Some Aspects of Impurity Grain Boundary Segregation in Low Alloy Cr-Mo-V Steels

Segregacije nečistoč v nizko legiranih Cr-Mo-V jeklih

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The present work is focused on theories of grain boundary segregation. An overview of different approaches to solution of surface enrichment phenomenon is given in the first part. The second part is devoted to the verification of introduced theories by means of experimental results.

Key words: low alloy steels, phosphorus, grain boundary segregation, non-equilibrium segregation, kinetics

V članku so predstavljene teorije različnih avtorjev o segregaciji po mejah zrn. V prvem delu je podan pregled različnih razlag obogatitve prostih površin. V drugem delu smo obravnavane teorije verificirali z eksperimentalnimi rezultati.

Ključne besede: nizko legirana jekla, segregacija po mejah zrn, neravnotežne segregacije, kinetika segregacije po mejah zrn

1 Introduction

Enrichment of solute or solvent atoms from bulk at the grain boundaries is referred to as grain boundary segregation. Segregation is mostly attributed to the grain boundary weakening due to lowering the interface cohesion. As a consequence, an intergranular embrittlement occurs. Because segregation phenomenon decisively influences properties of commercial materials, the grain boundary segregation has been intensively studied in last decades[1-8].

The present work deals with segregation theories[9-15] and their experimental verification. By use of multicomponental alloys in the verification, the introduction of some simplifications is necessary because the segregation theories were mostly derived for binary or ternary solid solutions. For example, low alloy steels containing Fe, Cr, Mo, V, Mn, Si, C and P were considered to be binary Fe-P or ternary Fe-Mo-P systems[13-15].

2 Segregation theories

2.1 Non-interactive equilibrium segregation

The theory of equilibrium segregation for dilute binary solid solution Fe-I (Fe - solvent, I - solute impurity) was derived by McLean to be the grain boundary analogous of Langmuir adsorption at free surfaces[1,16]. The Langmuir-McLean isotherm yields:

$$\frac{C_I^{Eeq}}{1-C_I^{Eeq}} = \frac{C_I^B}{1-C_I^B} \exp\left(-\frac{\Delta g_I}{kT}\right), \quad (1)$$

where C_I^{Eeq} is the equilibrium grain boundary concentration of impurity, C_I^B is the bulk concentration of impurity, Δg_I is the free energy of impurity segregation, and k is the Boltzmann constant.

The equilibrium segregation kinetics can be calculated as[1]:

$$\frac{C_I^E(t) - C_I^{E0}}{C_I^{Eeq} - C_I^{E0}} = 1 - \exp\left[\frac{4D_I t}{(\alpha_I^E)^2 (d^E)^2}\right] \text{erfc}\left(2\frac{\sqrt{D_I t}}{\alpha_I^E d^E}\right), \quad (2)$$

where $C_I^E(t)$ is the grain boundary concentration of impurity for the time t, $C_I^{E0} = C_I^E(t=0)$ is the initial concentration of impurity, d^E is the grain boundary thickness, D_I is the diffusion coefficient of impurity, and $\alpha_I^E = C_I^{Eeq}/C_I^{E0}$ is the enrichment factor.

2.2 Interactive equilibrium segregation (co-segregation)

Guttmann[4,17] modified the Langmuir-McLean isotherm to be suitable for the calculation of interactive equilibrium segregation in ternary Fe-M-I systems. He assumed for this system an attractive interaction between the impurity I and the solute metalic element M. If the M-I competition for convenient sites at the grain boundary exists, impurity grain boundary concentration can be calculated according to:

$$\frac{C_i^{Eeq}}{1-C_I^{Eeq}-C_M^{Eeq}} = \frac{C_i^B}{1-C_I^B-C_M^B} \exp\left(-\frac{\Delta g_i}{kT}\right), \quad i=I, M \quad (3)$$

The interaction leading to the M-I co-segregation was defined in terms of segregation free energy, Δg_i, i = I, M:

$$\Delta g_I = \Delta g_I^0 - 2\alpha_{FeI}C_I^{Eeq} + \alpha'_{MI}(C_M^{Eeq} - C_M^B), \quad (4)$$

$$\Delta g_M = \Delta g_M^0 - 2\alpha_{FeI}(C_M^{Eeq} - C_M^B) + \alpha'_{MI}C_I^{Eeq}, \quad (5)$$

where Δg_I^0 and Δg_M^0 are the free energies of segregation for I and M in their respective binary systems with

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Fe, while α'_{MI} and α_{FeI} are the relative chemical interaction energies between M-I and Fe-I, respectively. For non-competitive segregation the following expression was obtained[17,18]

$$\frac{C_i^{Eeq}}{1 - C_i^{Eeq}} = \frac{C_i^B}{1 - C_i^B} \exp\left(-\frac{\Delta g_i}{kT}\right), \quad i=I, M \qquad (6)$$

where Δg_i has the same meaning as in the previous case.

