Equilibrium Grain Boundary Segregation of P in Fe-P Binary Alloys

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This paper describes the work on the application of "AES" to the quantitative analysis of grain boundary fracture surfaces of Fe containing 0.05 to 1.7 wt% P quenched from the temperature in the range of 500 to 1150°C. In low P alloys the segregation levels of P at grain boundaries increased proportionally with the bulk concentration and inversely with the quenching temperature. The enrichment ratio was on the order of 10. In high P alloys the saturation level of segregation was about 15 at% P. On the basis of these experiments, the boundary structure at the saturation level was discussed.

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I. Introduction

It has been known for several decades that P is one of the principal impurities responsible for temper embrittlement in alloy steels⁽¹⁾. More recently, it has been shown by Auger electron spectroscopy (AES)⁽²⁾⁽³⁾ that P-induced embrittlement is associated with the build-up of P and other elements⁽⁴⁾ at grain boundaries. The equilibrium levels of these cosegregated elements increase proportionally with the bulk concentration of P and inversely with the temperature of equilibration. Rellick *et al.*⁽⁵⁾ proposed a "non-equilibrium model" for the phenomenon of "500°F embrittlement" which might also be nearly consistent with the "500°C temper embrittlement". In order to discuss the temper brittleness, the measurement of the equilibrium segregation of P to iron grain boundaries is deemed very essential. The isotherm for the segregation of P in δ -Fe at 1450°C was obtained by Hondros⁽⁶⁾ through the variation in grain boundary energy with bulk P content and the application of the Gibbs adsorption theorem. However, the temperature range between 450 and 1000°C is practically important.

This paper describes the work on the application of AES to the quantitative analysis of grain boundary fracture surfaces of Fe containing 0.05 to 1.7 wt% P, quenched

from the temperature in the range of 500 to 1150°C.

II. Experimental

The lower P alloys used were produced as follows; electrolytic iron was vacuum melted, refined with 10.7 kPa H₂ stream, Fe-24 wt% P alloy was added in an Ar atmosphere of 50 kPa, and the melt was cast. These alloys were hot forged in the form of round bars of ϕ 8 mm to break up the cast structure and followed by cold swaging up to ϕ 3.65 mm and used as AES specimens after heat treatment. The series of higher P alloys were sucked in ϕ 8 mm silica tubes after stepwise additions of Fe-P alloy and then hot-rolled. The chemical compositions are given in Table 1. AES

Table 1 Chemical composition of Fe-P alloys used.

Code	Chemical composition		
	P, wt%	P, at%	Others, wt%
0.05P	0.05	0.10	S; 0.004~0.005 N; 0.0013~0.0025 C; 0.0030~0.0039
0.1P	0.11	0.20	
0.2P	0.21	0.38	
0.5P	0.48	0.86	S; 0.004 C; 0.004~0.005 Si; 0.01 Mn; 0.01~0.02
0.6P	0.58	1.04	
0.9P	0.90	1.63	
1.0P	0.97	1.74	
1.5P	1.54	2.74	
1.6P	1.61	2.87	
1.9P	1.88	3.34	
2.6P	2.65	4.68	
2.7P	2.74	4.83	
eutec.	11.32	18.70	
Fe ₃ P	16.97	26.92	
Fe ₂ P	23.48	35.61	

