Grain Boundary Segregation of Phosphorus in 2.25wt% Chromium Steels with Variations in Molybdenum and Carbon Contents*

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Synopsis

The segregation behaviors of P, Cr, Mo and C to grain boundaries in low alloying steels, isothermally aged (embrittled) at 773 K have been examined by means of an Auger electron spectroscopy. All of these four elements segregated to the grain boundaries, but the amount of segregation varied widely in different grain boundary facets. The addition of Mo and/or C retarded the diffusion of P to the grain boundaries, and also lowered its saturation concentration at grain boundaries. In contrast to the enrichment of intergranular P concentration, depletion of grain boundary C concentration was found during the first step of aging. The aging temperature dependence of the equilibrium concentration of Cr and Mo was very weak compared with that of P and Ni. The change in the grain boundary energy due to impurity-segregation contributed to its equilibrium intergranular content, and this contribution has been discussed in a different way from the usual Gibbs adsorption theorem approach.

1. Introduction

It has been generally believed that Mo is an effective element for inhibiting temper embrittlement in low alloy steels, and this property of Mo arises partly from its retardation of the diffusion to grain boundaries of impurity-elements such as P, As and Sb, due to the strong affinity of Mo for these elements.¹⁻⁴⁾ However, is the role of Mo confined only to this retardation effect? It seems that this question has not yet been satisfactorily answered.

The present authors have considered two aspects of this question, with special reference to P doped 2.25wt%Cr-Fe alloys, studying the effects of the addition of Mo and/or C on 1) the grain boundary fracture strength and 2) the equilibrium grain boundary content of P and its diffusion rate to grain boundaries. The results of the former study are reported elsewhere⁵⁾ and those of the latter are shown here. The reason why C as well as Mo were chosen as an addition element is because the behavior of Mo in alloys containing C is somewhat different from that in C-free alloys. In fact, McMahon *et al.* have recently reported that the scavenging effect of Mo on P is rapidly lost with increasing C content in Ni-Cr steels.³⁾

In the present study, the concentrations of segregants were measured by means of Auger electron spectroscopy (AES), using a "fine" electron beam with a diameter smaller than the average size of a grain boundary facet.

II. Experimental Procedure

Six kinds of 2.25wt%Cr-Fe alloys with variations in Mo and C contents were vacuum induction melted

to produce Steels 1 to 6. Their chemical compositions are shown in Table 1. They were hot- and cold-worked into 10 mm dia. rod-blanks.

These rod-blanks were austenized for 1/2 h in a salt bath at 1 200°C (1 473 K), after which the high C alloys were oil quenched and the very low C alloys were quenched in water at ~10°C (283 K). They were subsequently tempered at 650°C (923 K) for 2 h, water cooled, and then isothermally aged (embrittled) at 500°C (773 K) for times up to 1 000~1 300 h. Some blanks of Steel 5 were tempered at 700°C (973 K) for 17 h and water cooled in order to study the effect of tempering conditions upon grain boundary segregation. These are called "Steel 5B" to distinguish them from "Steel 5A", which tempered at 650°C (923 K) with the other specimens, as shown in Table 1.

After aging the 10 mm dia. rod-blanks, they were machined into Auger specimens of 3.7 mm dia., which were fractured at -80°C (193 K) inside the test chamber of the Auger system, in a vacuum of $3 \times 10^{-11} \sim 2 \times 10^{-10}$ Torr (3~20 nPa). Auger spectra were obtained using a cylindrical mirror type AES instrument, with the following variables: a primary electron beam energy of 5 keV, a primary beam current of 0.3 μ A, an electron multiplier voltage of 1 500 V, a modulation energy of 6 eV, and a lock-in-amplifier gain of $40 \times$.

The typical electron beam diameter under these conditions was 10 to 15 μ m, which was less than the typical grain boundary facet diameter of the order of 100 μ m. At least 10, and sometimes more than 30, different grain boundary facets of each fractured sample were selected at random and the Auger peak-to-peak heights of P at 120 eV, Cr (529 eV), Mo (186 eV), C (272 eV) and of Fe at 703 eV were measured.

Table 1. Chemical composition (wt%)

Steels	C	Si	Mn	P	S	Cr	Mo
3	0.30	0.28	0.49	0.050	0.007	2.29	0.01
4	0.28	0.30	0.49	0.050	0.008	2.26	0.48
5A, 5B	0.30	0.30	0.49	0.052	0.008	2.28	0.98
6	0.008	0.30	0.49	0.053	0.008	2.24	0.01
7	0.002	0.30	0.49	0.054	0.008	2.29	0.49
8	0.003	0.30	0.50	0.053	0.007	2.23	0.99

Al<0.005, Sn<0.003, Sb<0.001, As<0.006, Cu<0.1 and Ni<0.01.