Kinetics of interactive segregation can be described by means of the regular solution model proposed by Seah[18]. In the model it is assumed a local equilibrium between concentrations of impurity at the grain boundary, $C_I^E(t)$, and in adjacent bulk layers, $C_I^B(t)$. Then

$$\frac{C_I^E(t)}{1 - C_I^E(t)} = C_I^B(t) \exp\left(-\frac{\Delta g_I}{kT}\right) \qquad (7)$$

The combination of equations (4) and (7) is frequently used in kinetic calculations, as firstly by Tyson[19].

In recently proposed theories, the grain boundary segregation is assumed to be a bulk-diffusion-controlled process. There are also kinetic models favouring other controlling mechanisms, for instance the fast diffusion path[20,21] or the grain boundary diffusion[22,23]. Du Plessis and Van Wyk[24], for instance, proposed a model considering the chemical potential gradient as a driving force of the grain boundary segregation.

2.3 Non-equilibrium segregation

Non-equilibrium segregation theory was established by Aust et al.[25] and Anthony[26]. They supposed that vacancies and impurities form vacancy-impurity complexes with a binding energy higher than the thermal energy. The controlling mechanism of non-equilibrium segregation is the vacancy concentration gradient. The higher temperature the higher is the equilibrium concentration of vacancies. The temperature decrease during rapid cooling leads to a loss of vacancies along grain boundaries due to their annihilation. This process is in accordance with the tendency to achieve a lower equilibrium concentration of vacancies at lower temperature. The vacancy concentration decrease near the grain boundaries results in the dissociation of vacancy-impurity complexes in this region. In the interior of grains, where less vacancy sinks are present, the concentrations of vacancies and vacancy-impurity complexes decrease lesser. Consequently, the diffusion of the complexes from interior to the grain boundaries occurs due to the concentration gradient between these two areas. The process leads to an excessive impurity concentration near the grain boundaries and causes the non-equilibrium segregation.

The model of non-equilibrium segregation was proposed by Faulkner[6] and extended by Xu Tingdong[27]. When a sample is held at the solution-treatment temperature T_0 and then quickly cooled to the lower temperature T, the maximum of the impurity grain boundary concentration C_I^{Nmax} induced during holding at the temperature T is calculated as[6,27]:

$$C_I^{Nmax} = C_I^B \left(\frac{E_b}{E_f}\right) \exp\left(\frac{E_b - E_f}{kT_0} - \frac{E_b - E_f}{kT}\right), \qquad (8)$$

where E_b is the vacancy-impurity atom binding energy and E_f is the energy of vacancy formation. The kinetic equation of non-equilibrium segregation has a form[27]:

$$\frac{C_I^N(t) - C_I^{N0}}{C_I^{Nmax} - C_I^{N0}} = 1 - \exp\left[\frac{4D_c t}{(\alpha_I^N)^2 (d^N)^2}\right] \text{erfc}\left(2\frac{\sqrt{D_c t}}{\alpha_I^N d^N}\right), \quad (9)$$

where $C_I^N(t)$ is the grain boundary concentration of impurity for time t, $C_I^{N0} = C_I^N(t=0)$ is the initial concentration of impurity, D_c is the diffusion coefficient of complexes, d^N is the thickness of grain boundary, and $\alpha_I^N = C_I^{Nmax}/C_I^{N0}$ is the enrichment factor. The equation (9) is used for times of impurity diffusion shorter than the critical time. The critical time t_c is given by[27]

$$t_c = \frac{\gamma^2 \ln(D_c/D_I)}{4\delta(D_C - D_I)} \qquad (10)$$

where γ is the average austenite grain size and α is the critical time constant[28]. For times of impurity diffusion longer than the critical time the process of desegregation occurs.