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specimens vacuum sealed in silica tubes were heated and water quenched as shown in Fig. 1. Samples of low P alloys were homogenized for 3 h at 1200°C and slowly cooled to the ferrite region. All samples were heated at a higher temperature in the ferrite region for the grain growth, cooled stepwise and quenched in water as shown in Fig. 1. All of the "0.2P" specimens (0.2PH) were heated in 0.1 MPa H₂ stream at 750°C for 36 h to promote grain boundary fracture before the above heat treatment.[†] Specimens were mounted in the AES apparatus operating at a base pressure of 13 nPa. The lower P alloys were fractured at about -70°C and the higher P alloys were fractured at room temperature and the fractured surfaces were analyzed, followed by continuous analysis during the ion-bombardment in an Ar atmosphere of 6.65 mPa. The sputtering speed was 0.8 nm/min calibrated by sputtering the known thickness vapour deposited Fe films. The operating conditions were as follows; acceleration voltage, 4 kV; beam diameter, about $\phi 0.1$ mm; beam current, 30 μ A; modulation amplitude, 6 V; time constant, 0.1 s; sweep rate, 6 eV/s. AES analyses were performed at different 3 to 5 positions on a fracture surface and averaged. On compensation of the fraction of the intergranular fracture surface to the total area, the topography was later observed by scanning electron microscopy (SEM). The peak height of P (120 eV) was normalized by the Fe peak (703 eV) height. These data are shown as relative peak heights (RPH).

Figure 2 is a calibration curve from (RPH) to the P content. The data indicated by the bar symbol were obtained from the intergranular fracture surfaces. Open circles show the data after sputtering for 30 min. The numbers in brackets show the sputtering voltage (kV). (RPH)-values obtained from the surface subjected to lower voltage sputtering

[†] By the annealing in H₂ stream the grain boundary fracture ratio increased from less than 40% to more than 80%. The grain boundary segregation levels of C and N decreased to less than half of those which were not treated. However the segregation of P had the tendency to increase slightly within experimental error.

Fig. 1 Heat treating schedules.

Fig. 2 Relationship between P content in bulk and relative peak height of P.

are lower than those with higher voltage sputtering, because of the higher sputtering efficiency for P than for Fe. Although the (RPH) from the as-fractured intergranular surface shows the expected grain boundary segregation, the segregation in higher P alloys is not so distinct. Crosses show the data from

cleavage-fractured surfaces; they are given by the equation

$$(\text{RPH})_{\text{CL}} = 8.35x/(1-x), \quad (1)$$

where $(\text{RPH})_{\text{CL}}$ is the (RPH) from the cleavage-fractured surface and x is the bulk concentration of P in atomic fraction. The factor, 8.35, is larger than Meyer's result, 5.5⁽⁷⁾, which was obtained with chemically vapour-deposited films on Si substrates. Equation (1) can be applied in the range up to $x=0.05$, and the broken line shown in Fig. 2 must be used over the range which is expressed as

$$(\text{RPH}) = 3.739\{x/(1-x)\}^{0.7286}. \quad (2)$$

When the fracture surface contains the transgranular area, the true intergranular $(\text{RPH})_{\text{GB}}$, is calculated from apparent $(\text{RPH})_{\text{ap}}$, as follows:

$$(\text{RPH})_{\text{GB}} = \{(\text{RPH})_{\text{ap}} - 8.35x(1-x)^{-1}(1 - S_{\text{GB}})\}/S_{\text{GB}},$$

where S_{GB} is the fraction of the intergranular part in the fracture surface.

III. AES Analyses

Figure 3 is a typical example of the AES spectrum from a fracture surface, which shows the segregation of not only P but also S, C, and N. The effects of C and N on the grain boundary segregation of P are small⁽⁸⁾, but S and P segregations are competitive to each other⁽⁹⁾. However, the effects of these residual impurities were neglected in the present work.

Photograph 1 shows SEM fractographs

Fig. 3 AES spectrum from the fracture surface of "0.1P" specimen quenched from 880°C.

Photo. 1 SEM fractographs of "0.1P" specimens quenched from 880°C.

of "0.1P" specimens of different grain size. The effect of grain size on $(\text{RPH})_{\text{GB}}$ was neglected because $(\text{RPH})_{\text{GB}}$ taken from specimens A and B gives almost the same value.

Figure 4 shows the isothermal segregation of P in boundaries. The experimental evidence that the segregation level of "0.9P" specimens quenched from the temperature range of 800 to 100°C is constant suggests that the saturation of P segregation occurs. Figure 5 shows

Fig. 4 $(\text{RPH})_{\text{GB}}$ from αFe boundaries as a function of quenching temperature.

