

PHOSPHORUS GRAIN BOUNDARY SEGREGATION IN POLYCRYSTALLINE ALLOY STEELS

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ABSTRACT

In the present work some of the still open questions concerning the grain boundary segregation in multicomponent alloys are discussed. There are reported non-traditional views of the applicability of the current models of equilibrium segregation. The cumulative effect between segregation and intergranular precipitation as well as the role of interface geometry in segregation processes are also subjected to the discussion.

KEYWORDS

Phosphorus grain boundary segregation, alloy steels, thermodynamics.

INTRODUCTION

Generations of scientists have sought for possibilities to apply theories derived mostly for simple ideal systems to real industrial conditions. This process has also affected the researcher dealing with the investigation of grain boundary segregation (GBS) of impurities in solid solutions. In the first attempt, they tried to use Langmuir-McLean isotherm [1] derived originally for the ideal dilute binary system in thermodynamic calculations related to multicomponent alloys [2-4]. Naturally, the alloy was considered as binary Fe-P system and the influence of other solute elements was neglected. Later the modified Langmuir-McLean equation reflecting the site competition between segregating species was introduced [5]. The completely new concept based on the chemical interactions between solute elements was proposed by Guttmann [6]. Guttmann and McLean [7] have introduced five models of the equilibrium segregation in multicomponent systems. In the models, combined effects of the following factors are considered: Fowler type interaction between atoms of the same solute, ternary interaction between atoms of different solutes, site competition, the formation of stable clusters consisting of two atoms (quasimolecules), and the formation of twodimensional compounds at grain boundaries. Even if Guttmann models represent the most complex and exact theory of equilibrium segregation, they did not fit always satisfactorily experimental data [8]. Grabke et al. [9,10] pointed out that carbon plays a dominant role in influencing the phosphorus GBS in Fe-M-C-P systems (M = carbide-forming metallic element). Due to the carbide formation the carbide-forming elements act as scavengers for free carbon, and in this way they indirectly enhance the phosphorus GBS (as a result of the P-C site competition). When a high affinity to phosphorus is attributed to a carbide-forming element, it can prevent from phosphorus segregation through the phosphide formation. Recently, the formation of Laves phase (also in the quasicrystalline form) at grain boundaries due to P and Mo segregation was described [11]. The Laves phase dissolving phosphorus promotes practically the phosphorus desegregation [12]. Lejček and Hofmann [13,14] have specified the influence of both basic boundary types (special, general) and misorientation angle on the segregation of C, P, and Si in Fe-Si. Their results confirmed the significant role of the interface geometry in segregation processes.

As evident from the above given theoretical outline, still are scientific problems waiting for the satisfactory clarification. Three of them, the quantification of equilibrium segregation in multicomponent alloys, the interaction between GBS and intergranular precipitation, and the concept of GBS reflecting the interface geometry, are also discussed in the present work.

