***In Situ* Observation of Preferential Anodic Dissolution of Phosphorus Compound in Fe–P Alloys Using Raman Spectroscopy**

Hiroyoshi TANABE, Teruo SHIBUYA,¹⁾ Noriaki KOBAYASHI¹⁾ and Toshihei MISAWA¹⁾

Department of Applied Chemistry, Muroran Institute of Technology, Mizumoto, Muroran, Hokkaido, 050 Japan.

1) Department of Materials Science and Engineering, Muroran Institute of Technology, Mizumoto, Muroran, Hokkaido, 050 Japan.

(Received on August 12, 1996; accepted in final form on November 12, 1996)

The solution chemistry of P in the Fe–P alloy electrodes containing P of 0.104, 0.028, and 0.004 mass% has been investigated by using *in situ* Raman spectroscopy in an electrochemical cell under controlled potential in 0.1 kmol·m⁻³ NaOH at 25°C. It is found that the segregation site of the precipitate with the chemical composition of F₃P dissolves preferentially. Using *in situ* Raman spectroscopy three dissolution species of PO₄³⁻, HPO₄²⁻, and H₂PO₄⁻ were detected on the surface at the segregation site, and these concentrations depend on the location of the precipitate of P compound whether at grain boundary or in grain. The detection of HPO₄²⁻ and H₂PO₄⁻ both of which are unstable in the solution of NaOH suggests that the localized corrosion at the segregation site of P induces decrease of pH.

KEY WORDS: *In situ* Raman spectroscopy; preferential dissolution; Fe–P alloy; localized corrosion.

1. Introduction

It has been well known that the impurities of P, As, and Sn *etc.* reduce the corrosion resistance as well as mechanical properties, such as embrittlement of iron steels due to segregation towards grain boundary. Therefore, the processing for purification of steels has been progressed. However, since the present process of iron refinement has employed the oxidation method which introduces difficulties to remove the inactive elements, some amount of the impurities stays behind in the steel.

Influence of both the kind and the concentration of impurities on the properties of iron steel has been widely studied using a number of techniques. These techniques employed give us only average information of substrate surface. The better understanding of the effects of impurities on corrosion control requires the chemical and structural information on corrosion products focusing on the solution side as well as the interface on the substrate side.

“Phosphate Corrosion¹⁾” has been widely noticed, whose attack is severe and which causes various kinds of wastage morphologies such as gouges, pits, and groves. This suggests that the phosphate corrosion will introduce serious problems during constructing an “Iron Recycle” system. In the present work, we investigate the behavior around the P precipitates in the Fe–P alloy electrode using *in situ* Raman spectroscopy measurement under potentiostatic control of the substrate electrode.

2. Experimental

2.1. Preparation of Test Samples

The Fe–P ingot alloys were prepared by electrorefining iron with a given amount of ferrophosphorus using high frequency induction furnace. The ingot samples were treated by the forging at 1100°C followed by the solution annealing at 900°C for 1220 min. Then, the samples were shaped to the thickness of 13 mm, which had average grain size of 300 μm.

2.2. Substrate Electrode

The substrate electrodes tested were pure iron and Fe–P alloys with the different P concentrations (P-1: 0.004 mass%, P-2: 0.028 mass%, P-3: 0.104 mass%) in the form of rod of φ5 mm in diameter. After the substrate electrode was treated by solution annealing again in ferrite-phase region at 900°C for 120 min in vacuum at 10⁻³ torr and was cooled in air, it was mounted in a glass tube with epoxy, ground until smooth, and polished to a mirror finish with 0.05 μm alumina. Following this procedure, the edge of the substrate electrode was sealed with epoxy except for the part of φ4 mm of the surface.