Fig. 5 Grain boundary concentration of P as a function of bulk P content.

the saturation with P content.

Photograph 2 shows the grain boundary precipitation of Fe_3P in the specimens quenched from temperature under that of the solubility limit shown in Fig. 6⁽¹⁰⁾.

In Fig. 7, open circles show $(\text{RPH})_{\text{GB}}$ of the as-fractured surface and solid circles show those after sputtering for about 30 min. The segregation of P to $\text{Fe}_3\text{P}/\alpha\text{Fe}$ interfaces may be very low because $(\text{RPH})_{\text{GB}}$ of "0.9P" specimens with Fe_3P precipitates quenched from the temperature range of 500 to 700°C is lower than that without Fe_3P precipitates quenched from that of 800 to 1000°C. Similar results have been reported in the case of C segregation to $\text{Fe}_3\text{C}/\gamma\text{Fe}$ interfaces⁽⁸⁾.

Fig. 6 Solubility limit⁽¹⁰⁾ and boundary precipitation zones (closed circles).

IV. Calculation of the Grain Boundary Concentration

Waugh and Southon⁽¹¹⁾ investigated oxygen segregation to Mo grain boundaries by means of field ion microscopy (FIM) and showed that the segregation zone was limited within 1 nm at either side of the boundary. Suzuki⁽¹²⁾ proposed a method to calculate the grain boundary concentration from AES data based on an assumption that the solute concentration, $X(nl)$, decreased exponentially with distance, nl/d , into grain boundary plane as follows:

Photo. 2 SEM fractographs of "0.9P" specimens quenched from 700°C (A) and from 600°C (B) and (C). The creased surface shows boundary precipitates.

Fig. 7 (RPH)_{GB} before (open circles) and after (closed circles) sputtering of "0.5P" and "0.9P" specimens.

$$X(nl) = x + X_e \exp(-nl/d), \quad (3)$$

where $n=0$ (boundary plane), 1, 2, 3, 4, $\dots$, n , l is the atomic size, x is the bulk concentration and X_e is the surface excess concentration at the boundary plane, d is the effective width of segregation from boundary plane (if $d=nl$, $X_e \exp(-nl/d) = X_e/e$). Then, the AES signal, I , is given by the relation

$$I = \Sigma I_0 X(nl) \exp(-nl/\lambda), \quad (4)$$

where I_0 is a constant as a function of experimental conditions, λ is the escape depth of Auger electrons. In the case of a uniform solid solution or a cleavage-fractured surface,

$$I \equiv I_u = I_0 x \{1 - \exp(-l/\lambda)\}^{-1}. \quad (5)$$

In the case of the Fe-P system, Suzuki⁽¹²⁾ approximated that λ_{Fe} was equal to λ_P . More exactly, the AES signals for Fe and P (I_{Fe} , I_P) are given by the relations

$$\begin{aligned} I_P &= \Sigma I_{OP} x_P \exp(-nl/\lambda_P) + \Sigma I_{OP} X_e \\ &\quad \times \exp(-nl/d) \exp(-nl/\lambda_P) \\ &= I_{OP} x_P \{1 - \exp(-l/\lambda_P)\}^{-1} \\ &\quad + I_{OP} X_e \{1 - \exp(-l/d - l/\lambda_P)\}^{-1}. \end{aligned} \quad (6)$$

$$\begin{aligned} I_{Fe} &= I_{OFe} x_{Fe} \{1 - \exp(-l/\lambda_{Fe})\}^{-1} \\ &\quad - I_{OFe} X_e \{1 - \exp(-l/d - l/\lambda_{Fe})\}^{-1}, \end{aligned} \quad (7)$$

where $x_{Fe} + x_P = 1$. The concentrations of P

and Fe on the grain boundary plane are given by $(x_P + X_e)$ and $(x_{Fe} - X_e = 1 - x_P - X_e)$, respectively.