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The grain boundary content of a species was, as is usual, evaluated from its peak's peak-to-peak height expressed as a percentage of the peak-to-peak height of the iron peak (simply described as “%P.H.” hereafter). Thus, “%P.H.” = $(I_i/I_{Fe}) \times 100$, where I_i and I_{Fe} are the peak-to-peak heights of i -species and iron peaks, respectively. Finally, the arithmetic mean and standard deviation for the grain boundary concentrations of each species on all measured facet faces were calculated.

III. Results

1. Metallography

Non-aged (or as-tempered) specimens of the high C alloys had a microstructure of the so-called tempered martensite type, with a prior austenite grain diameter of about 200 μm , and a facet length of $\sim 120 \mu\text{m}$.^{*} Nonaged specimens of the very low C alloys had a microstructure resembling tempered martensite, but the size of the prior-austenite grains was very uncertain. However, the facet length of these types of alloys was judged to be about 80 μm from fracture surface micrographs. No remarkable changes in microstructure or grain size were found in the specimens after aging, even if they were aged over 1 000 h at 500°C (773 K).

2. Segregation of P

The mean, standard deviation, maximum, and minimum values for the grain boundary P contents of each steel are summarized in Table 2, as a function of aging time. It can be seen that the grain boundary P concentration varies greatly in each specimen, depending on the facet measured. The degree of scatter is quantitatively represented by the value of standard deviation (S.D.) in Table 2. Some examples of the scatter in P concentration are shown in Figs. 1 and 2, from which it can be seen that the scatter remained unchanged with aging time.

Although the segregation concentration of P differed appreciably from facet to facet in each specimen, the mean concentration followed a trend. The average concentration of P in Steels 3 and 6, which were free from Mo, increased rapidly during the first ~ 30 h aging, and then remained nearly constant up to at least 1 000 h, whereas the values for Mo-doped Steels 4 and 5A attained their saturation level after ~ 70 h aging. The concentration for Steel 5B increased slowly with aging time, attaining 30%P.H., presumably the level of saturation, at 1 300 h, as shown in Fig. 2.

The saturation concentration of P varied in different alloys, although the differences were not large: the saturation values for Mo-free Steels 3 and 6 were 28.3 and 30.4%P.H., respectively, which were a little higher than the 27.0%P.H. for Steel 4 and the 27.3%P.H. for Steel 5A.

In Steels 7 and 8, little data on the grain boundary P concentration was obtained because they fractured

mainly by transgranular cleavage. However, it was clear that the saturation intergranular P concentration for Steel 8 was about 26–27%P.H., which was comparable to the levels for Steels 4 and 5A, and the intergranular P content in Steel 8 appeared to saturate in the same order of aging time as in Steels 4 and 5A.

3. Segregation of Cr, Mo and C

The changes in the average intergranular concentration of Cr are shown in Fig. 3 as a function of aging time for various alloys. In this figure the vertical

Table 2. Grain boundary P concentrations by AES (%P.H.)

Steels		As-tempered	10 h	30 h	70 h	290/ 370 h*	1 000/ 1 300 h**
3	(1)	14	18	21	15	20	20
	(2)	12.94	24.09	27.36	26.91	28.19	28.66
	(3)	2.81	5.19	5.28	3.72	8.30	5.34
	(4)	15.74	29.28	32.64	30.64	34.77	34.00
	(5)	10.13	18.89	22.09	23.19	21.62	23.32
4	(1)	19	10	10	15	15	35
	(2)	12.51	18.51	22.77	27.02	27.23	26.30
	(3)	3.00	4.26	3.40	4.17	5.38	5.70
	(4)	15.51	22.77	26.17	31.19	32.62	32.00
	(5)	9.51	14.26	19.36	22.85	21.85	20.60
5A	(1)	21	23	20	10	10	20
	(2)	12.70	20.72	22.64	27.87	27.87	26.98
	(3)	3.70	4.00	5.28	2.89	3.00	5.32
	(4)	16.40	24.72	27.91	30.13	30.87	32.30
	(5)	9.00	16.72	17.36	24.98	24.87	21.66
5B	(1)	3	16	20	21	17	23
	(2)	10.47	14.00	19.43	22.19	24.26	29.94
	(3)	—	1.68	4.74	4.66	5.40	6.47
	(4)	—	15.95	24.17	26.81	29.66	36.40
	(5)	—	12.02	14.68	17.53	18.85	23.47
6	(1)	21	17	25	23	23	25
	(2)	14.60	27.60	31.17	30.98	29.68	29.79
	(3)	3.70	1.22	5.04	5.98	7.96	8.83
	(4)	18.30	33.11	36.21	36.96	37.64	38.62
	(5)	10.89	22.15	26.13	25.00	21.72	20.96
7	(1)	—	2	1	—	—	2
	(2)	—	16.17	7.15	—	—	19.26
	(4)	—	16.17	—	—	—	20.96
	(5)	—	16.17	—	—	—	17.66
8	(1)	—	3	6	3	1	3
	(2)	—	18.00	24.74	26.34	15.62	27.23
	(4)	—	22.66	27.57	29.64	—	39.57
	(5)	—	15.21	13.17	22.28	—	6.60

