	42	56

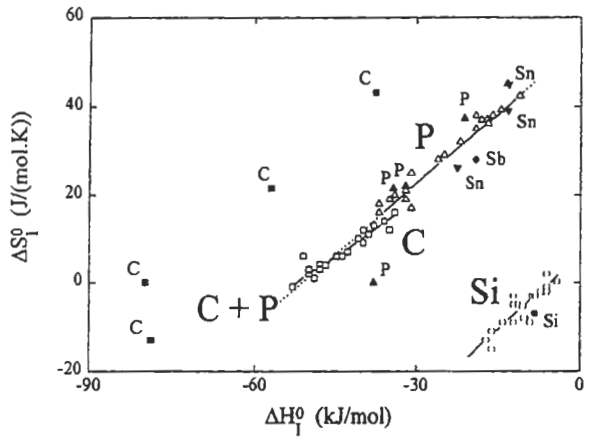

Figure 4. Dependence of entropy and enthalpy of Si, P and C segregation at [100] tilt GBs of α-Fe (empty symbols). Literature data on GB segregation of Si in a bicrystal, and P, C, Sb and Sn in polycrystals of Fe base materials (as summarized in [2]) are also plotted (solid symbols) [16].

It is seen from Fig. 4 and Table 2 that there are two branches of the linear dependence: One is fulfilled for Si and the other for C and P (and for all other elements for which the GB segregation in α-Fe was studied). The slopes of these lines are parallel suggesting a single value of parameter τ_I. It is also seen that systematically, the entropy of the Si segregation possesses negative values while they are positive for other elements. Both these findings can be explained by the tendency of individual elements to "order" (*negative* entropy) or "disorder" (*positive* entropy) the GB during segregation [16].

Based on the linear dependence between enthalpy and entropy of segregation (Eq. (6), Fig. 4), we can estimate the values of ΔS^0_I at a chosen GB knowing ΔH^0_I for this interface.

The existence of the temperature τ_I is very important for the anisotropy of GB segregation: Lower absolute values of ΔH^0_I (suggesting lower tendency to segregation) and higher values of ΔS^0_I (suggesting larger "disordering" due to segregation) are observed at special GBs as compared to general ones. Therefore, lower levels of solute segregation are observed at special GBs at low temperatures as compared to general interfaces. With increasing temperature, the differences between composition of special and general interfaces diminish and at τ_I, all boundaries possess the same chemical composition. Above τ_I, however, segregation levels are higher at special boundaries as compared to general ones, i.e., the character of anisotropy of GB segregation, if represented by orientation dependence of interfacial composition (e.g., by β_I), qualitatively changes although the orientation dependence of thermodynamic parameters remains unchanged. Therefore, *anisotropy of GB segregation should be represented exclusively by the orientation dependence of thermodynamic parameters* [16].

7. Grain boundary design of polycrystals based on anisotropy of solute segregation

Knowing enthalpy and entropy of segregation of a solute at single interfaces, the segregation behavior of individual GBs can simply be determined and thus the interfaces suitable for GB design of polycrystals can be selected. From the viewpoint of modeling the properties of polycrystals, the knowledge of thermodynamic parameters is more useful than the knowledge of chemical composition of GBs which is always related to specific external conditions. However, there is a very complex relationship between thermodynamic parameters of solute segregation obtained on one hand from the temperature dependence of composition of individual GBs and on the other hand from average chemical composition of the fracture surface of a polycrystal. Using Eq. (3), the average value of the segregation free energy can be expressed in the latter case as

$$\Delta \bar{G}_I = -RT \ln \left[\frac{\left(1 - X^B_I\right) \sum_{k=1}^{m} X^{\Phi}_{I,k}}{X^B_I \sum_{k=1}^{m} \left(1 - X^{\Phi}_{I,k}\right)} \right] \qquad (7)$$

Supposing that the free energy of segregation represents the arithmetic average of the free energy of individual GBs (former case), it is given by the geometric average of chemical concentration of individual interfaces, $X^{\Phi}_{I,k}$

$$\Delta\overline{G}_I = -RT \ln \left[\frac{\left(1 - X^{B}_{I}\right)\left(\prod_{k=1}^{m} X^{\Phi}_{I,k}\right)^{\frac{1}{m}}}{X^{B}_{I} \sum_{k=1}^{m} \left(1 - X^{\Phi}_{I,k}\right)^{\frac{1}{m}}} \right] \qquad (8)$$

Only in the special case when the *arithmetic* and *geometric* averages of chemical composition of different GBs are identical, average values of enthalpy and entropy of segregation determined according to Eq. (7) represent *arithmetic* averages of the values for individual GBs [17].

8. Conclusions

AES is a suitable tool for the study of chemical composition of internal interfaces in metallic materials. Its importance will increase with refining the detection limit using field emission AES (see Fig. 1) as well as with the present renaissance of demands of metallic materials [18]. The present resolution of AES is still good enough to measure concentrations of solutes at individual GBs and to determine thermodynamic parameters of segregation with satisfactory accuracy to specify, for example, anisotropy of GB segregation even in materials with low levels of segregation. Segregation parameters of single GBs in α-Fe determined from AES measurements on bicrystals of an Fe base alloy enabled us to construct the GB segregation diagram and to test the dependence between segregation entropy and enthalpy. Both these constructions allow to estimate the values of thermodynamic parameters of segregation of any element at any boundary in a given matrix and thus, to provide the necessary data for GB design of polycrystals.

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