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Non-equilibrium grain boundary segregation kinetics of phosphorus in 12Cr1MoV steel at different solution temperatures

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The non-equilibrium grain boundary segregation (NGS) concentrations of phosphorus in an industrial steel, 12Cr1MoV, at different solution temperatures, 1050 and 1300°C, were measured. The NGS kinetics curves of phosphorus at the isothermal holding temperature of 540°C are given. These results provide direct support for a NGS kinetic model, and also show that the higher the solution temperature, the higher the segregation concentration of phosphorus at the grain-boundaries, and also the longer the critical time. © *2004 Kluwer Academic Publishers*

1. Introduction

The non-equilibrium grain-boundary segregation (NGS) theory was established by Aust *et al.* [1] and Anthony [2]. They supposed that the mechanism of segregation is based on equilibrium where a sufficient quantity of vacancy-solute atom complexes exists. All three components (solute atom, vacancy and their recombined complex) are in equilibrium with each other at high temperature. The higher the temperature, the higher is the equilibrium concentration of vacancies. The temperature decrease during rapid cooling leads to 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 temperatures. The vacancy concentration decrease near the grain boundaries results in the dissociation of the complexes into vacancies and solute atoms. This in turn gives rise to the decrease in the complex concentration near the grain boundary. Meanwhile, in the interior of grains, where less vacancy traps are present, vacancies would recombine with solute atoms and reduce the vacancy concentration. This makes the complex concentration increase in this region. Consequently, diffusion of the complexes from interior to the grain boundaries occurs due to a concentration gradient between these two areas. This diffusion leads to excessive solute atoms concentration near the grain boundaries and causes the non-equilibrium segregation.

In 1980s, Faulkner [3] and Xu [4] proposed that the thermodynamics and kinetics of NGS depended on the diffusion of vacancy-solute atom complexes. According to the mechanism the processes of non-equilibrium grain boundary segregation can be classified into segregation and de-segregation processes. They suggested the concept of critical time and worked out a formula for the critical time [3, 5–7]:

$$t_c(T) = d^2 \ln(D_c/D_i)/[4\delta(D_c - D_i)] \qquad (1)$$

where d is the average grain size, δ is the critical time constant, D_c is the coefficient of complex diffusion and D_i is the coefficient of impurity diffusion in the matrix. A NGS kinetic model both for segregation and de-segregation processes were also derived from the above described theories [4, 5, 8, 9]. Experimental observations [10–12] provided evidences of the model.

In the present work, experimental studies of non-equilibrium grain-boundary segregation kinetics of phosphorus and the critical time in an industrial steel, 12Cr1MoV, at different solution temperatures are put forward.

2. Experimental procedures

Experimental studies were carried out on a low alloy industrial 12Cr1MoV steel of composition listed in Table I. Specimens were solution treated at different temperatures. The heat treatment included: solution treated at 1050°C/2 h, solution treated at 1300°C/0.5 h, water quenching to room temperature, tempering at 200°C/2 h, air cooling, isothermal holding at 540°C

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TABLE I Chemical compositions of experimental steel (wt%)

C	P	Mn	Si	Cr	Mo	V	S	Ni	Cu
0.14	0.019	0.62	0.22	1.05	0.27	0.17	0.015	0.02	0.008

TABLE II Grain boundary concentration of phosphorus of steel 12Cr1MoV

Isothermal holding time at 540°C (h)	1050°C		1300°C	
	C_P (120 eV) $S_\mathrm{P} = 0.53$	C'_P (at.%)	C_P (120 eV) $S_\mathrm{P} = 0.53$	C'_P (at.%)
0	0.9	3.15	1.1	3.85
5	3.2	11.20	–	–
10	3.4	11.90	–	–
15	–	–	4.1	14.3
75	–	–	5.0	17.5
100	4.1	14.35	5.5	19.25
150	4.4	15.40	–	–
300	4.6	16.10	–	–
400	5.6	19.60	–	–
500	6.1	21.35	–	–
800	5.7	19.95	–	–
900	5.6	19.60	–	–
1000	5.4	18.90	–	–
1200	4.9	17.15	–	–
1500	3.9	13.65	–	–
1800	3.8	13.30	–	–

for 0, 5, 10, 15, 75, 100, 150, 300, 400, 500, 800, 900, 1000, 1200, 1500, and 1800 h respectively.