(1) Number of observed facets (4) Maximum values

(2) Mean (5) Minimum values

(3) Standard deviation

* 290 h for Steels 3, 4, 5A and 5B. 370 h for the others.

** 1 300 h for Steels 3, 4, 5A and 5B. 1 000 h for the others.

* This length is defined as the mean length of the facets projected on a section cut by a number of grains.

Fig. 1. Solid circles: the average P concentrations
Scatter in the intergranular P content for different grain boundary facet faces for Steel 6

Fig. 2. Scatter in the intergranular P content for different grain boundary facets for Steel 5B

error bars indicate the magnitude of the S.D. of the concentrations measured. Similar curves for Mo are shown in Fig. 4. These figures show that the average intergranular concentrations of Cr and Mo are almost constant, independent of aging time, and that the magnitude of the S.D. for Mo is small compared with that for Cr. The mean intergranular contents of Cr and Mo saturated after about 70 h aging. The saturation level of Cr for the Mo-doped alloys is larger than that for the alloys free from Mo, and the saturation level of Mo increases as its bulk content is increased.

The grain boundary concentrations of Cr and Mo for Steels 7 and 8 are summarized in Table 3. From these it can be seen that the grain boundary concentrations of Mo in these alloys are close to, or greater than, those in Steels 4, 5A and 5B, and that the

Vertical error bars: the standard deviation in measurements

Fig. 3. Change in the average intergranular Cr content as a function of aging time

Fig. 4. Change in the average intergranular Mo content with aging time and the standard deviation in measurements

Table 3. Grain boundary concentrations of Cr and Mo in Steels 7 and 8 (average %P.H.)

Steels	Segregated species	Aging Time (h)				
		10	30	70	290	1000
8	Cr	10.39	10.06	9.36	7.77	10.13
	Mo	6.32 (3)	6.49 (6)	7.55 (3)	4.63 (1)	10.63 (3)
7	Cr	10.41	8.03	—	—	15.03
	Mo	4.65 (2)	3.57 (1)	—	—	6.96 (2)

The number in brackets: the total number of observed facets.

intergranular concentrations of Cr in Steels 7 and 8 are smaller than those in Steels 4, 5A and 5B, but comparable to that of Steel 6.

Figure 5 shows an example of the scatter in the C

Fig. 5. Scatter in the intergranular C content for different facets, and the effect of vacuum level on the C content

The data points marked by (*) are the ones at 2×10^{-10} Torr.
The others are at lower than 7×10^{-11} Torr.

Fig. 6. Change in the average intergranular C content as a function of aging time for various types of steels

concentration at grain boundaries for different facets, together with the change in the average concentration with aging time. In general, as the concentration of C on a surface is easily affected by carbon atoms from the environment, the AES measurements of C in the present study were carried out in a vacuum lower than $\sim 7 \times 10^{-11}$ Torr (~ 7 nPa), unless otherwise stated. Even at this high vacuum AES data obtained 1 h after the specimen fracture was discarded. From Fig. 5 it can be seen that the average intergranular concentration of C in Steel 3 decreases during approximately the first 30 h of aging and then remains almost constant. A similar tendency was found in the other types of alloy, as shown in Fig. 6. The stationary value of the average content of C was higher in the alloys doped with Mo than in the alloys free from Mo.

In the very low C alloys the segregation behavior of C was different from that in the high C alloys; in the former, some facet faces were found where no carbon segregation was detected within the present accuracy of the AES analysis, while in the latter type of alloy C was detected on all of the facet faces observed. However, if one considers the ratio of the number of

The number beside the data points shows the C content (%P.H.) averaged over the facets in which C was detected.

