

SOME ASPECTS OF CARBIDE PRECIPITATION AND PHOSPHORUS GRAIN BOUNDARY SEGREGATION IN Cr-V LOW ALLOY STEELS

NEKATERE ZNAČILNOSTI TVORBE KARBIDOV IN SEGREGACIJ NA KRISTALNIH MEJAH PRI MALOLEGIRANIH CrV JEKLIH

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Phosphorus grain boundary segregation was investigated at 773 and 853 K for three Cr-V low alloy steels with different vanadium contents. AES and TEM methods were used for determination of the segregating elements enrichment on grain boundaries and phase identification, respectively. Phosphorus segregation enthalpy and entropy, as well as the phase equilibria for both temperatures, were determined by means of thermodynamic calculations. Aging up to 1000 hours was sufficient to achieve the equilibrium state of phosphorus segregation at the aging temperatures. In agreement with Langmuir-McLean theory, the phosphorus grain boundary equilibrium concentration decreases with the temperature. The aging conditions, however, were not sufficient to achieve the phase equilibrium. According to thermodynamic calculations, the steels should consist of ferrite, M₇C₃, and MC phases while only the ferrite, M₃C and MC (M₇C₃ only in one state at the higher aging temperature) were found experimentally. Chemical composition changes of analyzed carbides also confirmed the non-equilibrium state of precipitation. The changes accompanying the non-equilibrium development of phases show a direct influence on phosphorus segregation, especially at 773 K. As a consequence, the supporting effect of vanadium on phosphorus segregation, observed at 853 K is not clear at this lower temperature.

Key words: low alloy steels, carbide precipitation, carbide composition, grain boundaries, phosphorus segregation

Raziskana je bila segregacija fosforja na kristalnih mejah pri 773 in 853 K pri treh malolegiranih jeklih z nizko vsebnostjo vanadija. Uporabljeni sta bili AES in TEM metodi. Entalpija in entropija segregacije ter fazna ravnotežja so bila termodinamično izračunana. Staranje 1000 ur je bilo zadostno za doseganje ravnotežne segregacije fosforja. V soglasju s teorijo Langmuir-McLean je ravnotežna segregacija fosforja manjša pri nižji temperaturi. Staranje v trajanju 1000 ur pa ni bilo zadostno za doseganje faznega ravnotežja. Na osnovi termodinamskih izračunov je pričakovana fazna sestava jekla ferit, M₇C₃ in MC, eksperimentalno pa so najdeni ferit, M₃C in MC ter M₇C₃ samo po žarjenju pri višji temperaturi. Tudi kemična sestava izločenih karbidov je dokazala neravnotežno izločanje. Nastanek neravnotežnih konstituent mikrostrukture kaže na neposreden vpliv segregacije fosforja, posebno pri 773 K. Kot posledica se pri nižji temperaturi ni jasno pokazal pospeševalen vpliv vanadija na segregacijo fosforja.

Ključne besede: malo legirano jeklo, precipitacija karbidov, sestava karbidov, kristalne meje, segregacija fosforja

1 INTRODUCTION

Low alloy steels are widely used in various industrial areas in conditions of high temperature and stress. However, in these circumstances the steels are relatively sensitive to intercrystalline embrittlement as a consequence of grain boundary impurity segregation^{1,2}.

This work deals with the influence of vanadium on the phosphorus grain boundary (GB) segregation and the influence of carbide reactions during aging.

The thermodynamic description of segregation is based on the Langmuir-McLean isotherm. There are many approaches³⁻⁷ modifying the isotherm. Individual models and approaches have been discussed in detail e.g. by Lejček⁸.

