# Phosphorus grain boundary segregation in polycrystalline low alloy steels

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16 different approaches (equations) to the calculation of thermodynamic parameters corelating the phosphorus grain boundary segregation ($\Delta H_P^0$, $\Delta S_P^0$, $a_{Fe,P}$, $a'_{PCr}$, $a'_{PMo}$, and $a'_{PV}$) in two low alloy steels were tested. It was shown that the Langmuir-McLean equation can be successfully used in routine calculations of phosphorus grain boundary segregation in multicomponent steels. Calculations according to equations containing the Fowler term lead in this case to physically meaningless results.

## 1. Introduction

Bulk chemical composition [1,2], type of grain boundaries [3,4], and microstructure [5] are the main factors influencing the grain boundary segregation (GBS) of impurities in steels. Because only average chemical composition of numerous grain boundaries is usually measured in polycrystals, obtained results do not reflect some of the above enumerated factors. According to current segregation theories, thermodynamic parameters of GBS in multicomponent polycrystalline steels can be calculated in two principal ways:

- using modified segregation equations and/or values of the equilibrium grain boundary concentration (GBC); this approach can be in contradiction with the current segregation theories,
- considering steels as simple systems and using particular generally accepted segregation equations; the values of equilibrium GBC can also be modified.

**Table 1.** Chemical compositions of the investigated steels in wt. %.

| Element | Cr-steel | Cr-Mo-V-steel |
|---|---|---|
| C | 0.12 | 0.11 |
| Mn | 0.68 | 0.70 |
| Si | 0.32 | 0.27 |
| Cr | 2.48 | 2.62 |
| Mo | 0.03 | 0.69 |
| V | 0.01 | 0.33 |
| S | 0.008 | 0.006 |
| P | 0.011 | 0.014 |
| Fe | bal. | bal. |

In the present work the second approach was used to test the applicability of different equations for description of phosphorus GBS in two low alloy steels.

**Table 2.** GBCs of P, Cr, Mo, and V ($X_P^S$, $X_{Cr}^S$, $X_{Mo}^S$, and $X_V^S$) measured by AES in the investigated Cr- and Cr-Mo-V-steels tempered at 773, 823, and 853 K for 1000 h. GBCs are given in at. %.

| | $X_P^S$ | $X_{Cr}^S$ | $X_{Mo}^S$ | $X_V^S$ |
|---|---|---|---|---|
| Cr-steel, 773 K | 17.0 ± 2.0 | 10.0 ± 2.0 | - - - | - - - |
| Cr-steel, 823 K | 13.5 ± 1.1 | 12.2 ± 2.4 | - - - | - - - |
| Cr-steel, 853 K | 12.2 ± 1.3 | 11.6 ± 1.6 | - - - | - - - |
| Cr-Mo-V-steel, 773 K | 9.4 ± 2.0 | 8.8 ± 2.0 | 6.0 ± 2.8 | 3.0 ± 0.8 |
| Cr-Mo-V-steel, 823 K | 15.3 ± 2.6 | 10.8 ± 1.6 | 6.0 ± 2.0 | 4.0 ± 0.4 |
| Cr-Mo-V-steel, 853 K | 13.8 ± 0.9 | 10.2 ± 1.2 | 5.8 ± 2.2 | 3.8 ± 0.8 |

## 2. Experimental

Multicomponent polycrystalline low alloy Cr- and Cr-Mo-V-steels (see Table 1) were austenitized at 1523 K for 0.75 h, water quenched, and tempered at 773, 823, and 853 K for 1000 h. After tempering, the samples were in-situ fractured at 163 K in UHV chamber of a PHI 4300 SAM system and achieved intergranular facets were immediately analyzed using primary electron beam of 5 kV / 60 nA. For each sample, 8-10 Auger spectra were recorded. In spectra of the Cr-steel, the peaks of P, Cr, C, O, and Fe were identified. The peaks of P, Cr, Mo, V, C, O, and Fe were found in spectra from fracture surfaces of the Cr-Mo-V-steel. The GBCs of P, Cr, Mo, and V were determined following the procedure described in more details in [5]. Because of contamination from the residual gas atmosphere and occurrence of carbide particles at grain boundaries, the C and O peaks were not taken into account. Average values of P, Cr, Mo, and V GBCs ($X_P^S$, $X_{Cr}^S$, $X_{Mo}^S$, and $X_V^S$) are given in Table 2.