Fig. 7. Change in the average intergranular C content as a function of aging time for Steel 6

Table 4. Correlations between the grain boundary concentrations for each pair of the species P, Cr, Mo and C

Steels	Aging treatments	Cr/P	Mo/P	Cr/C	Mo/C	Cr/Mo
7 & 8	All data involved	0.287	0.858	—	—	0.432
6	As-tempered Aged 1 000 h	0.450	—	0.509	—	—
		0.310	—	—	—	—
3	As-tempered Aged 1 300 h	0.551	—	0.654	—	—
		0.672	—	0.781	—	—
4	As-tempered Aged 1 300 h	0.657	0.503	0.613	0.062	0.312
		0.434	0.623	0.095	0.728	
5A	As-tempered Aged 1 300 h	0.659	0.512	0.709	0.438	0.255
		0.452	0.087	0.825	0.555	0.408
5B	As-tempered Aged 1 300 h	—0.166	0.661	0.769	0.399	0.212
		0.550	0.723	0.859	0.123	

facets where C was detected to the total number of facets analyzed, it turns out that the ratio decreases again at long aging times, as shown in Fig. 7. Moreover, the C content averaged over the facets, in which C was detected, also decreases with increasing aging times as indicated by the number beside each data point in Fig. 7.

4. Statistical Correlation between Pairs of Segregants

Table 4 shows the correlation coefficient for the intergranular concentrations of each pair of the four elements, in the as-tempered and 1 000/1 300 h aged specimens. Values of this coefficient close to unity imply that some kind of chemical interaction is expected to exist between the two elements considered. However, the converse is not necessarily true. It can be seen from Table 4 that the correlation is relatively strong between Mo and P, especially in Steel 7, and between Cr and C, especially in Steels 5A and 5B.

Compared with these, the coefficients for Cr/P, Mo/C and Cr/Mo are not so large so far as the present results are concerned.

IV. Discussion

1. Scatter in the AES Data with the Position of Measurement

Seah and Hondros have pointed out⁶⁾ that scatter in the AES data is due to 1) the measurement error associated with AES measurement, 2) the uneven partition of segregants between the paired fracture surfaces and 3) the inherently inhomogeneous segregation of species on grain boundaries. It is believed from what follows that the large scatter observed in this study was mainly due to the third reason.

Regarding reason (1), the effect of surface inclination* on the Auger spectra seems to be most important, because the effects of other factors such as surface roughness were generally minimized by normalizing the peak-to-peak height of each species with respect to the peak height of iron, and in addition the instrumental variables in each Auger measurement were kept nearly constant in the present study. The effect of surface inclination was examined in the following manner: Firstly, the Auger spectra were monitored whilst moving a facet along the beam axis in either direction from the reference position, where the 'elastic' peak height was at a maximum. The results showed that the difference in the Auger spectrum due to this movement was small. For example, the %P.H. of P increased by only 0.81, from 30.4 at the reference position, when the facet position was moved by 50 μm from the reference position toward the beam gun, while it decreased by only 0.81 while moving the facet position the same distance in the opposite direction. This small effect of positional change on the Auger spectrum suggests that the effect of surface inclination on the Auger spectrum is also small. Secondly, the degree of scatter in the Cr %P.H. results were compared for both cleavage and intergranular fracture surfaces. An example of the results obtained is shown in Table 5, indicating that the large scatter observed on the intergranular surfaces cannot be explained only in terms of the measurement errors, since the measurement errors are expected to be the same for both kinds of surfaces.

The results shown in Table 5 suggest at the same time that the effect of reason (2) on the Auger data scatter is also small, since this effect would manifest itself to the same degree—with the same ratio of the standard deviation to the mean—on both the cleavage and intergranular surfaces. Seah and Hondros have also reported that reasons (1) and (2) have little effect on the scatter in the Auger data.⁶⁾ Thus, it is concluded that most of the scatter observed in this study results from the inherently inhomogeneous segregation of species to grain boundaries. However, a question arises from this conclusion; is this inhomogeneous

Table 5. Comparison of the scatter on Cr concentration on two kinds of fracture surface

Specimen	On cleavage surfaces	On intergranular surfaces
Steel 5B, aged 30 h	$5.0 \pm 0.47^*$	$9.37 \pm 2.03^*$

* $\pm$ Standard Deviation (%P.H.)

geneous segregation of an equilibrium nature, or not? Taking account of the fact that the degree of scatter in the %P.H. of P does not change with aging time (Figs. 1 and 2), we can regard the inhomogeneous segregation being of an equilibrium nature. The distortion energy of grain boundaries is considered to be a function of the grain boundary angle or the coincidence site density.⁷⁾ The variation in distortion energy for different grain boundary facets might allow some species to segregate in different concentrations on different facets.

