

EFFECT OF ORDERING ON GRAIN BOUNDARY SEGREGATION

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ABSTRACT

A simple phenomenological model of solute segregation at partially ordered grain boundaries is proposed and used to correlate complex concentration and temperature dependences of silicon segregation in ordered Fe–Si alloys. The model assuming no segregation at ordered parts of the boundary while undisturbed segregation at its disordered parts, is shown to be consistent with present understanding of equilibrium segregation phenomena.

KEYWORDS

Grain boundaries, solute segregation, phase transitions, order–disorder, Fe–Si alloys

INTRODUCTION

Grain boundaries (GBs) in solids represent an important component of material structure since they strongly influence properties of a polycrystal. The most serious effect being responsible for intergranular brittle fracture of the material is the changed chemical composition of GBs, i.e., *grain boundary segregation* [1]. Due to this effect, GB concentration of impurities such as P, Sn, Sb and S has been measured in the past decades in iron and nickel base materials [2,3]. In 1990s, the chemistry of well-characterized GBs has been systematically examined in bicrystals of Fe–Si alloys [3]. As a result, sets of values of enthalpy and entropy of segregation of carbon, phosphorus and silicon were determined, that served for various kinds of generalization such as classification of [100] tilt GBs [4] and prediction of segregation enthalpy and entropy for chosen solute at chosen GB [5].

However, one result remained not interpreted for more than 10 years. The study of interfacial segregation at the {013} and {112} GBs in an Fe–12.9at.%Si by Auger electron spectroscopy (AES) revealed an anomaly of temperature dependence of silicon concentration at low temperatures suggesting, in the first approximation, a maximum of Si segregation at about 870 K. This fact was intuitively ascribed to the effect of the alloy ordering [6]. After years, a Mössbauer spectroscopic (MS) study of GBs in polycrystalline Fe–Si alloys that clearly detected a long-range ordering at interfaces in Fe–12at.%Si and Fe–17at.%Si alloys [7], initiated the development of a simple phenomenological model of solute segregation at partially ordered GBs. In the present work, this model is introduced and used for interpretation of the results of GB segregation in Fe–Si alloys [6,7].

MODEL OF SOLUTE SEGREGATION AT ORDERED GRAIN BOUNDARIES

Let us assume a partially ordered GB in an alloy. The portion of the ordered region can be described by the GB order parameter $m^{GB}(T)$ [8],

$$m^{GB}(T) = \left(\frac{T_c^{GB} - T}{T_c^{GB}} \right)^{\beta^{GB}} \quad (1)$$

where T_c^{GB} is the GB ordering temperature, and β^{GB} is the GB exponent. In fact, $m^{GB}(T)$ varies between 0 at the temperature T_c^{GB} , and 1 at $T = 0$ K. The value of the T_c^{GB} is generally different from the bulk ordering temperature T_c . Let us also assume that solute segregation at disordered parts of the GB will be unaffected by ordering and therefore, it can be described by the simple Langmuir–McLean segregation isotherm [1],

$$\frac{X_I^0}{1 - X_I^0} = \frac{c_I}{1 - c_I} \exp \left(- \frac{\Delta G_I^0}{RT} \right) \quad (2)$$

where X_I^0 and c_I are the GB and the bulk concentrations of element I , respectively, and ΔG_I^0 is the standard molar Gibbs free energy of segregation of the element I at GBs in a disordered dilute binary system N – I with matrix N . On the other hand, we will assume that solute segregation at ordered parts of GBs is suppressed, so that the concentration of the solute element is equal to the bulk concentration c_I there. Accepting that a $m^{GB}(T)$ portion of the boundary is ordered, we can write the average GB concentration X_I^{GB} as

$$X_I^{GB}(T) = X_I^0(T) \left[1 - m^{GB}(T) \right] + c_I m^{GB}(T). \quad (3)$$

According to eqs. (1) – (3), we can now determine solute segregation at ordered GBs.

