Chemical State of Phosphorus Segregated at Grain Boundaries in Iron*

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Synopsis

Knowledge on the chemical state of phosphorus (P) segregated at grain boundaries in iron is important in discussing the mechanism of grain boundary decohesion by P. In order to determine the chemical state of P at grain boundaries, X-ray photo-electron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used.

Fe-P alloy specimens with the P concentration between 0.05 mass% and 15.6 mass% was fractured in the analyzer chamber of which vacuum was better than 5×10^{-9} Pa (4×10^{-11} torr). Since the amount of P segregated at grain boundaries is small, XPS had to be measured for a long time to accumulate the signal from P. The prolonged measurement was possible without contamination by the residual gas because of the high vacuum. XPS of the segregated P was found to be identical to XPS of P in Fe_3P . This result supports the Losch model for the grain boundary decohesion by P, in which a segregated P atom forms a strong bond with surrounding Fe atoms and reduces the strength of bond between Fe atoms neighboring to the P atom.

The shape of Auger electron spectrum of P in solid solution varies with the P concentration, but that of the segregated P is independent of the P concentration and identical to that of P in Fe_3P . The importance of the variation of the shape of Auger electron spectrum with the P concentration in the quantitative analysis of the segregated P is discussed.

I. Introduction

It has been well known that the segregation of phosphorus (P) at grain boundaries causes the temper embrittlement in low alloy steels, e.g., Ni-Cr steels and Cr-Mo steels. The grain boundary embrittlement due to the segregation of P is also observed in Fe-P alloys based on electrolytic iron if the concentration of carbon (C) in them is small enough.¹⁾ The mechanism of the grain boundary decohesion by the impurity segregation such as P is not clarified as yet, although several hypotheses, atomistic and electronic, have been proposed. Seah²⁾ has assumed that the impurity atoms segregated at grain boundaries have the same chemical bond with the host atoms as in the solid solution of the matrix and that the fracture propagates between the impurity and host atoms. He has, then, discussed the degree of grain boundary decohesion for various impurities in iron. His model, however, does not explain well the effect of impurity on the grain boundary embrittlement.³⁾ Losch⁴⁾ considers that the bond of the segregated atoms with the surrounding metal atoms is of a covalent nature, and that the impurity atoms draw electrons around them and hence the bond between host Fe atoms neighboring the impurity atoms becomes weak. In this case the fracture path is not between an impurity atom and a host atom but between host atoms neigh-

boring the impurity atom. Similar models have been proposed by Ogawa and Ishida⁵⁾ and by Messmer and Briant.^{6,7)} Experimental supports to the covalent-like bond model are given by a Mössbauer effect study of Sn at grain boundaries in iron⁵⁾ and an investigation of the electronic state of S on the surface of nickel.⁷⁾ No investigation, however, has been reported on the chemical state of P, one of the most important impurities in steels, segregated at grain boundaries of iron.

We applied X-ray photo-electron spectroscopy (XPS) and Auger electron spectroscopy (AES) to investigate the chemical state of P segregated at grain boundaries of iron. XPS is a powerful technique to investigate the chemical state but the sensitivity is low. In order to apply this technique to segregation at grain boundaries, one has to accumulate the signal from the segregation for a long time, because the total amount of segregation to be analyzed is quite small. However, the fracture surface freshly revealed under an ultra high vacuum is usually contaminated by the residual gas in the analyzer during the long period measurement. A high enough vacuum is necessary to prevent the contamination, and no such investigation has been performed. We have succeeded to obtain such a high vacuum and analyzed the chemical state of P at grain boundaries of iron. AES is often used to identify elements existing at grain boundaries. It is, however, considered that the energy distribution of Auger electrons is rather insensitive to the chemical state of the element. We have examined the possibility of applying AES to the chemical state analysis. The present paper reports these results.