**Table 3.** Equations used in calculations of thermodynamic parameters characterizing the phosphorus GBS. $\Delta H_P^0$ is the phosphorus segregation enthalpy, $\Delta S_P^0$ is the phosphorus segregation entropy, $\alpha_{Fe,P}$ is the Fe-P interaction coefficient, $a'_{PCr}$, $a'_{PMo}$, and $a'_{PV}$ are the respective interaction coefficients of phosphorus with chromium, molybdenum, and vanadium.

| No. | Equation |
|---|---|
| 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 | $-RT\ln\frac{X_P^S}{X_P^B(1-X_P^S)} = \Delta H_P^0 - \Delta S_P^0 T + \alpha'_{PCr}(X_{Cr}^S - X_{Cr}^B) + \alpha'_{PMo}(X_{Mo}^S - X_{Mo}^B)$ |
| 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 | $-RT\ln\frac{X_P^S}{X_P^B(1-X_P^S)} = \Delta H_P^0 - \Delta S_P^0 T + \alpha'_{PV}(X_V^S - X_V^B) + \alpha'_{PCr}(X_{Cr}^S - X_{Cr}^B) + \alpha'_{PMo}(X_{Mo}^S - X_{Mo}^B)$ |
| 16 | $-RT\ln\frac{X_P^S}{X_P^B(1-X_P^S)} = \Delta H_P^0 - \Delta S_P^0 T - 2\alpha_{FeP}(X_P^S - X_P^B) + \alpha'_{PV}(X_V^S - X_V^B) + \alpha'_{PCr}(X_{Cr}^S - X_{Cr}^B) + \alpha'_{PMo}(X_{Mo}^S - X_{Mo}^B)$ |

## 3. Theoretical outlines

In calculations, the investigated steels were considered to be simplier systems: Fe-P, Fe-Cr-P, and in the case of Cr-Mo-V steel, Fe-Mo-P, Fe-V-P, Fe-Cr-Mo-P, Fe-Cr-V-P, Fe-Mo-V-P, and Fe-Cr-Mo-V-P. For the binary Fe-P system, the values of segregation enthalpy of phosphorus, $\Delta H_P^0$, and entropy, $\Delta S_P^0$, were calculated according to Langmuir-McLean equation [6]. In some cases, Fowler binary interaction coefficient $\alpha_{FeP}$ [7] between impurity (P) atoms in the matrix (Fe) was considered. In ternary and multicomponent systems, coefficients for ternary interaction [8] between phosphorus and alloying elements $a'_{PCr}$, $a'_{PMo}$, and $a'_{PV}$ were also taken into account. Equations used in calculations are listed in Table 3.

characterizing the GBS of phosphorus in α-Fe, as measured in ferritic steels, range from -10 to -50 kJ mol$^{-1}$ and from 10 to 45 J mol$^{-1}$ K$^{-1}$, respectively [3-5,8]. Interaction coefficients $a'_{PCr}$, $a'_{PMo}$, and $a'_{PV}$ should be negative, when an attractive interaction between phosphorus and alloying elements exists [8]. The last two criteria were fullfilled and acceptable data were obtained in calculations performed according to Eqs. (1) (Langmuir-McLean isotherm), (3), (5), (7), (9), (11), (13), and (15). Unacceptable data (the values differing from those given in literature evidently) belong to the second group. These data result from calculations performed according to Eqs. (2), (4), (6), (8), (10), (12), (14), and (16) which all consider the Fowler term. A comparison of the acceptable data as indicated in bolt in Tables 4 and 5 leads to following findings:

**Table 4.** Values of $\Delta H_P^0$, $\Delta S_P^0$, $\alpha_{FeP}$, and $\alpha_{PCr}$ calculated for the Cr-steel after equations 1, 2, 5 a 6 (see Table 3).

| Equation | $\Delta H_P^0$ [kJ mol$^{-1}$] | $\Delta S_P^0$ [J mol$^{-1}$ K$^{-1}$] | $\alpha_{FeP}$ [kJ mol$^{-1}$] | $a'_{PCr}$ [kJ mol$^{-1}$] |
|---|---|---|---|---|
| **1** | **-22.9** | **27.5** | - - - | - - - |
| 2 | 7.6 | 55.6 | 27.0 | - - - |
| 5 | -22.0 | 29.8 | - - - | 10.8 |
| 6 | 8.2 | 56.0 | 27.6 | -1.3 |

## 4. Results of calculations

Experimental data of GBCs (not only their average values given in Table 2) were used in calculations according to Eqs. (1) - (16) given in Table 3. To determine the values of $\Delta H_P^0$, $\Delta S_P^0$, $\alpha_{FeP}$, $a'_{PCr}$, $a'_{PMo}$, and $a'_{PV}$, the multiple linear analysis was used. Results achieved for the Cr-steel are summarized in Table 4. For the Cr-Mo-V-steel, only the GBCs at the tempering temperatures 823 and 853 K were taken into account, because equilibrium was not reached at 773 K (see Table 2). Obtained results are given in Table 5.