GRAIN BOUNDARY SEGREGATION IN Fe–Si ALLOYS

As mentioned in introduction, three polycrystalline Fe–Si alloys containing 4, 12 and 17 at.%Si were recently studied by combined MS in emission and transmission modes. In this way, both the amount of foreign atoms (Si) in the surrounding of Fe isotope atoms at the GBs and – on the basis of model calculations – the arrangement of the atoms there can be determined. The complete description of the experiment, models and obtained results are published in detail elsewhere [7]. Here, the most important results are summarized in Table 1.

Let us now correlate these results according to the above model of segregation at ordered GBs. First, we will consider the Fe–4at.%Si alloy as disordered and therefore, we will apply eq. (2) to determine the value $\Delta G_{Si}^0(873 \text{ K}) = -5340 \text{ J/mol}$. Let us remind that ΔG_{Si}^0 represents the thermodynamic quantity characterizing segregation of silicon in α -iron [3] and

Table 1. Summary of experimental results of the MS study of GBs of three Fe–Si alloys [7].

	Fe–4at.%Si	Fe–12at.%Si	Fe–17at.%Si
Bulk	A2 disordered	D0 ₃ ordered	D0 ₃ ordered
GBs	disordered	D0 ₃ ordered	D0 ₃ ordered
X_{Si}^{GB} (at.%)	8.0 ± 1.5	17.7 ± 1.1	24.5 ± 0.5

therefore, it does not depend on silicon concentration. From this point of view, the above value of ΔG_{Si}^0 is independent of alloy composition and thus, characteristic for the Langmuir–McLean type of GB segregation in both the Fe–12at.%Si and Fe–17at.%Si alloys at 873 K.

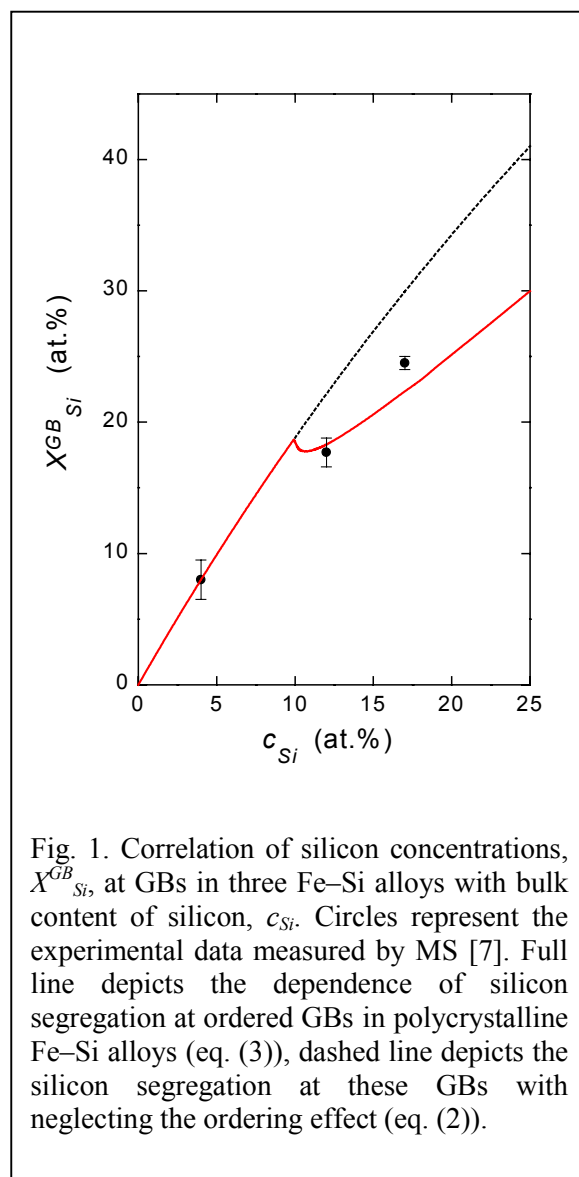


Fig. 1. Correlation of silicon concentrations, X_{Si}^{GB} , at GBs in three Fe–Si alloys with bulk content of silicon, c_{Si} . Circles represent the experimental data measured by MS [7]. Full line depicts the dependence of silicon segregation at ordered GBs in polycrystalline Fe–Si alloys (eq. (3)), dashed line depicts the silicon segregation at these GBs with neglecting the ordering effect (eq. (2)).