Thermodynamic aspects of phosphorus GB segregation in low alloy CrMoV steels have recently been studied by Janovec et al.⁹. One of the main conclusions was that the above mentioned Langmuir-McLean equation for a binary ideal solid solution can be

successfully used in routine thermodynamic calculations for multicomponent steels. In accordance with this finding, the following form of the Langmuir-McLean equation⁸ was used in this paper:

$$\Delta H_p^0 - \Delta S_p^0 T = -RT \ln \frac{X_p^S}{X_p^B (1 - X_p^S)} \quad (1)$$

where: ΔH_p^0 and ΔS_p^0 are the enthalpy and entropy of phosphorus segregation, respectively, R is the gas constant, T is the aging temperature, and X_p^S and X_p^B are the grain boundary and bulk phosphorus concentrations, respectively.

2 EXPERIMENTAL

Three experimental low alloy steels with different vanadium contents were used for the investigation, see **table 1**. The experimental material was heat treated as follows:

1. austenitization 1323 K/0.5h → quenching in 10% water solution of KOH (average grain size 100-150 μm),
2. tempering 953 K/2h → water cooling,
3. aging 773 and 853 K for 0.1, 0.5, 1, 5, 10, 100, and 1000 h → water cooling.

The grain boundary concentration of segregated elements was evaluated from Auger spectra achieved by means of an AES microprobe operating at UHV 10⁻⁸ Pa, with energy 5 keV, primary beam current 3 μA, and primary beam size 50 μm. Carbon extraction replicas were used for phase analysis by TEM and EDX.

Table 1: Chemical composition of investigated steels [mass %]

Steel	C	Cr	Mn	P	Si	S	V
11	0.12	0.89	0.33	0.045	0.23	0.004	0
33	0.13	0.88	0.34	0.047	0.24	0.004	0.26
37	0.13	0.88	0.33	0.040	0.23	0.004	0.51

3 RESULTS

Auger peak heights P_{120eV}, C_{272eV}, Cr_{529eV}, V_{473eV}, and Fe_{703eV} were used for calculation of the GB concentration of appropriate elements according to Eq. 2 [11]:

$$X_i^S = \frac{K_i}{S_i} \left(\sum_j \frac{K_j}{S_j} \right)^{-1} \quad (2)$$

where K_i and K_j are the Auger peak heights of the elements i and j , respectively, and S_i and S_j are the relative Auger sensitivities of the corresponding elements. In **Figs. 1 and 2**, the concentrations of P, V and Cr are plotted as a function of aging time.

The phosphorus segregation kinetics in ideal solid solution can be described by the McLean equation [10]:

$$\frac{X_P^S(t) - X_P^S(0)}{X_{P_{eq}}^S - X_P^S(0)} = 1 - \exp\left(\frac{4D_P k}{\alpha^2 d^2}\right) \operatorname{erfc}\left(\frac{2\sqrt{D_P t}}{\alpha d}\right) \quad (3)$$

where the term $X_P^S(t)$ represents the GB concentration of phosphorus at time t , $X_P^S(0)$ is the initial GB concentration of phosphorus (after tempering and cooling), d is the GB thickness, the term D_P is the coefficient of phosphorus bulk diffusion in α -iron. The enrichment factor α represents the ratio of $X_{P_{eq}}^S / X_P^B$. In the calculations the value $d = 5.5 \cdot 10^{-10}$ m was used.

By fitting Eq. 3 to the measured GB phosphorus concentration in **figs. 1a and 2a**, the values of $X_{P_{eq}}^S$ (**tab. 2**) and D_P were determined [in m²/s]: $D_P = 3.4 \cdot 10^{-10} \cdot \exp(-137 \text{ kJmol}^{-1}/RT)$ for steel 11, $D_P = 5.7 \cdot 10^{-9} \cdot \exp(-141 \text{ kJmol}^{-1}/RT)$ for steel 33, and $D_P = 1.7 \cdot 10^{-8} \cdot \exp(-148 \text{ kJmol}^{-1}/RT)$ for steel 37.