## 5. Discussion

Calculated thermodynamic data summarized in Tables 4 and 5 can be divided into two groups. In the first group, values of $\Delta H_P^0$ and $\Delta S_P^0$ are included that are comparable with those earlier published in literature for similar steels. For instance, the values of $\Delta H_P^0$ and $\Delta S_P^0$

- The values of $\Delta H_P^0$ (of about -22 kJ mol$^{-1}$) and $\Delta S_P^0$ (of about 28 J mol$^{-1}$ K$^{-1}$) determined according to the Langmuir-McLean equation (1) are comparable to each other regardless of chemical composition the steel. This should be expected, because $\Delta H_P^0$ and $\Delta S_P^0$ are thermodynamic parameters of phosphorus GBS in α-Fe independent of presence of other elements in the system [4]. Similarly, the values of $\Delta H_P^0$ and $\Delta S_P^0$ for the Cr-Mo-V-steel determined according to Eqs. (1), (3), (5), (7), (9), (11), (13), and (15) are also comparable. This indicates that the „simple" Langmuir-McLean equation can be successfully used for routine calculations of phosphorus GBS in multicomponent low alloy steels.
- Thermodynamic calculations considering the Fowler term lead to physically meaningless results (e. g., positive values of $\Delta H_P^0$ and ternary interaction coefficients).

**Table 5.** Values of $\Delta H_P^0$, $\Delta S_P^0$, $a_{Fe,P}$, $a'_{PCr}$, $a'_{PMo}$, and $a'_{PV}$ calculated for the Cr-Mo-V-steel according to Eqs. (1)-(16).

| Eq. | $\Delta H_P^0$ [kJ mol$^{-1}$] | $\Delta S_P^0$ [J mol$^{-1}$ K$^{-1}$] | $\alpha_{Fe,P}$ [kJ mol$^{-1}$] | $a'_{PCr}$ [kJ mol$^{-1}$] | $a'_{PMo}$ [kJ mol$^{-1}$] | $a'_{PV}$ [kJ mol$^{-1}$] |
|---|---|---|---|---|---|---|
| **1** | **-21.3** | **28.7** | --- | --- | --- | --- |
| 2 | 5.9 | 52.3 | 25.7 | --- | --- | --- |
| **3** | **-22.1** | **26.1** | --- | --- | **-23.7** | --- |
| 4 | 6.2 | 52.6 | 25.9 | --- | 1.0 | --- |
| **5** | **-20.5** | **29.4** | --- | **-2.4** | --- | --- |
| 6 | 7.0 | 53.2 | 25.7 | -3.2 | --- | --- |
| **7** | **-20.8** | **27.5** | --- | --- | --- | **-44.6** |
| 8 | 6.0 | 52.5 | 25.8 | --- | --- | 3.4 |
| **9** | **-20.7** | **27.3** | --- | **-4.7** | **-24.0** | --- |
| 10 | 7.1 | 53.4 | 25.9 | -3.2 | 0.8 | --- |
| **11** | **-21.9** | **26.0** | --- | --- | **-22.0** | **-11.4** |
| 12 | 6.1 | 52.6 | 25.9 | --- | 0.6 | 2.6 |
| **13** | **-19.7** | **28.4** | --- | **-3.5** | --- | **-45.0** |
| 14 | 7.0 | 53.4 | 25.8 | -3.2 | --- | 3.0 |
| **15** | **-20.4** | **27.3** | --- | **-4.8** | **-22.2** | **-11.8** |
| 16 | 7.1 | 53.5 | 25.9 | -3.2 | 0.4 | 2.4 |

- Negative values of the interactive coefficients ($\alpha_{PCr} \approx$-3.8 kJmol$^{-1}$, $\alpha_{PMo} \approx$ -23.0 kJmol$^{-1}$, and $\alpha_{PV} \approx$ -11.0 or -45.0 kJmol$^{-1}$) indicate existence of attractive interactions between phosphorus and alloying elements (Cr, Mo, V) in the Cr-Mo-V-steel.

## 6. Conclusions

Based on the correlation of phosphorus GBS for two low alloy steels using 16 different equations, following conclusions can be drawn:

- The Langmuir-McLean isotherm can be successfully used in routine calculations of phosphorus GBS in multicomponent low alloy steels.
- Correlations including the Fowler term lead to physically meaningless results.
- Negative values of interaction coefficients describe existence of attractive interactions between phosphorus and alloying elements (Cr, Mo, and V) in the Cr-Mo-V-steel.

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