	in multicomponent steels
No	Equation
1.0.	
1	$-RT\ln\frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T$
2	$-RT\ln\frac{X_{P}^{S}}{X_{P}^{B}(1-X_{P}^{S})} = \Delta H_{P}^{0} - \Delta S_{P}^{0}T - 2\alpha_{FeP}(X_{P}^{S}-X_{P}^{B})$
3	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T + \alpha'_{PMo}(X_{Mo}^{S} - X_{Mo}^{B})$
4	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T - 2\alpha_{FeP}(X_{p}^{S}-X_{p}^{B}) + \alpha'_{PMo}(X_{Mo}^{S}-X_{Mo}^{B})$
5	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T + \alpha'_{PCr}(X_{Cr}^{S} - X_{Cr}^{B})$
6	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T - 2\alpha_{FeP}(X_{p}^{S}-X_{p}^{B}) + \alpha'_{PCr}(X_{Cr}^{S}-X_{Cr}^{B})$
7	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T + \alpha'_{PV}(X_{V}^{S}-X_{V}^{B})$
8	$-RT ln \frac{X_{P}^{S}}{X_{P}^{B}(1-X_{P}^{S})} = \Delta H_{P}^{0} - \Delta S_{P}^{0}T - 2\alpha_{FeP}(X_{P}^{S}-X_{P}^{B}) + \alpha'_{PV}(X_{V}^{S}-X_{V}^{B})$
9	$-RTln\frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T + \alpha'_{PCr}(X_{Cr}^{S} - X_{Cr}^{B}) + \alpha'_{PMo}(X_{Mo}^{S} - X_{Mo}^{B})$
10	$-RT \ln \frac{X_{p}^{s}}{X_{p}^{B}(1-X_{p}^{s})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T - 2\alpha_{FeP}(X_{p}^{s}-X_{p}^{B}) + \alpha'_{PCr}(X_{Cr}^{s}-X_{Cr}^{B}) + \alpha'_{PMo}(X_{Mo}^{s}-X_{Mo}^{B})$
11	$-RT \ln \frac{X_{p}^{s}}{X_{p}^{B}(1-X_{p}^{s})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T + \alpha'_{PV}(X_{V}^{s}-X_{V}^{B}) + \alpha'_{PMo}(X_{Mo}^{s}-X_{Mo}^{B})$
12	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T - 2\alpha_{FeP}(X_{p}^{S}-X_{p}^{B}) + \alpha'_{PV}(X_{V}^{S}-X_{V}^{B}) + \alpha'_{PMo}(X_{Mo}^{S}-X_{Mo}^{B})$
13	$-RT \ln \frac{X_{p}^{s}}{X_{p}^{B}(1-X_{p}^{s})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T + \alpha'_{PV}(X_{V}^{s}-X_{V}^{B}) + \alpha'_{PCr}(X_{Cr}^{s}-X_{Cr}^{B})$
14	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T - 2\alpha_{FeP}(X_{p}^{S}-X_{p}^{B}) + \alpha'_{PV}(X_{V}^{S}-X_{V}^{B}) + \alpha'_{PCr}(X_{Cr}^{S}-X_{Cr}^{B})$
15	$-RTln\frac{X_{P}^{S}}{X_{P}^{B}(1-X_{P}^{S})} = \Delta H_{P}^{0} - \Delta S_{P}^{0}T + \alpha'_{PV}(X_{V}^{S}-X_{V}^{B}) + \alpha'_{PCr}(X_{Cr}^{S}-X_{Cr}^{B}) + \alpha'_{PMo}(X_{Mo}^{S}-X_{Mo}^{B})$
16	$-RT ln \frac{X_{p}^{S}}{X_{p}^{B}(1-X_{p}^{S})} = \Delta H_{p}^{0} - \Delta S_{p}^{0}T - 2\alpha_{FeP}(X_{p}^{S}-X_{p}^{B}) + \alpha'_{PV}(X_{V}^{S}-X_{V}^{B}) + \alpha'_{PCr}(X_{Cr}^{S}-X_{Cr}^{B}) + \alpha'_{PMo}(X_{Mo}^{S}-X_{Mo}^{B})$

Table 1.	Equations used in calculations	of thermody	<u>ynamic</u>	parameters	of	phosphorus	GBS
	in multicomponent steels						

PHOSPHORUS GBS IN MULTICOMPONENT ALLOYS

To compare the applicability of different models of equilibrium segregation for the calculation of thermodynamic parameters characterising the GBS in multicomponent alloys the specific approach was proposed [15,16]. It consists in the consideration of multicomponent alloy steel as simpler systems. For instance, a Cr-Mo-V low alloy steel was considered to be Fe-P, Fe-Cr-P, Fe-Mo-P, Fe-V-P, Fe-Cr-Mo-P, Fe-Cr-V-P, Fe-Mo-V-P, and Fe-Cr-Mo-V-P system, if the GBS of phosphorus investigated. For each of the enumerated systems segregation equations were set-up. The site competition effect and the influence of intergranular carbides on Auger spectra were omitted. Finally, the values of phosphorus segregation enthalpy (ΔH_P^{0}) , phosphorus segregation entropy (ΔS_P^{0}) , binary interaction coefficient α_{FeP} , and ternary interaction coefficients a'_{PCr} , a'_{PMo} , and a'_{PV} were calculated from values of P, Cr, Mo, V, and Fe grain boundary concentrations using methods of regression analysis. The equations used are listed in Table 1. The results of calculations for one of the investigated low alloy steels (0.12C-0.015P-2.57Cr-0.95Mo-0.34V, mass contents in %) are summarised in Table 2. The physically acceptable values of thermodynamic parameters are marked in bolt. Because the findings for all the investigated steels are comparable, it can be generalised:

- The Langmuir-McLean isotherm (Eq. 1 in Table 1) can be successfully used for routine calculations of phosphorus GBS in multicomponent steels.
- Correlations including the binary interaction term lead to physically meaningless results (Eqs. 2, 4, 6, 8, 10, 12, 14, 16 in Table 1).
- The physically acceptable values of segregation enthalpy (entropy) calculated according to the Langmuir-McLean (Eq. 1 in Table 1) or Guttmann (Eqs. 3, 5, 7, 9, 11, 13, 15 in Table 1) models are comparable.
- Negative values of the ternary interaction coefficients indicate the possibility of attractive interactions between phosphorus and alloying elements (Cr, Mo, and V). However, higher grain boundary concentrations of alloying elements can also originate from intergranular carbides.