II. Experimental Procedure

1. Specimen Preparation

Electrolytic iron (MAIRON) was melted in a high frequency induction vacuum furnace and deoxidized with white pig iron. The melt was added with an Fe-25mass%P mother alloy (commercial, but remelted under vacuum for purification) and cast. The ingot was forged at high temperatures (1 270 to 1 070 K) to a bar of 4 mm in diameter. It was machined to specimens of 3.6 mm in diameter and 32 mm long. They were decarburized to 10 to 20 mass-ppm C by hydrogen treatment at 1 070 K (12 h with wet hydrogen and 12 h with dry hydrogen).

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The decarburized specimens were held for 0.5 h at 1170 K and oil-quenched, and hence they were of the single α -phase. No precipitate particle of carbide or phosphide was revealed with optical or transmission electron microscopy ($\times 50\,000$). The P concentrations were 0.05, 0.11, 0.53, 1.0, 1.7, 2.0, 2.8 and 15.6 mass%, and the concentration of other impurities was as follows: Si: 0.005; Mn: 0.005; Al: 0.003; S: 0.003; O: <0.005 mass%.

Specimens were V-notched and fractured below 170 K in the chamber of the analyzer under an ultra high vacuum, and XPS and AES measurements were performed. The specimens and the specimen holders for XPS were vapor-deposited with gold of about $0.1\ \mu\text{m}$ thick on the whole surface after being notched. The X-ray beam diameter for XPS was about 5 mm, so that, besides the fracture surface, the notch surface is involved in XPS analysis. The gold surface layer covers the notch surface and the undesirable signal from the notch surface is eliminated. Besides, the gold ($\text{Au}_{4f_{7/2}}$ binding energy) was used as the standard (83.8 eV) for the photoelectron energy calibration, and the accuracy of the energy measurement is improved.

2. XPS and AES Analyses

XPS analysis was performed with PHI-550 under the following conditions:

Degree of vacuum when the specimen was fractured:

$(5\text{ to }9)\times 10^{-9}\text{ Pa } ((4\text{ to }6)\times 10^{-11}\text{ Torr})$

Degree of vacuum during measurement:

$<3\times 10^{-8}\text{ Pa } (<2\times 10^{-10}\text{ Torr})$

X-ray source and accelerating voltage:

$\text{MgK}\alpha$ and 10 kV

Emission current: 40 mA

Pass-energy: 50 eV

Time for the XPS measurement: $\leq 10\text{ h}$.

AES analysis was performed with PHI-590 under the following conditions:

Degree of vacuum when the specimen was fractured:

$(5\text{ to }9)\times 10^{-9}\text{ Pa } ((4\text{ to }6)\times 10^{-11}\text{ Torr})$

Degree of vacuum during measurement:

$(5\text{ to }10)\times 10^{-9}\text{ Pa } ((4\text{ to }8)\times 10^{-11}\text{ Torr})$

Accelerating voltage: 3 kV

Modulation: 3 eV or 1 eV

Current: 100 nA

Primary electron beam diameter: $5\ \mu\text{m}$

Time for the AES measurement: $\leq 1\text{ h}$.

It should be noted here that the specimen current, 100 nA, was much smaller than that usually used in AES. The current density is so low, $5\times 10^3\text{ A/m}^2$ which is about 1/100 of the current density usually used, that no severe local heating occurs to affect the surface state.

III. Experimental Results and Discussion

1. Contamination of the Fracture Surface with the Residual Gas during Measurement

Figure 1 shows the Auger electron spectrum of a grain boundary facet in the fracture surface of an Fe-1.0%P alloy. The contamination due to the

Fig. 1. AES from a grain boundary fracture surface taken 1 h and 30 h after breaking the specimen under ultra high vacuum better than $4\times 10^{-11}\text{ Torr}$.