The concentration level of impurity at grain boundaries during the desegregation can be calculated according to[29,30]:

$$C_I^N(t) = C_I^B + \frac{1}{2}[C_I^N(t_C) - C_I^B] \cdot$$

$$\cdot[\text{erf}(\frac{d^N/2}{[4D_I(t - t_c)]^{1/2}}) - \text{erf}(\frac{-d^N/2}{[4D_I(t - t_c)]^{1/2}})]; \quad t > t_c \quad (11)$$

The process in which the desegregation is dominant can only occur when $C_I^N(t_c) > C_I^{Eeq}$ for a given temperature. It means the desegregation is limited by reaching the equilibrium grain boundary concentration. The migration of grain boundaries during austenitizing and recrystallization can also contribute to the non-equilibrium segregation in term of a sweep effect. The nature of this phenomenon resides in embedding and subsequent dragging of solute species by moving grain boundary. As a consequence the grain boundary enrichment of solute species occurs[31,32].

2.4 Segregation under stress

Stress and thermal energy does not affect the equilibrium grain boundary concentration of impurities during the tempering (aging) significantly, but it influences segregation kinetics. Grain boundary segregation of impurities with higher diffusivity can be enhanced effectively by applied stress. Atoms of some impurities (e.g. carbon, nitrogen, boron) fastly occupy the convenient sites on grain boundaries and they prevent subsequently due to competition effect the segregation of other elements[33-35].

Shinoda and Nakamura[36] studied the grain boundary segregation of phosphorus in low carbon steel during long-term tempering and subsequent aging under stress at the same temperature. In the first step of aging under

tension (compression) phosphorus grain boundary concentration increases (decreases), then its value approximate to the initial one[36]. Changes in impurity concentration at the grain boundaries oriented normal to the applied stress ΔC_I^S can be calculated as follows[37]:

$$\Delta C_I^S = \frac{4\phi C_I^{S0} D_I \rho \sigma \Delta t}{\gamma^2 RT} , \qquad (12)$$

where ϕ is a numerical factor of the order of unity, C_I^{S0} is the initial grain boundary concentration of impurity, ρ is the specific volume of alloy, σ is the stress related to the grain boundary, and Δt is the aging time under stress.

3 Verification of segregation theories

To verify the above described theories the phosphorus grain boundary segregation in five low alloy steels was investigated, **Table 1**. Schedules of heat treatment and phases identified in individual investigated steels termed 1, 2, 3, 4, and 5 are given in **Table 2**. Grain boundary concentrations of relevant elements were calculated after Davis et al.[38] from Auger spectra. Peaks of P_{120eV}, S_{152eV}, Mo_{186eV}, C_{272eV}, N_{379eV}, V_{473eV}, Cr_{529eV} and Fe_{703eV} were used in calculation. The peak of oxygen was not considered because of additional adsorption of this element on freshly fractured surface. Parameters, at which Auger spectra were achieved are given in Ref.[13,15].

Table 1: Chemical composition of investigated steels in wt.%

Steel	C	P	Mn	Si	Cr	Mo	V	Ni	S
1	0.110	0.004	0.525	0.385	2.685	0.694	0.355	-	0.010
2	0.100	0.014	0.700	0.270	2.620	0.690	0.330	-	0.007
3	0.110	0.027	0.665	0.340	2.700	0.733	0.357	-	0.010
4	0.060	0.013	0.650	0.290	2.660	0.700	0.310	-	0.009
5	0.160	0.014	0.460	0.290	2.700	0.640	0.300	0.060	0.015

Table 2: Schedules of heat treatment and phases identified in investigated steels

Steel	Heat treatment	Phases identified
1	1250°C/0.75h, water quenching,	
2	680°C/20 h, water cooling, Ferrite+M$_7$C$_3$+MC	
3	aging at 500°C for 0.33h,1h,5h,150h	
4	1250°C/0.16h, water quenching, 680°C/20h, water cooling, aging 580°C for 5 min and 150h	Ferite+M$_7$C$_3$+MC
5	welding cycle:T$_{max}$=1300°C $\Delta t_{8/5}$=30s, 580°C/100h	Ferrite+M$_3$C+M$_7$C$_3$
	welding cycle:T$_{max}$=1300°C,$\Delta t_{8/5}$=30s, 600°C/120s under stress(strain rate 300mm.h^{-1})	Ferrite+M$_3$C