Using the value $\Delta G_{Si}^0(873 \text{ K}) = -5340 \text{ J/mol}$, the values of silicon segregation, X_{Si}^0 , at disordered parts of the boundaries in the Fe–12at.%Si and Fe–17at.%Si alloys can be determined. Comparing the values of X_{Si}^0 and corresponding experimental (E) values $X_{Si,E}^{GB}$, we can determine the values of $m_{E}^{GB}(873 \text{ K})$ for both ordered alloys according to eq. (3). We can now correlate these values with the values of $m_{M}^{GB}(873 \text{ K})$ calculated according to eq. (1). The value of the exponent β^{GB} lies, in principle, between 0.3 that corresponds to the bulk with full number of the nearest neighbors, and 0.8 that was obtained for reduced number of nearest neighbors at the surface [8]. Therefore, we will assume the value of the exponent $\beta^{GB} \approx 0.5$ for GBs with smaller number of the nearest neighbors as compared to the bulk but with higher number of them comparing to a free surface. In fact, the value of β^{GB} can be improved according to a new experimental knowledge, however, if once chosen, it will be then used for *all* considerations of solute segregation at ordered GBs. Using $\beta^{GB} = 0.5$ throughout the whole paper, the best fit is obtained for the value $T_c^{GB} = T_c + 120 \text{ K}$. Knowing the model values of $m_{M}^{GB}(873 \text{ K})$, we can calculate the concentration dependence of silicon segregation at ordered GBs according to eqs. (1)–(3). This correlation is shown in Fig. 1.

Let us now apply the present approach to our previous results [6]. In that work, silicon segregation was measured at the {112} and {013} GBs in the Fe–12.9at.%Si alloy in the

temperature range 773 K – 1173 K by means of AES. As it is seen from Table 2, abnormally low silicon concentration was found at both GBs at 773 K. Based on eq. (2) and accepting $\Delta G_I^0 = \Delta H_I^0 - T\Delta S_I^0$, the values of segregation enthalpy, ΔH_I^0 , and entropy, ΔS_I^0 , were determined for both GBs from the data at high temperatures where none or only weak ordering occurs [6]. These values are also shown in Table 2. Using these values and supposing the T_c^{GB} to be more close to the bulk value ($T_c^{GB} = T_c + 60$ K) in this case of special GBs characterized by a transition behavior between general GBs (the case of polycrystalline Fe–Si alloys) and bulk, we can calculate the values of silicon segregation at ordered GBs and correlate the experimental data using the model temperature dependence (Table 2, Fig. 2).