The NGS concentrations of phosphorus were carefully measured with Auger Electron Spectroscopy (AES). Cylindrical samples of $\phi 3.68$ mm with sharp notch were fractured by impact at about −100°C. On the freshly prepared fracture surfaces, 20 inter-granular facets were observed and subsequently analyzed. The phosphorus grain boundary concentration was calculated according to [13]:

$$C_\mathrm{X} = \frac{\frac{I_\mathrm{X}}{S_\mathrm{X} d_\mathrm{X}}}{\sum_\alpha \frac{I_\alpha}{S_\alpha d_\alpha}} \tag{2}$$

where C_X is the surface concentration of element X in at.%, I_X is the peak-to-peak amplitude of element X, S_X is the relative elemental sensitivity factor, d_X is the scale factor. The relative elemental sensitivity factors of S_P, S_Cr, S_Mo and S_Fe were 0.53, 0.32, 0.34 and 0.182, respectively [13]. C_X is the approximate atomic fraction of element X remaining on each side of the boundary after fracture, averaged over the mean escape depth of the element X Auger electrons.

The more careful analysis has been done by Seah [14]. Corrected values of the grain boundary concentration of element X were established according to [14]:

$$C'_\mathrm{X} = (2AL\cos\theta)\cdot C_\mathrm{X} \tag{3}$$

where C'_X is the atomic concentration of element X expressed as a fraction of a monolayer, AL is the attenuation length of the Auger electrons in iron and θ is the angle of emission from the surface normal. For phosphorus, the factor $2AL\cos\theta$ is about 3.5 [14], i.e., $C'_\mathrm{P} = 3.5C_\mathrm{P}$.

3. Results and discussion

Experimental results of NGS concentrations of phosphorus, both at solution temperature 1050 and 1300°C, are shown in Table II. The NGS kinetic curves of phosphorus at the isothermal held temperature of 540°C are shown in Fig. 1.

An intergranular fracture in Auger samples (solution treated at 1050°C and held at 540°C for 100 h) is shown in Fig. 2. Fig. 3 gives the AES patterns of samples held at 540°C.

Experimental results of specimens solution treated at 1050°C, show that from the start to about 500 h, the grain-boundary segregation concentration of phosphorous increasing continuously with increasing isothermal holding time. When the holding time is longer than 500 h, the phosphorus segregation concentration decreasing continuously with increasing holding time, and the maximum value of segregation degree appears

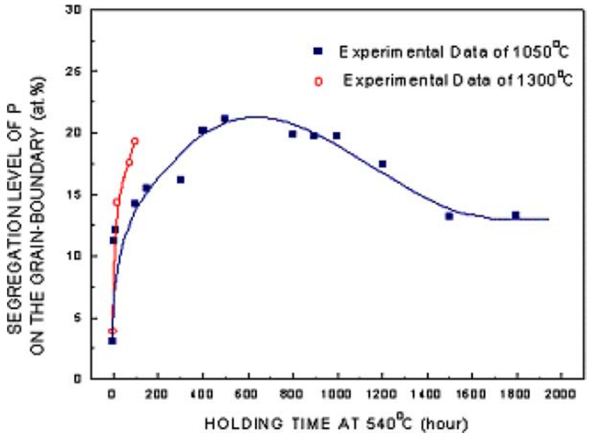

Figure 1 The non-equilibrium grain-boundary segregation kinetics curves of phosphorus in 12Cr1MoV steel.

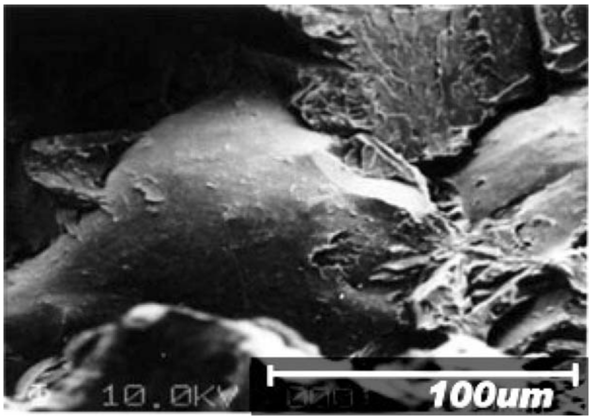

Figure 2 Intergranular fracture in Auger samples of steel 12Cr1MoV (Solution treated at 1050°C and held at 540°C for 100 h).