Phosphorus grain boundary concentrations measured for steels 1, 2, 3 aged at 500°C for different times showed the best fit with McLeans non-interactive kinetic equation (2), (**Figure 1**). The segregation can be characterized as slow, because after 150 h aging the equilibrium was not reached for any of the steels. A completely different situation was observed for steel 4 aged at 580°C
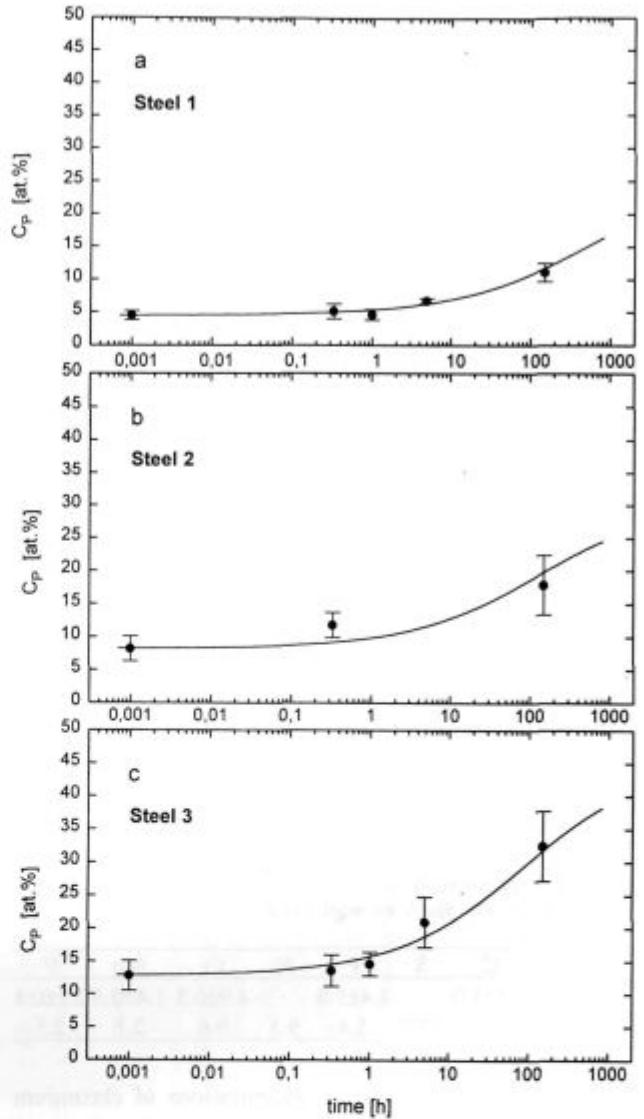

Figure 1: McLean's non-interactive equilibrium kinetic equation fitted to values of phosphorus grain boundary concentration for steels: 1 (a), 2 (b), and 3 (c), aged at 500°C (after[15])
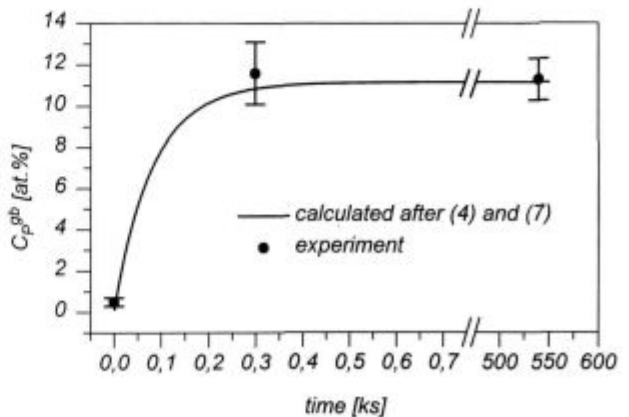

Figure 2: Interactive kinetic equations (4) and (7) fitted to values of phosphorus grain boundary concentration for steel 4 aged at 580°C (after[13])

(**Figure 2**). Here, the measured values of phosphorus grain boundary concentrations correlate with the curve, calculated according to equations (4) and (7). The equilibrium was reached after 5 min, and that indicates to very rapid segregation process. The obtained results showed that both rate of equilibrium segregation and also participations of interactions in this process are temperature dependent. McLean's non-interactive kinetic theory seems to be available for the description of segregation kinetics at lower aging temperatures (slower segregation rates) and interactive equations are more convenient for higher ones (accelerated segregation rates).