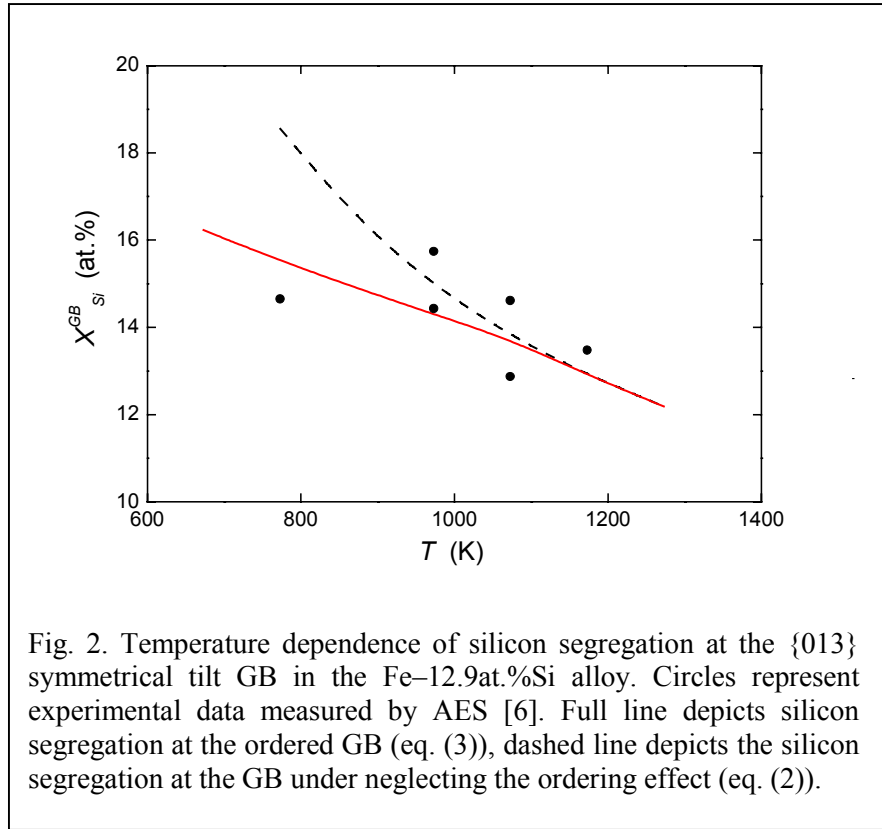
Table 2. Temperature dependence of silicon segregation at the {112} and {013} symmetrical tilt GBs in an Fe–12.9at.%Si alloy [6].

($X_{Si,E}^{GB}$ and $X_{Si,M}^{GB}$ are the silicon concentrations at the GB measured by AES and calculated according to the present model, respectively. Experimentally determined values of ΔH_{Si}^0 and ΔS_{Si}^0 are also listed for both boundaries.)

T (K)	Bulk order	$m^{GB}(T)$	{112}		{013}	
			$X^{GB}_{Si,E}$ (at.%)	$X^{GB}_{Si,M}$ (at.%)	$X^{GB}_{Si,E}$ (at.%)	$X^{GB}_{Si,M}$ (at.%)
773	D0 ₃	0.494	12.5	13.7	14.7	15.5
			12.8			
			12.9			
			13.2			
873	D0 ₃ + B2	0.382	14.7	13.7		14.9
			15.4			
973	B2	0.219	13.3	13.0	14.4	15.0
					15.7	
1073	B2	–	11.9	12.6	12.9	13.7
			12.6		14.6	
1173	–	–	13.5	12.1	12.5	12.9
					13.5	
			$\Delta H^0_{Si} = -4$ kJ/mol		$\Delta H^0_{Si} = -8.1$ kJ/mol	
			$\Delta S^0_{Si} = -4$ J/(mol.K)		$\Delta S^0_{Si} = -6.9$ J/(mol.K)	

DISCUSSION

The above proposed model represents a very simple correlation of solute segregation at (partially) ordered GBs. There is only one parameter, the GB ordering temperature T_c^{GB} , the value of which is not completely known. Since it also has a physical meaning, it represents a “fitting” parameter to a limited extent only. The model enables a very good correlation of the



dependence of solute segregation on both concentration and temperature, under the effect of GB ordering.

Let us compare this model with present understanding of solute segregation at ordered interfaces or at interfaces with limited segregation sites. Recently, Polak *et al.* [9] developed a model of solute segregation at free surface exhibiting short-range order. Based on Ising model Hamiltonian for an A_xB_{1-x} alloy and Bragg-Williams approximation for

segregation enthalpy, they found that

$$\Delta H_p^{(1)} = \Delta H_p^0 + V \sum_q z_{pq} \left\{ (2c_q - 1) + \frac{2V}{kT} c_q (1 - c_q) (2c_p - 1) \right\} - Vz(2c - 1) \left\{ 1 + \frac{2V}{kT} c(1 - c) \right\} \quad (4)$$

where ΔH_p^0 is the Langmuir–McLean type segregation enthalpy, V is the surface and effective pair interaction, z and z_{pq} are the bulk coordination number and the coordination number of a p -plane atom with respect to neighboring q -plane atoms, respectively. c and $c_{p,q}$ are the bulk solute concentration and the solute concentrations in the planes p and/or q parallel to the surface plane, respectively. Supposing analogously in our case that $\Delta G_I = \Delta G_I^0 + \Delta G_I^{ORD}$, we can write

$$\Delta G_I = \Delta G_I^0 + RT \ln \left[\frac{X_I^0}{1 - X_I^0} \frac{1 - X_I^{GB}}{X_I^{GB}} \right]. \quad (5)$$