2. Equilibrium Intergranular Concentrations of Segregants

1. A Modified Relationship for the Equilibrium Segregation

In earlier theories of equilibrium segregation, as first suggested by McLean⁸⁾ and then developed by Guttman,⁴⁾ the grain boundary energy change which is induced by the intergranular segregation of a species has not been included explicitly in the formulations. Therefore, a modified relationship has been derived on the basis of the thermodynamical equilibrium conditions for a ternary alloying system of Fe-Metal-Impurity (see Appendix I):

$$RT \cdot \ln X_I^g/X_I^b \cong Q_I - W_{MI}(X_M^g - X_M^b) \\ RT \cdot \ln X_M^g/X_M^b \cong Q_M - W_{MI}(X_I^g - X_I^b) \dots\dots\dots(1)$$

where,

$$Q_i \cong -V/\omega(\partial\gamma^g/\partial X_i^g) + (\Omega_{Fei}^b - \Omega_{Fei}^g) \\ + 2X_i^g\Omega_{Fei} \quad (i = I \text{ or } M)$$

In these equations suffix *I* and *M* mean 'impurity' and 'metal', respectively, and superscripts '*g*' and '*b*' denote grain boundary and bulk, respectively. X_i^g (hereafter '*X*' denotes atomic concentration and the suffix '*i*' denotes *I* and *M*) is the equilibrium grain boundary content of *i*-species, X_i^b is the bulk content of *i*, *V* is the specific volume per mol of the ternary alloy, ω is the grain boundary thickness, and γ^g is the grain boundary free energy per unit area of the interface between *b* and *g*. *RT* has the usual meaning. Q_I , Q_M and W_{MI} are thermodynamic parameters which correspond to α_{FeI} , α_{FeM} and $-\alpha_{MI}$ respectively in Guttman's terminology.⁴⁾ Ω_{FeI} and Ω_{FeM} are the so-called interaction coefficients for each of binary alloying systems, Fe-*I* and Fe-*M*. The special character of Eq. (1) lies on the respect that a term for the change in grain boundary energy due to impurity segregation, $-V/\omega(\partial\gamma^g/\partial X_i^g)$, is included explicitly.

* This means the inclination of a facet to the incident electron beam.

Equation (1) can be applied, in place of the Gibbs adsorption theorem, to correlate the equilibrium impurity segregation with the change in grain boundary energy due to the impurity segregation, especially in a solid at lower temperatures, in which the work done by the grain boundary tension is negligible.

Now, let us evaluate, for example, the magnitudes of Q_P , Q_{Cr} and W_{CrP} for a Fe-Cr-P system, by applying the data for Steel 6 to Eq. (1). Firstly we must evaluate the magnitude of X_i^g from the Auger peak-to-peak heights for i , I_i . For this purpose the following relationships are available:

$$\begin{aligned} X_P^g &= X_P^b + 1.9(X_P^{g'} - X_P^b) \\ X_{Cr}^g &= X_{Cr}^b + 2.9(X_{Cr}^{g'} - X_{Cr}^b) \end{aligned} \quad \dots\dots\dots(2)$$

and

$$X_i^{g'} = (I_i/S_i)/\sum_j (I_j/S_j) \quad j = \text{Fe, P and Cr} \dots\dots\dots(3)$$

Equation (3) relates I_i to $X_i^{g'}$ the atomic concentration of i in a specimen where i is uniformly dissolved. $X_i^{g'}$ should be discriminated from X_i^g , the average concentration of i in a specimen where the concentration of i rapidly decreases from the surface to interior. Equation (2) relate $X_i^{g'}$ to X_i^g (see Appendix II). In Eq. (3), S_i is the so-called "relative sensitivity" for i -species, and is here taken as 0.215, 0.46, 0.30 for Fe, P and Cr, respectively.⁹⁾ In Eq. (2), X_P^b and X_{Cr}^b are the bulk concentration of P and Cr.

In Table 6 are shown the calculated values of Q_P , Q_{Cr} and W_{CrP} , and some of the concentrations required for the calculations for Steel 6. The concentrations at 650°C (923 K) were obtained from the data for the non-aged specimens. An assumption was made in these calculations, for the sake of fitting the data, that Q_{Cr} and W_{CrP} are independent of temperature but that Q_P is dependent on it. The magnitude of 230 for $\beta_P(\equiv X_P^g/X_P^b)$, the grain boundary enrichment factor for P, in Table 6, is comparable to the values for P listed by Seah.¹⁰⁾ The value of approximately 13 kJ/mol for $-W_{CrP}$ is only different by a factor of about two from the value of 26 kJ/mol reported by Guttman¹¹⁾ and the value of approximately 34 to 38 kJ/mol for Q_P is in close agreement with the value of about 40 kJ/mol, estimated by Seah¹⁰⁾ for Ni-Cr steel.