The relation between I_P and the apparent surface concentration of P obtained from the calibration curve shown in Fig. 2, $X_{P,ap}$, is given by

$$I_P = I_{OP} X_{P,ap} \{1 - \exp(-l/\lambda_P)\}^{-1}. \quad (8)$$

Similarly,

$$I_{Fe} = I_{OFe} X_{Fe,ap} \{1 - \exp(-l/\lambda_{Fe})\}^{-1}. \quad (9)$$

From eq. (1),

$$I_P/I_{Fe} = (RPH)_{GB} = 8.35 X_{P,ap}/X_{Fe,ap}. \quad (10)$$

Therefore,

$$\begin{aligned} (RPH)_{GB} &= I_{OP} X_{P,ap} \{1 - \exp(-l/\lambda_P)\}^{-1} \\ &\quad / I_{OFe} X_{Fe,ap} \{1 - \exp(-l/\lambda_{Fe})\}^{-1} \\ &= 8.35 X_{P,ap}/X_{Fe,ap}. \end{aligned} \quad (11)$$

Thus,

$$\begin{aligned} I_{OP}/I_{OFe} &= 8.35 \{1 - \exp(-l/\lambda_P)\} \\ &\quad \times \{1 - \exp(-l/\lambda_{Fe})\}^{-1}. \end{aligned} \quad (12)$$

Provided that $l=0.287$ nm, $\lambda_P=0.4$ nm, $\lambda_{Fe}=1.0$ nm⁽¹³⁾, eq. (12) reduces to

$$I_{OP}/I_{OFe} = 17.13. \quad (13)$$

In reference to Waugh's FIM result⁽¹¹⁾, a reasonable value for d may be 0.4 nm which was given by Suzuki⁽¹²⁾.

From eqs. (10), (11) and (13), the P concentration of the boundary plane, X_{GB} , is given by

$$\begin{aligned} X_{GB} &= x_P + \{12x_{Fe}(RPH)_{GB} - 100x_P\} \\ &\quad / \{4.7(RPH)_{GB} + 67\}, \end{aligned} \quad (14)$$

providing $x_P \leq 0.05$. Similarly for $x_P > 0.05$

$$\begin{aligned} X_{GB} &= x_P + \{16.4x_{Fe}[(RPH)_{GB}]^{1.37} - 100x_P\} \\ &\quad / \{6.45[(RPH)_{GB}]^{1.37} + 67.2\}. \end{aligned} \quad (15)$$

Figure 8 rewritten from Fig. 4 shows the relationship between grain boundary concentration and reciprocal temperature.

Hondros⁽¹⁴⁾ predicted thermodynamically that the P content in α Fe boundaries was extrapolated from that in δ Fe boundaries and monotonously increased with decreasing temperature. As shown in Fig. 8, however, the saturation of P segregation level appears at

Fig. 8 Boundary concentration of P as a function of reciprocal temperature of quenching.

the lower temperature and/or for the higher P content alloys and the value of the grain boundary concentration is approximately 0.15.

Ramasubramanian and Stein⁽¹⁵⁾ reported that the boundary enrichment ratio of P in a Fe-0.2 wt% P alloy at 1000°C was 134, but our data are on the order of 10. The difference between them is very large.

V. Discussion

As shown in Figs. 6 and 7, a "0.9P" alloy (1.63 at% P) is a single phase of α Fe at 800°C, and from Fig. 8 the boundary concentration is 15.7 at% P. From Fig. 6, at 700°C the matrix concentration is 0.9 at% P (solubility limit), and Fe_3P precipitates at boundaries as shown in Photo. 2. The average concentration of the fractured surface after sputtering, $X_{\text{GB}}^{\text{sp}}$, which is calculated to be 3.5 at% P by putting the $(\text{RPH})_{\text{GB}}^{\text{sp}}$ -value at 700°C in Fig. 7 into eq. (14), is a function of the fraction of area occupied by Fe_3P on the fractured surface, $S_{\text{Fe}_3\text{P}}$, as shown in Fig. 9(b). That is,

$$X_{\text{GB}}^{\text{sp}} (=0.035) = (\text{P in bulk; } 0.009)(1 - S_{\text{Fe}_3\text{P}}) + (\text{P in Fe}_3\text{P; } 0.25)S_{\text{Fe}_3\text{P}},$$

and we obtain $S_{\text{Fe}_3\text{P}} = 0.107$.