Ea Na	ΔH^{θ}_{P}	ΔS^{θ}_{P}	α_{FeP}	α'_{PCr}	α'_{PMo}	α'_{PV}
Eq. No.	[kJ mol ⁻¹]	$[J mol^{-1} K^{-1}]$	[kJ mol ⁻¹]			
1	-30,3	17,1				
2	7,2	52,	29,0			
3	-32,0	14,8			-4,6	
4	6,5	51,3	28,9		-1,5	
5	-31,8	14,6		-6,5		
6	7,1	52,0	28,9	-0,2		
7	-33,1	13,4				-8,9
8	5,6	50,0	28,8			-4,6
9	-33,6	12,0		-6,7	-5,2	
10	6,4	51,1	28,8	-0,3	-1,5	
11	-33,4	12,9			-2,6	-6,9
12	5,5	50,0	28,8		-0,1	-4,5
13	-32,7	13,4		-5,9		-3,5
14	5,7	50,2	29,0	0,8		-5,3
15	-33,4	12,3		-7,1	-5,7	-1,9
16	5,6	50,2	29,0	0,9	0,3	-5,6

Table 2.Thermodynamic parameters of phosphorus segregation for 0.12C-0.015P-2.57Cr-0.95Mo-0.34V steel

INTERACTION BETWEEN GBS AND INTERGRANULAR PRECIPITATION

In the last decade, specific foil-shape particles showing forbidden five-fold rotation symmetry were observed at grain boundaries in 9-12%Cr [11,17,18], austenitic [19], superferritic [20], and duplex Cr-Ni [21] steels. They were classified as quasicrystalline approximants (QA), because the diffraction patterns of them were less clear in comparison to the true quasicrystals. QA exhibited the similar chemical composition as detected for Laves phase of Mo₂Fe (W_2Fe) type. Janovec [12] characterised the sequences of segregation and precipitation processes at grain boundaries in 12Cr-1Mo-0.3V steel during longterm aging at 773 K as follows, Fig. 1:

- During the first stage (up to 10 000 h), P and Mo segregate to grain boundaries and M₂₃C₆matrix interfaces. This leads to the interface enrichment with mentioned elements.
- During the second stage (for terms preceding 10 000 h) foil-shaped QA particles precipitate preferentially along M₂₃C₆ - ferrite interfaces because of an intensive



Figure 1. Mechanism of the QA formation in 9-12 % Cr steels during long-term aging (schematic illustration). Demonstrated for the 12Cr-1Mo-0.3V steel aged at 773 K:

- a) <u>initial state</u>, P and Mo atoms are even distribution in solid solution and $M_{23}C_6$ particles occur at grain boundaries,
- b) for aging terms below 10 000 h, P and Mo segregate at grain boundaries and $M_{23}C_6$ -matrix interfaces,
- c) for aging terms above 10 000 h, thin QA foils dissolving phosphorus precipitate along $M_{23}C_6$ -matrix interfaces and grain boundaries, the grain boundary concentration of phosphorus decreases.

mass transfer. QA dissolves up to 9 at. % of phosphorus [11] what evokes the diffusion of this element from the interfaces into the foil particles (some kind of desegregation). As a result the grain boundary concentration of phosphorus starts to decrease with increasing aging time.

• If the aging is prolonged, the growth of QA foils continues. It was observed almost continuous coverage of grain boundaries by thin QA film [12,22].