2.3. *In Situ* Raman Spectroscopy with Electrochemical Potentiostatic Control

The experimental set up used in this study is shown in Fig. 1. The characterization of reaction species containing P was performed in 0.1 kmol·m⁻³ NaOH solution under a microscope objective on a selected area (φ2 μm) of the surface of substrate electrode, whose potential was controlled by a potentiostat. The light source

Fig. 1. Micro cell for *in situ* Raman spectroscopy measurement.

for Raman excitation was argon laser ($\lambda = 514.5$ nm), and the scattering Raman light was analyzed with a triple monochromator (JASCO, NR-1800S). The power of laser beam was 100 mW and at the substrate surface it was about 7.5 mW. The signal was detected using a charged-coupled device multi-channel detector. Raman spectra were recorded at the given polarization potentials. A microelectrochemical cell was consisted of a Fe-P working, a Pt counter, and a Ag/AgCl reference electrodes, as described in Fig. 1. The working electrode surface was covered with an electrolyte layer of 3 mm in thickness.

2.4. Polarization Measurement

Potentiodynamic polarization curves were measured at a potential sweep rate of $10 \text{ mV} \cdot \text{min}^{-1}$ in deaerated $0.1 \text{ kmol} \cdot \text{m}^{-3}$ NaOH solution at 298 K. The electrode potentials were measured with respect to a Ag/AgCl reference electrode in a saturated KCl solution. The counter electrode was a Pt spiral wire.

2.5. SEM-EDX Measurements

A potentiostatic etching method²⁾ using non-aqueous solution has been applied to the observation and analysis of precipitates in the test samples. The samples were etched electrochemically at a given constant potential in the mixed solution of 10 vol% acetylacetone–1 wt% tetramethylammonium chloride–methyl alcohol. Precipitates were observed and analyzed by employing analytical SEM-EDX instruments (SEIKO DENNSHI Co. Ltd., SED 8600) after the etched surface of the sample was washed with methyl alcohol. The quantitative accuracy of the SEM-EDX analysis is about 1 mass% of P and Al.

3. Results and Discussion

3.1. Current–Potential Curves

Figure 2 shows typical potentiodynamic polarization curves of three test electrodes in $0.1 \text{ kmol} \cdot \text{m}^{-3}$ NaOH solution at 25°C under N_2 atmosphere. Corrosion poten-

Fig. 2. Anodic polarization curves of Fe-P alloy electrodes containing 0.004 mass%P (P-1), 0.028 mass%P (P-2), and 0.104 mass%P (P-3) in deaerated $0.1 \text{ kmol} \cdot \text{m}^{-3}$ NaOH solution.

Fig. 3. SEM micrograph (a) and enlarged image (b) around the pit in (a) for P-3 electrode after the anodic polarization at 300 mV for 3 h in deaerated $0.1 \text{ kmol} \cdot \text{m}^{-3}$ NaOH solution.

tials (E_{corr}) of P-1, P-2, and P-3 test electrodes are -560 , -580 , and -630 mV, and passive current densities 0.4 , 2.2 , and $2.8 \mu\text{A} \cdot \text{cm}^{-2}$, respectively. These indicate that the corrosion resistance of electrodes tested is inferior in the order, P-1, P-2, and P-3, as the concentration of P in a test electrode increases. Figure 3 shows the SEM images of P-3 test electrode after the anodic polarization at 300 mV vs. Ag/AgCl for 360 min. The SEM images indicates the presence of the sites of preferential anodic dissolution.

In order to characterize the location and the chemical

Fig. 4. SEM micrographs (a) and the P K α line image (b) by EPMA of P-3 electrode.

(A) P compound segregation site in grain, (B) P compound segregation site at grain boundary, (C) Site in grain without P precipitate

Table 1. Chemical composition of the precipitate at the segregation site of P-3 electrode.