In **Figure 3** Auger spectra for the steel 5 after tempering (a) and short-term aging under stress (b) are shown. For loaded state the peaks of C, S, N, and Cr were evidently higher than for tempered one (**Table 3**). Differences between carbon, sulphur and phosphorus grain boundary concentrations for the loaded state can be explained by different diffusivity of these elements in iron at 600°C[20,39,40]. Atoms of carbon and sulphur diffuse faster than phosphorus atoms and occupy earlier convenient sites at grain boundaries. Site competition between P-C and P-S[5,41] make impossible an additional phosphorus enrichment at grain boundaries. With prolonging the aging an increase in phosphorus and a decrease in carbon grain boundary concentrations occur because of carbide precipitation[5,42,43].

Table 3: Experimentally measured grain boundary concentrations of C, S, P, N, Cr, Mo, and V for steel 5 in at.%

	C	S	P	N	Cr	Mo	V
tempered	9.5±1.0	-	4.4±1.6	-	4.9±0.5	1.4±0.5	2.7±0.4
stressed	26.9	17.7	5.4	9.3	9.6	2.1	2.5

Higher grain boundary concentrations of chromium and nitrogen in the first period of aging under stress are probably caused by Cr-N interactive segregation. Misra and Balasubramanian[34,35] supposed a Cr-N co-segregation (stressing up to 5 min at 580°C) due to strong chemical interaction between these elements. After reaching the maximum coverage (depending on aging temperature), a continuous decrease in Cr and N grain boundary concentrations occurs.

The shape of carbon peaks (**Figure 3**) indicates the occurence of carbide particles on the grain boundaries[44]. Then, also peaks of alloying elements, preferentially Cr, must originate partially from these particles[45-47]. Reflexes originating from intergranular carbide particles mostly influence the achieved spectra and they can not be neglected in interpretation of grain boundary segregation in multicomponent alloys.

4 Concludig remarks

An overview of the theories of grain boundary segregation is given in the present work. The verification of
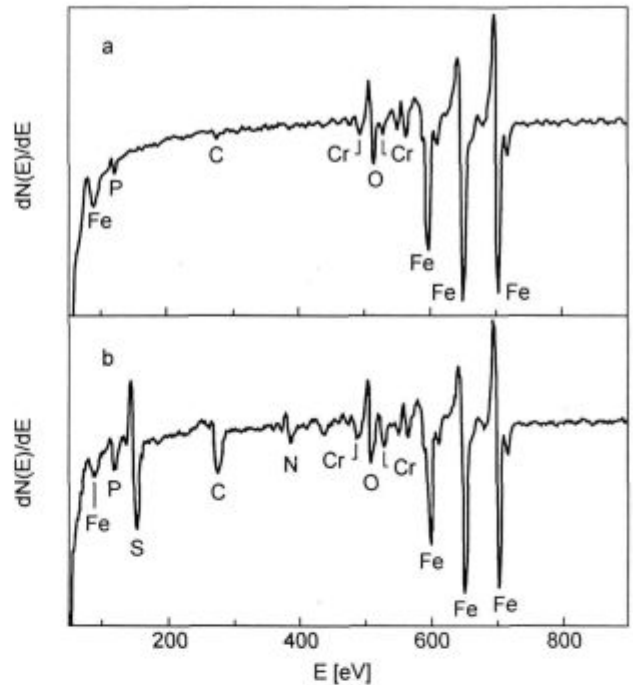

Figure 3: Characteristic Auger spectra taken on intergranular facets of steel 5: a) tempered at 580°C for 100 h, b) aged under stress for 120 s at 600°C

the theories for multicomponent Cr-Mo-V low alloy steels leads to the following findings:

1. The McLean's non-interactive equation is the most convenient for the description of equilibrium segregation kinetics at lower temperatures (500°C), while the interactive equations are more suited for the description of equilibrium segregation kinetics at higher temperatures (580°C)

2. In comparision with unstressed aging, the higher rates of C, S, N and Cr grain boundary segregation in the first period of the aging under stress (600°C) were observed

3. In the investigated multicomponent steels, an influence of carbide particles on achieved Auger spectra can not be neglected.

5 References

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