residual gas is detected with the appearance of C and O peaks. Here, these peaks are not seen until 30 h after the fracture in a vacuum of $5\times 10^{-9}\text{ Pa } (4\times 10^{-11}\text{ Torr})$. The peak height ratio of the P peak (120 eV) to the Fe peak (703 eV), P_{120}/Fe_{703} , is 40.5 % and remains so within 30 h. Although not being shown in the figure, the transgranular fracture surface is easier to be contaminated than the grain boundary facet; detectable peaks of C and O appear 10 h after the fracture. The values of P_{120}/Fe_{703} from the transgranular fracture surface decreases slightly with increasing contamination. This decrease occurs because the amount of P analyzed is small and the P Auger electron, of which energy is smaller than that of the Fe Auger electron, is more effectively absorbed by the C and O contamination layer at the surface. Although the result depends on the amount and composition of the residual gas and hence may be difficult to be generalized, we may conclude that, under a vacuum better than $5\times 10^{-9}\text{ Pa } (4\times 10^{-11}\text{ Torr})$, it is possible to differentiate the Auger peaks of the segregated C and O from those of contamination and to analyze them in detail with a sufficient time.

In the case of XPS analysis, the vacuum could not be kept so good as in the case of AES, because a rather large amount of heat is generated at the X-ray source filament. The vacuum was $(2.6\text{ to }4)\times 10^{-8}\text{ Pa}$ for 10 h during which the measurement was repeated to improve the S/N ratio. AES analysis was made before and after XPS measurement, and slight contamination by C and O was detected after XPS measurement. If the chemical state of P segregated at grain boundaries is affected by the C and O contamination, two or more peaks may be observed or the shape of the P peak may broaden. The observed peak of P, however, is single and its width is similar to P peaks in other cases, e.g., P in Ar ion sputtered Fe_3P surface. Hence, we may conclude that the chemical state of P is not affected by the C and O contamination.

2. XPS Analysis of P Segregated at Grain Boundaries

Figure 2 shows XPS of P (P_{2p}) of the fracture surface of an Fe-1.0%P alloy. The fracture is almost 100 % intergranular, and hence the spectrum is of P segregated at grain boundaries. The peaks of $Fe_{2p1/2}$ and $Fe_{2p3/2}$ are also shown in Fig. 2, which are at 720.4 eV and 707.0 eV, respectively. These peaks are of metallic iron.^{8,9)} The peak of P_{2p} is at 128.8 eV, and different from one at 129.7 eV of element P (P_{2p})¹⁰⁾ or 135.0 eV of P_{2p} in P_2O_5 .¹¹⁾ It is not known as yet the kind of phosphide of which P gives the observed 128.8 eV peak; P segregated at grain boundaries of iron is in an unknown chemical state. The chemical state, however, is expected to be similar to or the same as that of P in Fe_3P , and comparison is made between the segregated P and P in Fe_3P . Since there had been no measurement of XPS of P in Fe_3P , we examined it. Figure 3 shows the result of XPS analysis of an Fe_3P specimen, of which surface was exposed to the air and contaminated with O_2 , H_2O and CO_2 . The Fe peak shows that Fe in this specimen is in a state of Fe(II) similar to that in wüstite.¹²⁾ There are two peaks for P_{2p} ; the 128.8 eV peak is the unknown one just described above and the 133.0 eV peak is very close to the of

P in $(C_6H_5)_3PO$, 132.7 eV, among various peaks so far reported for P.¹³⁾ These results show that no accurate measurement to determine the chemical state of P in Fe_3P is possible with the surface already exposed to the air for a long time. Hence, the surface was subjected to Ar ion sputtering to reveal a fresh surface, and XPS was measured, Fig. 4. The $Fe_{2p1/2}$ and $Fe_{2p3/2}$ peaks are of the same binding energy as those for metallic Fe. The 133.0 eV peak for P_{2p} disappears and the 128.8 eV peak is left. Thus, the 128.8 eV peak is concluded to be the P_{2p} peak for Fe_3P . Therefore, P segregated at grain boundaries in iron is in the same chemical state as P in Fe_3P , as far as the XPS investigation is concerned. Exactly the same result was obtained for segregated P in an Fe-0.1%P and an Fe-0.005%P alloys.