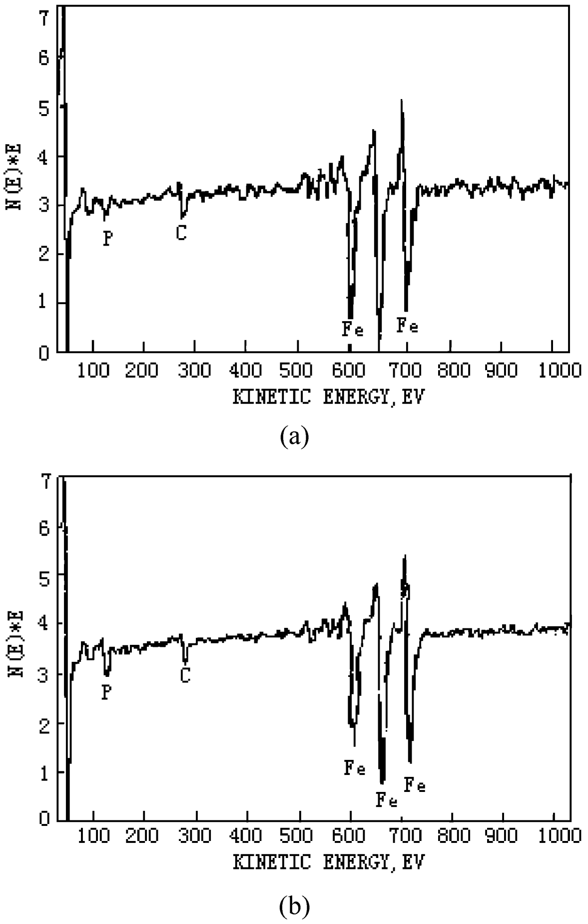

Figure 3 Peaks of AES patterns of steel 12Cr1MoV held at 540°C for 100 h: (a) Solution treated at 1050°C and (b) Solution treated at 1300°C.

at about 500 h. When the holding time is longer than 1500 h, the segregation reaches full equilibrium.

Usually, the equilibrium grain boundary segregation (EGS) and non-equilibrium grain boundary segregation (NGS) both contribute to the segregation concentration of phosphorous on grain boundaries. According to the theory of EGS [15], the equilibrium grain boundary concentration of phosphorous can be determined from the Langmuir-McLean isotherm equation [15]:

$$\frac{X_{\mathrm{Peq}}}{1-X_{\mathrm{Peq}}} = X_{\mathrm{P}}^{\mathrm{B}} \exp\left(\frac{-\Delta G_{\mathrm{P}}}{RT}\right) \tag{4}$$

where X_{Peq} is the equilibrium grain boundary concentration of phosphorous, $X_{\mathrm{P}}^{\mathrm{B}}$ is bulk phosphorous concentration, ΔG_{P} is the Gibbs free energy of phosphorous grain boundary segregation in binary αFe-P system. In the calculations, the following parameters were used: X_{Peq} (at 1800 h) $= 13.30$ at.%, $X_{\mathrm{P}}^{\mathrm{B}} = 0.0343$ at.%, $T = 540$°C. The ΔG_{P} value was -42.73 kJmol^{-1}. It is in good agreement with those values of ΔG_{P} in Ref. [16–18]. According to the calculations, the equilibrium (X_{Peq} (at 1800 h) $= 13.30$ at.%) was reached after 1500 h. At a fixed temperature (540°C), the magnitude of the equilibrium segregation was constant for all of the times held.

The grain boundary concentration value of phosphorous is higher than the value of EGS (X_{Peq} (at 1800 h) $=$ 13.30 at.%) when the holding time is shorter than 1500 h. It implies that the grain boundary concentration of phosphorous in specimens is NGS and EGS additively.

The experimental phenomenon can be easily explained by the mechanism of diffusion of vacancy-solute atom complex for NGS proposed by Xu in [4]. When the isothermal holding time is shorter than the critical time which corresponding to the maximum value of segregation level, 500 h, the process of segregation is dominant. When the holding time exceeds 500 h, the process of desegregation is dominant.

In the segregation process, complex diffusion to the grain boundary is dominant, at first, a high gradient of complex concentration drives the complexes to diffuse to the grain boundary and the rate of phosphorus segregation is high due to a large diffusivity of the complex, D_{c}. Then the rate of phosphorus segregation decreases due to a decreasing complex concentration gradient.