On the basis of Eq. 1, the values of the Gibbs free energy for phosphorus GB segregation in the form $\Delta G_P^0 = \Delta H_P^0 - \Delta S_P^0 \cdot T$ were achieved by linear regression:

$$\text{steel 11: } \Delta G_P^0 = -24041 - 18.8 \cdot T \text{ [kJ/mol]}$$

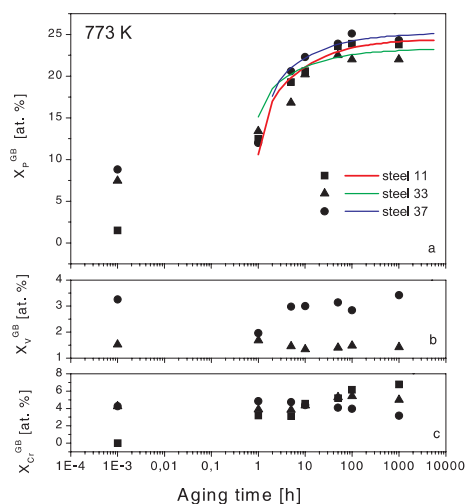


Figure 1: GB concentration of P, V, Cr in steel 11 (0% V), steel 33 (0.26% V) and steel 37 (0.51% V) at 773 K

Slika 1: Koncentracija P, V in Cr na mejah v jeklu 11 (0%V), jeklu 33 (0.26%V) in jeklu 37 (0.51%V) po staranju pri 773 K

$$\text{steel 33: } \Delta G_P^0 = -13778 - 31.2 \cdot T \text{ [kJ/mol]}$$

$$\text{steel 37: } \Delta G_P^0 = -10212 - 37.5 \cdot T \text{ [kJ/mol]}$$

Phase analyses of the experimental states showed the presence of ferrite, MC and M₃C phases. In steel 11, without vanadium, MC carbide was absent, however MX particles, most probably Cr₂N, were found. In steel 37, with 0.5 mass % V, M₃C carbide was not found at all. Moreover, traces of M₇C₃ carbide were found in steel 33, aged at 853 K for 1000 h.

According to the thermodynamic phase equilibria calculations provided by the PD-pp software package¹², the systems in equilibrium should contain the carbide M₇C₃, instead of M₃C. Experimentally measured ratios of V/Cr in MC, and calculated volume fractions of M₇C₃ and MC are given in **Tab. 2**.

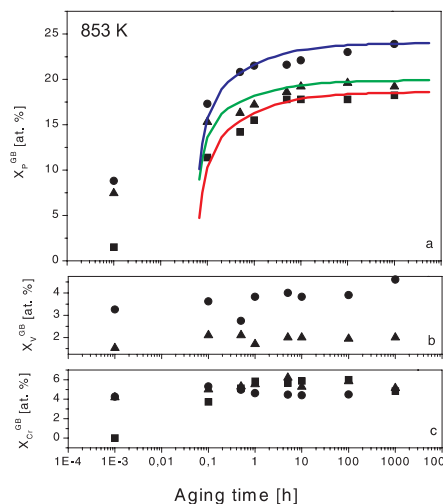


Figure 2: GB concentration of P, V, Cr in steel 11 (0% V), steel 33 (0.26% V) and steel 37 (0.51% V) at 853 K

Slika 2: Koncentracija P, V in Cr na mejah v jeklu 11 (0%V), v jeklu 33 (0.26%V) in v jeklu 37 (0.51%V) po staranju pri 853 K

Table 2: Some experimental and calculated data for investigated steels

Steel	T [K]	$X_{\text{Peq}}^{\text{S}}$ [at. %]	Volume portion (calc.) [vol. %]		V/Cr [at. %/at. %] in MC (exp.)		
			M_7C_3	MC		100h	1000h
11	773	24.5	1.77	-	-	-	-
	853	18.6	1.75	-	-	-	-
33	773	23.3	1.07	0.61	4.7	-	4.4
	853	19.9	1.21	0.54	4.7	6.1	2.98
37	773	25.2	0.38	1.05	9.8	-	7.3
	853	24.0	0.38	1.05	9.8	26.3	6.02

4 DISCUSSION

The kinetics of phosphorus GB segregation for the lower aging temperature is slower than at the higher temperature in all the investigated steels, **Figs. 1a and 2a**. Grain boundaries are approximately saturated after 100 hours in the former case, while this state is achieved after one hour at the higher temperature. The phosphorus grain boundary concentrations at 773 K are higher (24.5, 23.3, 25.2 at.%) than at 853 K (18.6, 19.9, 24.0 at.%) which is in agreement with the Langmuir-McLean theory.