Location	Fe at%	P at%	Al at%
Average composition	99.79	0.19	0.02
Precipitate at grain boundary*	73.33	22.29	4.38
Precipitate in grain**	80.91	13.04	6.05
Matrix in grain*** (without precipitate)	97.99	0.41	1.60
Matrix at grain boundary (without precipitate)	98.13	0.16	1.71

* corresponding to the site B in Fig.4

** corresponding to the site A in Fig.4

*** corresponding to the site C in Fig.4

composition of the preferential site for anodic dissolution, analytical SEM-EDX instrument was employed. Typical SEM and EDX images of P-3 electrode are shown in Figs. 4(a) and 4(b), respectively, after the potentiostatic etching method mentioned above. Figure 4(b) shows the image of P K α line, in which the location of highlight coincide with the location of the precipitate in Fig 4(a). The chemical compositions at the segregation sites on the electrode surface are analyzed, as shown in Table 1. Site A, B, and C in Fig. 4(a) are the precipitate in grain, that at grain boundary, and alloy matrix without precipitate, respectively. As seen from the results of EDX

Fig. 5. *In situ* Raman spectra for P-3 electrode in 0.1 kmol·m⁻³ NaOH solution at 300 mV.

(A) P compound segregation site in grain, (B) P compound segregation site at grain boundary, (C) Site in grain without P precipitate. Spectra of A, B, and C obtained at (A), (B), and (C) sites in Fig. 4, respectively.

analysis, the site B has a near chemical composition of F₃P, and that of A in grain slightly deviate from that of F₃P. The higher amount of Al at the P compound segregation sites both in grain and at grain boundary suggests that Al₂O₃ stabilized at high temperature during the sample preparation works as to nuclei for segregation of Fe₃P or P.

3.2. *In Situ* Raman Spectra

The identification of dissolution chemical species from the site A, B, and C at the electrode/electrolyte interface is very useful in better understanding preferential dissolution of Fe-P electrodes. Figure 5 shows the *in situ* Raman spectra of the segregation site A in grain, the segregation site B at grain boundary, and on the site C in grain without the precipitate of P compound for P-3 test electrode at 300 mV vs. Ag/AgCl. It is found that the Raman spectra at the site A and B, which have characteristic peaks around 915, 955, and 990 cm⁻¹, are significantly different from those at the site C. These peaks were not detected at any location without the precipitates of P compound, even at grain boundary. In addition to these significant peaks, a peak around 1050 cm⁻¹ is observed at every site analyzed on the electrode, which is also observed in the Raman spectra for P-1 and P-2 electrodes. This peak has not yet been identified.

To know the dependence of polarization potential on the behavior of these three peaks of 915, 955, and 990 cm⁻¹ is of very importance in understanding the behavior and chemistry at the preferential dissolution site of Fe-P alloys. Figure 6 shows the dependence of Raman spectra around 955 cm⁻¹, which is attributed to HPO₄²⁻ species as discussed below (Sec. 3.3.), on the polarization potential. The intensity of the peak of 955 cm⁻¹ increases as the electrode potential increases and then shows a maximum at 300 mV. The intensities of 915 and 990 cm⁻¹ indicated in Fig. 5 show the same potential-dependence as that of 955 cm⁻¹. The intensities of these peaks decrease even if the electrode potential is biased to more anodic potential near to the transpassive state

Fig. 6. Dependence of *in situ* Raman spectra at the segregation site at grain boundary of the P compound of P-3 electrode on anodic polarization potential in $0.1 \text{ kmol} \cdot \text{m}^{-3}$ NaOH solution.

and at 900 mV these peaks disappear. *In situ* CCD monitor TV caught the change of electrode surface morphology corresponding to the change of the Raman spectra. Although the presence of the precipitate of P compound was able to be confirmed until 500 mV, at the potential beyond 700 mV the site of the precipitate was transformed to a pit with an area of about $\phi 40 \mu\text{m}$ due to complete dissolution of the precipitate. On the other hand, no change was observed in both the Raman spectra measured at grain boundary and in grain without the precipitates of P compounds, even if the electrode potential was polarized to the anodic direction. Pure iron electrode also shows no evidence of change in spectra at any electrode potentials within the test potential range.