In the desegregation process, the diffusion of phosphorus atom from grain boundary to grain center is dominant and the segregation concentration of phosphorus decreasing with increasing holding time t ($t > t_{\mathrm{c}}$). However, the rate of phosphorus desegregation from grain boundaries to center is slower compared with that in the segregation for the diffusion coefficient of phosphorus atoms in the matrix, D_{i}, is lower than the complexes, D_{c} [4].

It is at critical time a kinetic process in which the reverse phosphorus atoms diffusion from the grain boundaries to the center balances the complex diffusion to grain boundaries, and the concentration of phosphorus atoms in grain boundaries reaches a maximum. When the holding time is longer than 1500 h, the diffusion process reaches full equilibrium.

The critical times $t_{\mathrm{c}}(T)$ were calculated for specimens solution heated both at 1050 and 1300°C according to Equation 1. The parameters used in the calculation are given in Table III.

TABLE III Parameters used in kinetic calculation

Measured average grain size d (μm)	66.67 (1050°C) 100.00 (1300°C)	
D_{c} (m^2 s^{-1})	5×10^{-5} exp(−1.80/kT)	[19]
D_{i} (m^2 s^{-1})	2.9×10^{-4} exp(−2.39/kT)	[20]
δ	11.5	[7]

The isothermal holding temperature is 540°C, i.e., 813 K. The calculated value of $t_c(T)$ for 1050°C is 516 h, which is in good agreement with the experimental results. The value of $t_c(T)$ for 1300°C is 1160 h. We see that the higher the solution temperature, the longer is the critical time.

Besides, Fig. 1 shows that the grain boundary segregation concentrations of phosphorus for specimens solution treated at temperature 1300°C are higher than those at temperature 1050°C. Fig. 3 also shows that the peak values of phosphorus for specimens solution treated at 1300°C are higher than those at 1050°C.

Above results give evidence to implicate the important effect of solution temperature on the characteristic of NGS kinetics of phosphorus and show that the higher the solution temperature, the higher is the segregation level of phosphorus, and also the longer are the critical times.

It can also be explained by the mechanism of NGS kinetics by Xu and Song [4, 9].

According to the thermodynamics of lattice defects, the concentration of vacancies in thermal equilibrium in a perfect lattice may be written as [21]:

$$C_v = A \exp(-E_F/kT) \tag{5}$$

$$E_F = 9kT_m \tag{6}$$

where A is an entropy term of vacancy, E_F is the energy required to form one vacancy. T is the solution temperature, T_m is the melting point, and k is the Boltzmann's constant.

From the Equations 5 and 6, we can see that, the higher the solution temperature, the higher is the concentration of vacancies, and therefore, the more the impurity (phosphorus) atoms diffuse to grain-boundary. This explains why the segregation levels of phosphorus for specimens solution treated at 1300°C are higher than those at 1050°C.

In addition, C_b^m, the maximum concentration of solute atoms at the grain boundary, cooled down from solution treated temperature T_0 down to an arbitrary temperature $T(T_0 > T)$ is as fellow:

$$C_b^m(T) = C_g(E_b/E_f)\exp\{[(E_b - E_f)/kT_0] - [(E_b - E_f)/kT]\} \tag{7}$$

where C_g is the concentration of solute atoms within the grain, E_b is the energy of formation of the recombined complex (usually $E_b < E_f$). In the present work, T_0 is solution temperature 1300 or 1050°C respectively and T is isothermal holding temperature 540°C. It is obvious that the maximum concentration C_b^m in Equation 7 is only dependent on the temperatureT_0 and T. When T is a constant ($T = 540$°C in the present work), the higher the solution temperature T_0, the higher is the maximum concentration of solute atoms at the grain boundary. It also explains why the segregation levels of phosphorus for specimens solution treated at 1300°C are much higher than those at 1050°C.

4. Conclusions

The non-equilibrium grain-boundary segregation concentrations of phosphorus at grain boundaries in steel 12Cr1MoV at different solution temperatures 1050 and 1300°C, have been measured, and the NGS curves of phosphorus at isothermal holding temperature of 540°C are given. Which provide direct support for a NGS kinetic model. Solution treatment temperature has an important effect on the characteristic of NGS kinetics of phosphorus and that the higher the solution temperature, the higher is the segregation level of phosphorus. The critical time $t_c(T)$ ($T = 540$°C) of phosphorus NGS is 516 h for 1050°C and 1160 h for 1300°C respectively. The higher the solution temperature, the longer is the critical time.

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