The above conclusion for the chemical state of the segregated P does not mean that P is precipitated as Fe_3P compound at boundaries. Microscopic investigation, optical and electron, do not reveal any precipitate at boundaries except for oxides which are observed very seldom, and AES analysis after Ar ion sputtering show that the layer concentrated P is limited only within a few atomic layers from the surface. If a second phase with a structure close to

Fig. 2.

XPS for Fe and P from the fracture surface of an Fe-1.0%P alloy specimen. The specimen was fractured in the analyzing chamber.

Fig. 3.

XPS (for Fe and P) from an Fe_3P specimen exposed to the air.

Fig. 4.

XPS (for Fe and P) from the same specimen as in Fig. 3, but cleaned by Ar ion sputtering.

Fe_3P is considered, it should be more or less two-dimensional. We, together with Hirokawa and Oku, have proposed a new method of estimating the thickness of the layer containing segregated P.¹⁴⁾ It has been assumed in the paper, for the convenience of expression, that P atoms are distributed uniformly within the layer with concentration of 25 at.% P, *i.e.*, that in Fe_3P , and the thickness of the layer is calculated. However, the distribution of P at each grain boundary facet is not necessarily uniform. It is quite possible that islands of a high P concentration with a fixed thickness are dispersed on the surface. The present result only shows the chemical state of segregated P to be the same as or similar to that of P in Fe_3P , and no conclusion may be drawn about the crystallographic structure or the distribution of P.

The above result supports the Losch model for the grain boundary decohesion by the P segregation. The Seah model, although its assumptions and approximations are not necessarily agreeable, cannot be ruled out by the present result. One of the important assumptions in the Seah model is that the chemical state of P at grain boundaries is the same as in solid solution. The concentration of P at the transgranular fracture surface is so small that XPS analysis of P is impossible, and hence no comparison can be made between the segregated P and P in solid solution with XPS to test the assumption.

3. The P Concentration Dependence of the Shape of the Auger Electron Spectrum

It is generally considered that the shape and position of the Auger electron spectrum peak are rather insensitive to the chemical state of the element. A few results, however, have been reported to show that the shape of the differential curve of AES depends on the chemical state.¹⁵⁾ Since AES can detect a much smaller amount of element than XPS, it can analyze solute elements such as P in solid solution at transgranular fracture surface. Hence, it is possible to compare AES of P at grain boundaries with that of P in solid solution.

Figure 5 shows the Auger peak of P taken at a transgranular fracture surface of Fe-P alloys with 0.05 to 15.6 mass% P. The 15.6 mass% P alloy is the composition of Fe_3P . This alloy was specially prepared from the electrolytic iron and phosphorus, and much purer than the commercial alloy. The peak to peak height (PPH) is normalized by changing the scale of the dE/dN axis. Figure 6 shows the Auger peak of P at grain boundary facets of Fe-0.05~1.0mass%P alloys. The curves shown in Fig. 6 coincide with each other and with the curve for Fe_3P (Fig. 5, Fe-15.6mass%P) if dE/dN is normalized; P segregated at grain boundaries has an Auger electron spectrum with exactly the same shape as P in Fe_3P . Here, the same shape means that two curves coincide with each other by changing the scale of the ordinate. If the detail of the shape of an Auger electron spectrum reflects the chemical state of an element, the result shown in Fig. 6 means that the chemical state of P segregated at grain boundaries is the same as that

Fig. 5. AES of P taken from the cleavage fracture surface of Fe-P alloys. The P concentration (mass%) is shown in the figure. The number on the right of each spectrum is the actual peak-to-peak height ratio (P_{120}/Fe_{703}).