2. The Ratio of $-V/\omega(\partial\gamma^g/\partial X_P^g)$ to Q_P

It is interesting to evaluate what proportion of Q_P , that is 34 to 38 kJ/mol in the present case is due to the term $-V/\omega(\partial\gamma^g/\partial X_P^g)$ in Eq. (1). To determine this ratio we must estimate the value of $(\partial\gamma^g/\partial X_P^g)$. Unfortunately we have at present no direct method for determining this. Therefore, it is assumed that $(\partial\gamma^g/\partial X_P^g) \cong 1/\beta_P(\partial\gamma^{g'}/\partial X_P^b)$, where β_P is the value defined above and $\gamma^{g'}$ is the so-called grain boundary

energy per unit area. Then $-V/\omega(\partial\gamma^g/\partial X_P^g)$ works out to about 8.3 kJ/mol, if we substitute as follows: $V \cong 7.108 \text{ cm}^3$, $\omega \cong 1 \text{ nm}$, $\beta_P \cong 230$ and $-\partial\gamma^{g'}/\partial X_P^b \cong 2.8 \times 10^{-2} \text{ J/cm}^2/\text{at}\%$. This last value is taken from Hondros.¹²⁾ Thus, the ratio of $-V/\omega(\partial\gamma^g/\partial X_P^g)$ to Q_P becomes about 0.2.

Q_P would vary for different grain boundary facets if the magnitude of $-V/\omega(\partial\gamma^g/\partial X_P^g)$ was different for each facet. If we suppose that the change in Q_P , ΔQ_P , for different facets is 3 or 4% of Q_P (that is about 1.25 kJ/mol for $Q_P = 34 \sim 38 \text{ kJ/mol}$), the value of $\Delta X_P^g/X_P^g$ is estimated to be about 0.2 at 773 K, based on the approximate relationship $\Delta X_P^g/X_P^g \cong \Delta Q_P/RT$ which is obtained from Eq. (1). This value of $\Delta X_P^g/X_P^g$ is of the same order of magnitude as the scatter in the Auger data for P in the present study.

3. Observed Results for P, Cr and Mo

Figure 8 shows the aging temperature dependences of the equilibrium intergranular concentrations of P, Cr and Mo. In this figure the data at 650°C (923 K) and 700°C (973 K) is taken from the data on the as-tempered specimens, and that at 600°C (873 K) is taken from the data on the specimens which allowed to recover at 600°C for 1 h after being aged 100 h at 500°C (773 K). It is apparent from this figure that the equilibrium concentration of P is comparatively strongly dependent on aging temperature, whereas those of Cr and Mo are very weakly dependent on it. This weak temperature dependence of Cr and Mo is in strong contrast with that of Ni, which has been re-

Dotted (1) and dash-dotted (2) lines: the calculated curves for Steel 6, based on Eq. [1]. Full lines: the experimental data for Steel 6
Fig. 8. Aging temperature dependences of the equilibrium intergranular concentrations of P, Cr and Mo for various steels

Table 6. Calculated values of Q_P , Q_{Cr} and W_{CrP} for Steel 6 and the various concentrations necessary for calculating them

	X_P^b	X_{Cr}^b	$X_P^{g'}$	X_P^g	$X_{Cr}^{g'}$	X_{Cr}^g	$\beta_P \equiv X_P^g/X_P^b$	Q_P	Q_{Cr}	W_{CrP}	(kJ/mol)
773K	9.5×10^{-4}	2.4×10^{-2}	1.2×10^{-1}	2.2×10^{-1}	5.4×10^{-2}	1.1×10^{-1}	232	33.87	6.93	-13.33	
923K			6.1×10^{-1}	1.2×10^{-1}	4.9×10^{-2}	7.2×10^{-2}	122	36.19			

ported to be comparable in magnitude to the temperature dependence of P.¹³⁾ In Fig. 8 the calculated temperature dependences of P and Cr, based on Eq. (1), are shown by dotted (1) and dash-dotted (2) curves. In Curve (1), Q_P was assumed to be a function of temperature of the form $0.884T + 1\,251.2$ (kJ/mol), whereas in Curve (2), Q_P was taken to be constant. In both cases Q_{Cr} and $-W_{CrP}$ were set at 7.0 and 13.3 kJ/mol, respectively. Curve (1) is in good agreement with experimental data for Steel 6, as far as the P content is concerned.