Replacing the logarithmic term by a series

$$\ln y = 2 \frac{y-1}{y+1} \left[1 + \sum_{n=1} \frac{1}{2n+1} \left(\frac{y-1}{y+1} \right)^{2n} \right] \quad (6)$$

for $y < 1$ [10], by neglecting the terms with $n \geq 2$ we obtain

$$\Delta G_I = \Delta G_I^0 - \frac{8}{3} RT \left(1 - 2X_I^0\right) \left[1 - X_I^0 \left(1 - X_I^0\right)\right] - \frac{4}{3} RT \left(1 - 2X_I^{GB}\right) \left[1 - X_I^{GB} \left(1 - X_I^{GB}\right)\right] \quad (7)$$

This expression is qualitatively similar to eq. (4) supposing solute enrichment in one atomic layer along the interface. As was found in AES experiments, the equilibrium segregation in Fe–Si system is really confined in one boundary monolayer [11]. A more deeper comparison of the present model (eq. (7)) with that of Polak *et al.* (eq. (4)) reveals, however, that – due to phenomenological nature of our derivations – neither pair interaction potentials nor coordination numbers are involved in our considerations. In addition, the solute concentration at a disordered interface, X_I^0 , is involved in eq. (7) instead of the bulk concentration c_I that appears in eq. (4). In fact, an application of the model of Polak *et al.* with the pair interaction potential for Fe–Si alloys determined according to Ref. [12], was unsuccessful to correlate the above mentioned data on GB segregation in the Fe–Si alloys. This might suggest that the mechanisms of segregation under short-range ordering and long-range ordering are different.

Combining eqs. (2) and (3) and introducing a general concentration

$$Y_I^{GB} \equiv X_I^{GB} - c_I m^{GB}(T), \quad (8)$$

we obtain

$$\frac{Y_I^{GB}}{X^* - Y_I^{GB}} = \frac{c_I}{1 - c_I} \exp\left(-\frac{\Delta G_I^0}{RT}\right) \quad (9)$$

where

$$X^* = 1 - m^{GB}(T). \quad (10)$$

If the product $c_I m^{GB}(T)$ is small comparing to X_I^{GB} , eq. (9) transforms into

$$\frac{X_I^{GB}}{X^* - X_I^{GB}} = \frac{c_I}{1 - c_I} \exp\left(-\frac{\Delta G_I^0}{RT}\right) \quad (11)$$

which is identical to the well-known modification of the Langmuir–McLean segregation isotherm (2) introduced by Hondros and Seah [1,3]. It means that for solute segregation at partially ordered GBs, X^* represents the maximum attainable coverage of the GB at a given temperature.

Looking at the phase diagram of the Fe–Si system (e.g. [13]), we can learn that there occur different kinds of long-range ordering in dependence on temperature and alloy composition. Supposing the concentration range 9–25at%Si, we can distinguish in the phase diagram the region of Fe base disordered solid solutions α (A2), the region of the FeSi (B2) base ordered solid solutions α_2 , and the region of the Fe₃Si (D0₃) base ordered solid solutions α_1 . In addition, a region composed of mixtures of α_1 and α_2 phases also appears in the phase diagram. The complexity of the order states can be documented for example of the Fe–

12.9at.%Si alloy at different temperatures (Table 2). However, the final form of the phase diagram of the Fe–Si system in the concentration range of interest is still under discussion. In this respect, mainly the existence of the B2-ordered alloy in this concentration range is not clear. Its existence as well as the existence of the above mentioned two-phase region $\alpha_1 + \alpha_2$ was detected by transmission electron microscopy and X-ray diffraction experiments suggesting the phase transition of the second order [14]. On the other hand, a detail neutron scattering study of a wide spectrum of Fe–Si alloys did not detect the B2-ordering at any temperature: Therefore, it is concluded that there exists only the D0₃ long-range order with small antiphase domains and the lines in present Fe–Si phase diagrams are connected only with the size of these domains [15].