Figure 7(a) which is a photo obtained by a video printer shows a segregation site of the precipitate of P compound with a diameter of $10 \mu\text{m}$ on P-3 electrode. Figure 7(b) shows the intensity image of Raman spectra over the same segregation site. In Fig. 7(a) the surface of the electrode was scanned by moving the electrochemical cell in $1 \mu\text{m}$ increments with computer controlled stepper motors. X and Y axis are established as shown in Fig. 7(a). The scanning time for this area was in less than 2 min. The spectra around 955 and 915 cm^{-1} reveal the highest intensities at the center of the location of the precipitate of P compound, and the intensity decrease rapidly at the both side.

3.3. Identification of Dissolution Species at P Segregation Sites

The measured Raman peaks of 915 , 955 , and 990 cm^{-1} are attributed to PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^- , respectively, by the Raman measurements of the chemical reagent themselves and the literature³⁾ of Raman spectra data. From comparison among the relative intensities of the three Raman peaks at the different sites, it is found that the dissolved species around the segregation site of the P compound at grain boundary are H_2PO_4^- and HPO_4^{2-} and that in grain HPO_4^{2-} and PO_4^{3-} .

Fig. 7. CCD camera image of P-3 electrode (a) and the line analysis of *in situ* Raman spectra across the identical P segregation site.

Fig. 8. Potential-pH equilibrium diagram for the phosphorus-water system at 25°C .

Potential–pH diagram is shown in Fig. 8 to refer to the relation between the obtained results and the equilibrium diagram of P–H₂O.⁴⁾ From the pH of bulk solution (pH 13) and the polarization potential, the stable species is expected to be PO₄³⁻ (>pH 12). However, in addition to PO₄³⁻, HPO₄²⁻ and H₂PO₄⁻ were detected, both of which are, respectively, formed stably at lower pH regions of pH 7–12 and pH 2–7. The presence of H₂PO₄⁻ and HPO₄²⁻ at grain boundary and the presence of HPO₄²⁻ in grain indicate that the preferential dissolution of the precipitate of Fe₃P brings about the local decrease of the solution pH, and that the degree of pH decrease is larger on the precipitate at grain boundary than that on the precipitate in grain. This is very interesting in the study on the linkage between the localized solution circumstances and the localized corrosion kinetics at an impurity segregation site at grain boundary or in grain.

4. Conclusions

(1) Analysis of both the *in situ* Raman spectroscopy and the SEM-EDX indicates that the preferential dissolution site of Fe–P alloy electrodes is the location with the chemical composition of Fe₃P.

(2) For dissolution species from Fe₃P precipitate, PO₄³⁻, HPO₄²⁻, and H₂PO₄⁻ are identified using in

Raman spectroscopy. Relative concentrations of the three dissolution species are different between the Fe₃P precipitates at grain boundary and in grain.

(3) It is suggested that the preferential dissolution of the precipitate of Fe₃P brings about local decrease of the solution pH. The decrease of pH is larger on the precipitate at grain boundary than that on the precipitate in grain.

Acknowledgments

This work was supported by the Grant-in-Aid of Scientific Research from the Ministry of Education, Science, Culture and Sports (07455283), and the Grant-in-Aid of Scientific Research from NEDO (A-543). The authors are grateful to Dr. A. Sakai for his help in Raman spectroscopy study.

REFERENCES

- 1) H. M. Herro and A. Banweg: *Mater. Perform.*, **34** (1995), 49.
- 2) F. Kurosawa, I. Taguchi and R. Matsumoto: *J. Jpn. Inst. Met.*, **43** (1979), 1068.
- 3) Raman Data Series, Nihonbunkou Co. Ltd., Tokyo, (1993).
- 4) J. Van Muylder and M. Pourbaix: *Atlas of Electrochemical Equilibria in Aqueous Solutions*, ed. by M. Pourbaix, Pergamon Press, Oxford, (1966), 504.