The weak temperature dependence of the equilibrium concentrations of Cr and Mo may be explained by the following: At lower aging temperatures, Cr and Mo atoms segregate on grain boundaries because of their interaction with P, whereas they can segregate at higher temperatures because of their stable interaction with C atoms. This concept is supported by the fact that the equilibrium concentration of Ni, which does not form carbide, is strongly dependent on aging temperature.¹³⁾ It should be noted that the intergranular concentration of C decreases during the first step of aging. It would appear that a proportion of the C atoms are displaced from the grain boundaries by invading P atoms. This behavior of C might be related to the situation mentioned above, in that the affinity of Cr or Mo for C would become less than that for P below a certain temperature.

3. Segregation Kinetics of P

According to McLean's kinetic theory for grain boundary segregation,⁸⁾ the grain boundary concentration of i -species, X_i^g , in a specimen aged for a time, t_a , at a given temperature is evaluated by;

$$\frac{X_i^g - X_i^g(0)}{X_i^g(\infty) - X_i^g(0)} \equiv \eta_i = 1 - \exp(-y_i^2) \operatorname{erfc}(y_i) \\ y_i^2 = 4D_i t_a / \beta_i^2 \omega^2 \dots\dots\dots (4)$$

where, $X_i^g(0)$: the initial grain boundary concentration of i

$X_i^g(\infty)$: the equilibrium grain boundary concentration of i

D_i : the apparent diffusion constant of i

β_i : the grain boundary enrichment factor of i

ω : the grain boundary thickness.

The apparent diffusion constant of P, D_P , can be calculated by using the experimental relationship between η_P and t_a for P, and by using Eq. (4) with reasonable values of β_P and ω . Figure 9 shows the relationship between the bulk content of Mo and the value D_P thus obtained. Here D_P is obtained by averaging the three values of D_P for $\eta_P = 1/3$, $1/2$ and $3/5$, with the value of β_P replaced by the ratio $X_P^g(\infty)/X_P^g$ (see Table 6), and taking ω as 0.85 nm. The data marked by asterisks, that is the data for Steels 7 and 8, was not obtained from the AES data, but from the change in the ductile to brittle transition temperature, which we have discussed in detail elsewhere.⁵⁾

From Fig. 9, it can be seen that D_P is at a minimum at around 0.5wt% of Mo in the very low C alloys.

Full line: the very low C type of alloys

Dotted line: the high C type of alloys

△: the diffusion constants for Fe and Fe-0.47% Mo¹⁸⁾

Fig. 9. Effect of the bulk content of Mo on the apparent diffusion constant of P, D_P , calculated from Eq. (4)

This is in qualitative agreement with results that have been reported in the literatures.^{2,14,15)} On the other hand, in the high C alloys the data appears to be in some confusion. However, it is consistently explainable if we consider that the effective concentration of Mo available for scavenging P in a matrix decreases, due to the formation of Mo carbides, in these high C types of alloys. The effective concentration of Mo that has been lost by this method is displaced schematically by horizontal lines in Fig. 9. In this case the effective concentration of Mo in Steel 5B tempered at 700°C (973 K) for 17 h is expected to show more loss, and hence be lower than in the other two alloys which were tempered at 650°C (923 K) for 2 h. Such loss in the effective concentration of Mo in the presence of C has also been reported by McMahon *et al.*³⁾

For comparison, the diffusion constants of P at 773 K in iron and Fe-0.47%Mo alloy, obtained by Gruzin and Murall,¹⁶⁾ are indicated by triangle symbols in Fig. 9. It is of interest that these are in good agreement with the values of D_P obtained in the present study.

V. Summary

The segregation behaviors of P, Mo and C to grain boundaries have been examined by Auger electron spectroscopy, using a fine electron beam, on 2.25wt% Cr-Fe alloys varied in Mo and C contents, isothermally aged at 773 K.

It has been found that these four elements segregated to the grain boundaries, but their segregation concentrations showed an unexpected scatter in measurements on different grain boundary facets. The degree of this scatter remains unchanged over aging times up to 1 000~1 300 h. The grain boundary segregation behavior of P is greatly affected by the tempering conditions, for non-aged specimens. The addition of Mo and/or C lowers the equilibrium intergranular content of P and Mo, together with C, also

affects the segregation kinetics of P. In C-free alloys there exists an optimum content for Mo to retard P-diffusion, whereas such an optimum phenomenon is masked in high C alloys, presumably because of the formation of Mo carbides, the degree of which is dependent on C content.

Contrary to the increase in the intergranular concentration of P with aging time, that of C decreases during the first part of aging. The equilibrium intergranular contents of Cr and Mo are very weakly dependent on aging temperature, the reason for which has been discussed. The change in the grain boundary energy due to the segregation of P contributes to its equilibrium concentration, and this contribution has been discussed in a different way from the usual Gibbs adsorption theorem approach.