The experimental results also show a positive correlation between bulk vanadium concentration and phosphorus GB concentration at 853 K. This behaviour can be explained by the indirect influence of vanadium through the P-C site competition effect^{13,14}. Strong V-C affinity and precipitation of the V-rich carbides leads to a decrease of carbon activity and thus enables P atoms to segregate at the GB. At the lower aging temperature, differences between phosphorus GB concentrations are smaller. Also, in contrast to 853 K, the experimental values in steel 33 with a higher bulk content are lower than the values in steel 11, without vanadium. This could be ascribed to the precipitation processes that are discussed later.

The GB concentration of vanadium can be said to be practically constant during the aging treatment, **Figs. 1b and 2b**. In the case of Cr, especially at the lower temperature, a slight tendency for a concentration increase (steel 11) and concentration decrease (steel 37) can be seen, **Figs. 1c and 2c**, respectively.

Comparison of the experimentally determined phases and the calculated equilibrium phase composition shows clearly that after 1000 hours of aging the phase equilibrium has not yet been achieved for both temperatures. The applied aging conditions are not sufficient for precipitating the M_7C_3 carbide^{15,16}, the amount of which, according to thermodynamic calculations, decreases from 1.77 to 0.38 vol.% in the investigated steels with increasing vanadium bulk content. The conditions were suitable for the precipitation of M_3C in which the Fe/Cr atomic ratio decreases with increasing time from 16.6 to 2.6 in steel 11 and from 4 to 0.81 in steel 33, which means

enrichment of the carbide by Cr. This, together with Cr_2N precipitation at the GB¹⁷ leads to the increase in Cr concentration at the GB in steel 11. Precipitation of Cr_2N particles results in a decrease of Cr activity which can also be a cause of M_7C_3 carbide precipitation delay.

No M_3C was found in steel 37, but there is a large quantity of MC, in particular (V,Cr)C, which precipitates mainly in the matrix. During aging, this carbide is enriched by Cr as can be seen from the decreasing V/Cr ratio, **Tab. 2**. Simultaneously, the amount of (V,Cr)C carbide increases, the carbon activity reduces which worsens the conditions for precipitating both M_3C and M_7C_3 carbides. Such behaviour is known in steels with a high V content (similar to steel 37) without any other strong carbide-forming element and a Cr content of about 2 mass¹⁵. This could explain the decrease in Cr concentration at the GB in steel 37.

It can be stated that the phosphorus GB concentration values will become constant only after the systems achieve equilibrium from the point of view of phase composition.

5 CONCLUSIONS

By investigating GB segregation and precipitation processes in three Cr-V low alloy steels it was found that after aging at 773 K and 853 K, equilibrium values of phosphorus GB segregation were achieved. Concerning the phase composition, 1000 h aging at both temperatures was not sufficient to achieve phase equilibria.

The following further conclusions can be drawn:

1. at the lower aging temperature, the phosphorus GB segregation is slower and achieves higher equilibrium values than at the higher temperature;
2. vanadium indirectly influences the phosphorus GB segregation, the higher the bulk vanadium content the higher the GB concentration of phosphorus;
3. precipitation of MX (Cr_2N) at GBs leads to a delay in M_7C_3 carbide formation and to the slight increase in GB chromium concentration in the steel without vanadium;
4. precipitation of (V,Cr)C in the matrix results in the delay of M_7C_3 carbide formation and a slight decrease of GB chromium concentration in the steel with the highest vanadium bulk content.

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