Similar course in the kinetic dependence of phosphorus grain boundary concentration as stated for 9-12 % Cr steels was also observed for the low alloy 2.5Cr-0.4Mo-0.25V steel aged



Figure 2. Dependence of the phosphorus grain boundary concentration on aging time at 853 K for 2.5Cr-0.4Mo-0.25V steel. Solid points and solid curve represent the experimental results, dashed curve the theoretical ones.

at 853 K, Fig. 2. For shorter aging times (up to about 1 000 h) the phosphorus grain boundary concentration increases (solid curve) in agreement with the theoretical expectation (dashed line). After about 1 000 h aging the grain boundary concentration of phosphorus starts to decrease with increasing time what is associated with the precipitation of thin Mo-Fe-rich particles (Laves or M_6C phases) containing phosphorus along grain boundaries, Fig. 3. This indicates the mechanism of interaction between segregation and precipitation processes

proposed for 9-12 % Cr steels, Fig. 1, is also applicable for some low alloy steels. The Mo-Fe-rich phase is more probably M_6C , because the occurrence of Laves phase in low alloy steels is not expected according to the thermodynamic calculations [23,24].



Figure 3. Mo-Fe-rich phase identified in 2.5Cr-0.4Mo-0.25V steel after aging for 5 000 h at 853 K:

- a) TEM micrograph showing the substructure of the investigated steel, Mo-Fe-rich particles are marked by arrows,
- b) EDX spectrum corresponding to the phase.

CONCEPT OF GBS REFLECTING INTERFACE GEOMETRY

Lejček and Hofmann [13], Fig. 4, have evidenced the segregation level of P and C in Fe-Si-P-C bicrystals is evidently lower at special grain boundaries than at general ones. They showed

system.



grain boundary concentration of phosphorus (a), and carbon (b), at [100] symmetric tilt grain boundary in the Fe-Si-P-C

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significant also the influence of aging temperature on differences in segregation behaviour of special and general grain boundaries. The differences in P and boundary C grain concentration decrease increasing with aging temperature. This evokes the question, if changes in segregation behaviour of different grain boundaries approximate to some zero point (limit temperature). If yes, what happens at temperatures higher than the limit temperature?

According to the classical thermodynamics, the free energy of segregation (ΔG_i^0) of a solute *i* in the binary system is the function of temperature (T):

$$\Delta G_i^0 = \Delta H_i^0 - T \Delta S_i^0, (1)$$

where enthalpy (ΔH_i^0) and entropy (ΔS_i^0) of

segregation are considered to be constant. It was shown recently the segregation enthalpy and entropy are not constant, but they are dependent on the interface geometry [14]. As stated by Lejček [14], there is a linear relationship between the above quantities, Fig. 5:

$$\Delta H_i^0 = \tau_i \Delta S_i^0 + \omega_i, \qquad (2)$$

where ω_i is the segregation enthalpy of the solute *i* for the grain boundary with $\Delta S_i^0 = 0$. Parameter τ_i represents the segregation analogue to compensation temperature [25] at which ΔG_i^0 is constant for all grain boundaries of different geometry. This makes possible to consider the free energy of segregation as a function of two variables (temperature and interface geometry):

$$\Delta G_i^0 = \Delta S_i^0(\tau_i - T) + \omega_i, \qquad (3)$$

where changes in the interface geometry are reflected in the entropy term ΔS_{i}^{0} . The term ($\tau_{i} - T$) in Eq. 3 indicates all lines representing the temperature dependence of ΔG_{i}^{0} for different interface geometries must intersect the point [τ_{i} ; ω_{i}], Fig. 6. In other words, at lower

temperatures ($T < \tau_i$) the segregation behaviour of two grain boundaries with different geometries (also different values of ΔS^0_i) can be confused in comparison with the segregation behaviour of the same boundaries at higher temperatures ($T > \tau_i$). The introduction of compensation temperature τ_i in the segregation theories led to the new thermodynamic suggestions, which are still waiting for the experimental confirmation.



Figure 5. Dependence of ΔH_i^0 on ΔS_i^0 (*i* = P and C) for different [100] tilt grain boundaries in α -iron (empty symbols). The dashed line represents the summary fit of both C and P data. Additional data taken over from the literature are marked by solid symbols. According to [14], partially modified.



Figure 6. Schematic illustration of dependence of ΔG^{θ}_{i} on *T* for grain boundaries with different geometries (also different values of ΔS^{θ}_{i}): GB1 and GB2. Lines related to the individual boundaries intersect one another in the point $[\tau_i; \omega_i]$, where τ_i is the compensation temperature. At temperature $T_1 < \tau_i$, GB1 exhibit the more negative value of ΔG^{θ}_{i} , at temperature $T_2 > \tau_i$, the more negative value of ΔG^{θ}_{i} corresponds to GB2.

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