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Appendix I

An alloy system is considered to consist of two

phases; bulk, *b*, and grain boundary, *g*. Both phases are assumed to be a regular solution composed of solvent, iron (Fe), solute impurity (*I*), and solute metal (*M*). Let the total number of atoms in '*b*' be *N* (Avogadro number) and that in '*g*' be *n*. When small amounts of *I*, δn_I mol, and of *M*, δn_M mol, migrate from '*b*' to '*g*', the change in the Helmholtz free energy for the system, δF^{b-g} , is given as

$$\begin{aligned}\delta F^{b-g} &= \delta F^b + n/N \cdot \delta F^g + A \cdot \delta \gamma^g \\ &= \left(\frac{\partial F^g}{\partial X_I^g} - \frac{\partial F^b}{\partial X_I^b} + A \cdot \frac{N}{n} \frac{\partial \gamma^g}{\partial X_I^g} \right) \delta n_I \\ &\quad + \left(\frac{\partial F^g}{\partial X_M^g} - \frac{\partial F^b}{\partial X_M^b} + A \cdot \frac{N}{n} \frac{\partial \gamma^g}{\partial X_M^g} \right) \delta n_M \dots (A-1)\end{aligned}$$

where, δF^b , δF^g : the free energy changes per mol in the *b* and *g* phases, respectively

$\delta \gamma^g$: the grain boundary free energy change per unit area due to the migration of atoms

'*A*': the total area of the interface between *b* and *g*

X_I^g , X_I^b : the atomic fractions of *i*-atom in *g* and *b*, respectively.

From the equilibrium condition of the system, that is $\delta F^{b-g}=0$ for any variations of δn_I and δn_M , we can obtain the following equations:

$$\begin{aligned}\mu_I^g + A \cdot \frac{N}{n} \frac{\partial \gamma^g}{\partial X_I^g} &= \mu_I^b \\ \mu_M^g + A \cdot \frac{N}{n} \frac{\partial \gamma^g}{\partial X_M^g} &= \mu_M^b \dots \dots \dots (A-2)\end{aligned}$$

where, μ_I^g and μ_I^b are substituted for $\partial F^g / \partial X_I^g$ and $\partial F^b / \partial X_I^b$, respectively.

On the other hand, on the basis of the assumption of a regular solution for both phases of *g* and *b*, the chemical potentials, μ_I^j and μ_M^j (superscript *j* denotes *b* and *g*) are approximated by,*

$$\begin{aligned}\mu_I^j &\cong F_I^j + (1 - 2X_I^j) Q_{FeI}^j + X_M^j W_{MI}^j + RT \ln X_I^j \\ \mu_M^j &\cong F_M^j + (1 - 2X_M^j) Q_{FeM}^j + X_I^j W_{MI}^j + RT \ln X_M^j \\ &\dots \dots \dots (A-3)\end{aligned}$$

where, F_I^j , F_M^j : the Helmholtz free energies per mol of *I* and *M* in the *j*-phase.

From Eqs. (A-2) and (A-3), we can obtain Eq. (1) neglecting some small terms. In Eq. (1), the quantity $A \cdot N/n$ is replaced by V/ω , because *n*, the number of atoms in *g*, can be evaluated by $(A\omega/V)N$, where *V* is the volume of *b*-phase and $A\omega$ is the volume of *g*-phase. Since $V \gg A\omega$, we know that *V* is nearly equal to the volume of the system, i.e., 1 mol of the alloy of Fe-M-I.

Appendix II

If the concentration of *i*-species in a homogeneous specimen (where *i* distributes uniformly) is X_0 when measured by AES, it can be correlated with the *i*-concentration in an inhomogeneous specimen in terms

* T. Nishizawa: *Bull. Japan Inst. Metals*, **12** (1973), 401.

of Suzuki's calculation* as follows:

$$X_e = X_{h0} + (X_0 - X_{h0}) \times [1 - \exp \{ -l(1/\lambda + 1/d) \}] / [1 - \exp (-l/\lambda)]$$

.....(A-4)

where, X_e , X_{h0} : the i -concentrations at a surface and at the position far from it in the inhomogeneous specimen

- λ : the escape depth for i ,
- l : the atomic distance
- d : the attenuation length for the distribution of i in the inhomogeneous specimen.

We can obtain in Eq. (2) by substituting $l=0.286$ nm (for Fe), $\lambda=0.4$ nm and $d=0.1$ nm for P , and putting $l=0.286$ nm, $\lambda=0.85$ nm and $d=0.2$ nm for Cr into Eq. (A-4).

* H. G. Suzuki: *Bull. Japan Inst. Metals*, **14** (1975), 173.