In higher P alloys (eutectic alloy, Fe_3P , and Fe_2P) the (RPH) -values from the as-fractured intergranular surfaces decrease slightly by sputtering with 2 kV, and in Fig. 7, $(\text{RPH})_{\text{GB}}$ of "0.9P" specimens with Fe_3P precipitates is lower than those without Fe_3P precipitates.

Fig. 9 Schematic representation of the near-surface section of a fractured "0.9P" alloy quenched from 700°C.

It is considered therefore that the segregation of P to $\text{Fe}_3\text{P}/\text{Fe}$ interfaces would be very low. From this experimental result, the following speculation may be deduced. Whereas the P atoms adsorbed in $\text{Fe}_3\text{P}/\text{Fe}$ interfaces are regarded as a part of surface atoms of Fe_3P , the matrix side surface separated from precipitates is not covered by the P-enriched layer as shown in Fig. 9(a). In this case, the P-concentration of Fe/Fe boundary, X_{GB} , is found to be 0.145 from the calculation by substituting the experimental values into eqs. (2), (15), and

$$\begin{aligned} & (\text{RPH})_{\text{GB}} \\ &= 3.739 \left[\frac{(\text{P in Fe}_3\text{P; } 0.25)}{(\text{Fe in Fe}_3\text{P; } 0.75)} \right]^{0.7286} S_{\text{Fe}_3\text{P}} \\ &+ 8.35 \frac{(\text{P in bulk; } 0.009)}{(\text{Fe in bulk; } 0.991)} S_{\text{Fe}_3\text{P}} \\ &+ (1 - 2S_{\text{Fe}_3\text{P}})(\text{RPH})_{\text{GB, true}} \\ &= 0.734 \\ & \quad \text{("0.9P" alloy quenched from 700°C)} \end{aligned}$$

where $(\text{RPH})_{\text{GB, true}}$ presents the true intergranular (RPH) and $(\text{RPH})_{\text{GB}}$ does the intergranular (RPH) with Fe_3P precipitates. On the other hand, the X_{GB} value at 800°C for the boundary without precipitates is similarly given by 0.157, which is very close to the abovementioned value and/or to the saturation value, 0.15, shown in Figs. 5 and 8.

It is tempting to draw a free energy-concentration diagram of the boundary phase

in a binary alloy system besides that of the bulk phase with the help of common tangent construction. By extending Guttman's representation⁽¹⁶⁾, the present results can be illustrated schematically as shown in Fig. 10. That is, as increasing P content in bulk, the grain boundary concentration increases more rapidly, but any secondary "boundary phase" does not form before the matrix concentration reaches the solubility limit (X^B in Fig. 10). If it is not so, the boundary segregation must jump discontinuously at a critical matrix concentration as an example illustrated by Guttman⁽¹⁶⁾.

To be more exact, whereas the boundaries present sites with a spectrum of activities⁽¹⁷⁾, the P-concentration in the strongest sites increases continuously beyond the average value of saturation, 0.15, and the concentra-

tion in the weakest sites is restricted to a value smaller than 0.15.

VI. Conclusions

(1) Equilibrium segregation of P to α Fe boundaries is obtained by means of a quantitative analysis of "AES", and the results are summarized in Fig. 8. The saturation value of grain boundary concentration is found to be 0.15 and the enrichment ratio is on the order of 10.

(2) The boundary structure at a saturation level was discussed.

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Fig. 10 Schematic representations of free energy-concentration diagram and change in concentration of fractured surface in the case of the Fe-P system.