Fig. 6. AES of P segregated to grain boundaries in Fe-P alloys with various P concentrations. Since fracture mode is not intergranular but cleavage in alloys with more than 1.7 % P, their spectra are not shown.

of P in Fe_3P . This is in agreement with the above conclusion with XPS. On the other hand, the shape of curves for the transgranular fracture surface of alloys with P less than 2.1 mass% (Fig. 5) differs from each other and from that of Fe_3P ; the peak at 114 eV decreases relative to the level above 125 eV. It would be concluded that the chemical state of P in a solid solution of iron would vary with the P concentration and that the state of P in a solid solu-

tion would be different from the state of P at grain boundaries. However, it is difficult to draw such a conclusion at present, because the shape of the Auger electron spectrum may depend on the characteristics of the apparatus itself, *e.g.*, the method to subtract the background of the spectrum. In order to determine whether the change in the shape of the Auger electron spectrum is only apparent or real, the detail of the Auger transition process of P should be studied.

Although the results shown in Figs. 5 and 6 cannot give a definite conclusion about the chemical state of P in a solid solution or at grain boundaries, they are important for a quantitative analysis of P segregated at grain boundaries. For a quantitative analysis with AES, the height between peak to peak in a dE/dN curve, I_P , is used to compare with that in a standard specimen of a known concentration of the element. In order for I_P to be used as a measure of the quantity of the element, the shape of the dE/dN curve must be independent of the concentration and state of the element. *The concentration is proportional to*

$$I_0 = \int_{-\infty}^{+\infty} N(E)dN.$$

If the shape of the normalized dE/dN curve is the same, *i.e.*, two curves coincide with each other by changing the scale of dE/dN , the ratio of the integrals from two specimens, I_{01} and I_{02} is equal to the factor changing the dE/dN scale. Hence I_P is proportional the concentration of the element to be analyzed. The result shown in Fig. 6 confirms this criterion for P segregated at grain boundaries in iron. It is not accurate to use the result in Fig. 5 for calibration, although, as shown in Fig. 7,* a linear relation exists between I_P of P in solid solution measured at the transgranular fracture surface and the bulk concentration of P, C_P . If we use an I_P -P concentration relation obtained with specimens of lower P concentrations (dotted line), we underestimate the grain boundary P concentration.

Fig. 7. Peak-to-peak height for P_{120} AES spectra taken on the transgranular fracture surface (normalized with that for Fe_{70s}) against the bulk concentration of P. The modulation is 3 eV. The line drawn for data for alloys with small P concentrations does not pass through the origin. This is due to rather large back ground.

In AES quantitative analysis reported so far by other authors, the shape of dE/dN curves have not been paid proper attention. There has been a report in which I_P 's for Cr, Ni and Mo in iron are shown to be proportional to the concentration of each element, respectively, and hence I_P is considered to be a proper measure of the concentration of these elements.¹⁶⁾ It is now obvious that the linear relation between I_P and the bulk concentration is not a sufficient condition for the quantitative analysis. The shape of dE/dN curves must be shown to be independent of the concentration and the state of the element. In case of P in iron, I_P for Fe_3P may be taken as a standard, the concentration of P being taken to be 25 at.%, or a calibration curve may be made with I_P for a transgranular fracture surface in Fe-P alloys with P more than 3 mass%. It is seen in Fig. 7 that data for alloys with more than 3 mass% P fall on the line connecting the origin and the point for Fe_3P .

IV. Conclusions

XPS and AES analyses were made for Fe-P alloys with various amount of P on the fracture surface freshly revealed under an ultra high vacuum. The vacuum was good enough to prevent the surface from contamination by the residual gas for more than 10 h.

The chemical state of P segregated at grain boundaries is the same as or similar to that of P in Fe_3P . This conclusion does not necessarily mean that P is precipitated at grain boundaries as Fe_3P . The segregated P is confined within a few atomic layers from the fractured surface. The conclusion for the chemical state of P supports the grain boundary decohesion model due to Losch, in which the bond of P atoms with surrounding Fe atoms is assumed to be of a covalent nature.

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* The shape of the dE/dN curve and I_P depend on the experimental conditions, such as the modulation, as well as on each instrument. Hence the relation between I_P and C_P shown in Fig. 7 may not be considered to be a universal calibration curve for P segregated at grain boundaries of iron. Figure 7 is only to show the linear relation between I_P and C_P and the difference between two lines.

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