It is clear that it is rather complicated to make quantitative correlation of experimental data in such a situation taking into account ordering tendencies. Therefore, it is necessary to accept some simplifying assumptions. Since no B2-ordering was detected either at GBs or in the bulk [7], we did not consider this kind of ordering: If any occurs at all, it should be rather weak and probably negligible as compared to pronounced D0₃-ordering. The temperature of the D0₃-ordering of GBs in Fe–Si polycrystals, T_c^{GB} , was supposed to be constantly shifted by 120 K to higher temperatures as compared to the temperature T_c of the bulk D0₃-ordering [7]. This fact could seem to be surprising if we accept that GB structure is principally less compact (i.e., “less ordered”) than crystal lattice. However, due to GB segregation, the GB composition is changed as compared to the bulk so that at $T_c^{GB} = T_c + 120$ K the concentration of silicon at GBs is higher than the bulk one at T_c (cf. Fig. 1). From this point of view, the value of $T_c^{GB} > T_c$ is acceptable. Let us also notice that the best fit of the data measured at the {013} and {112} GBs provides us with the values $T_c^{GB} = T_c + 60$ K, i.e., closer to T_c as compared to the case of polycrystalline Fe–Si alloys. This becomes clear taking into account the fact that the {112} and {013} special GBs possess more compact structures than general interfaces in polycrystals and therefore, the properties of the former interfaces are more closer to the bulk ones than those of the latter GBs [1,3].

The concentration dependence of silicon segregation at ordered GBs (Fig. 1) provides us with some interesting conclusions. First, we can observe a local maximum of GB segregation near to the concentration at which – at a given temperature – the GB ordering starts. This finding is understandable since the changes of the GB order parameter m^{GB} with the bulk concentration are the highest there and therefore, the contribution of the quickly increasing non-segregated “ordered” area with the bulk concentration c_I prevails the increase of solute segregation at disordered areas of GBs. Therefore, a decrease of GB concentration should be observed. With further increasing bulk concentration, m^{GB} does not change so quickly and therefore, after reaching a local minimum, GB segregation increases again, however, it is suppressed as compared to solute segregation in a hypothetical case of completely disordered GBs (compare full and dashed lines in Fig. 1). Second, since $m^{GB}(T) < 1$ at $T > 0$, there should still exist the disordered regions at GBs and therefore, GB concentration of silicon should be principally higher than the bulk concentration. From this point of view we can understand the fact that even in the case of the stoichiometric D0₃ ordered Fe₃Si alloy, a GB enrichment of silicon still exists.

CONCLUSIONS

In this work, a simple model of solute segregation at ordered GBs is proposed based on the assumption that a portion of the boundary, given by the order parameter $0 < m^{GB}(T) < 1$, is

ordered and no segregation is allowed there. The only parameter which is not known till now from physical measurements, is the GB ordering temperature, T_c^{GB} . This temperature is thus fitted for given experimental data but only to a limited extent since it should comply with the physical reality. It is shown that the model is physically consistent with present understanding of GB segregation. Two interesting features are predicted for GB segregation: (i) there are two local extremes (maximum and minimum) of solute segregation on concentration dependence of solute segregation at ordered GBs, both close to the start of the ordering, and (ii) since principally $m^{GB}(T) < 1$ for $T > 0$, a segregation at ordered GBs exists at all $T > 0$. As a result, GB segregation will appear even in the case of stoichiometric intermetallic alloys at all temperatures of interest. In contrast to the classical segregation isotherms, the proposed model enables us to explain the previously measured concentration and temperature dependences of GB segregation of silicon in the Fe–Si system.

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