Observation of Chemical State for Interstitial Solid Solution of Carbon in Low-carbon Steel by Soft X-ray Absorption Spectroscopy

Kakeru NINOMIYA,¹⁾ Kazutaka KAMITANI,²⁾ Yusuke TAMENORI,³⁾ Kazuki TSURUTA,³⁾ Toshihiro OKAJIMA,⁴⁾ Daisuke YOSHIMURA,⁴⁾ Hideaki SAWADA,⁵⁾ Keisuke KINOSHITA⁵⁾ and Maiko NISHIBORI^{1,6)*}

1) Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka, 816-8580 Japan.

2) Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan.

3) Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198 Japan.

4) Kyushu Synchrotron Light Research Center, 8-7 Yayoigaoka, Tosu-shi, Saga, 841-0005 Japan.

5) Advanced Technology Research Laboratories, Nippon Steel Corporation, 1-8, Fuso-Cho, Amagasaki, Hyogo, 660-0891 Japan.

6) Faculty of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka, 816-8580 Japan.

(Received on April 8, 2019; accepted on July 17, 2019; originally published in *Tetsu-to-Hagané*, Vol. 104, 2018, No. 11, pp. 628–633; J-STAGE Advance published date: September 25, 2019)

The near-edge X-ray absorption fine structure at the carbon *K* edge was measured for determining the chemical state of interstitial carbon in a low-carbon steel. In addition, the wavelength dependence of the photoelectron spectrum of the surface of the steel was evaluated, and a contamination and oxidation layer of 3 nm thickness was found. As a result, it was possible to observe a change in the chemical state of carbon existing in bulk iron located deeper than the oxidation and contamination layers, by evaluating the difference spectra between the sample and a reference. Furthermore, by evaluating the shape change of the difference spectra based on the heat treatment time, it was found that the chemical state of carbon in bulk iron changes with heat treatment.

KEY WORDS: low-carbon steel; aging; chemical state analysis; X-ray absorption spectroscopy; photoelectron spectroscopy.

1. Introduction

The development of high strength steel is important to achieve weight reduction, essential for the improvement of fuel economy of automobiles.^{1–3)} To enhance mechanical strength, precipitation of iron carbide in steel has been attempted. The use of steel with a martensitic structure having the highest hardness has also been considered.^{4–8)} However, although it shows high strength, the steel made by these methods has poor ductility and processability.^{9,10)}

Recently, carbon clusters have attracted attention in the steel industry as an effective material for overcoming this disadvantage. Ferritic steel with a supersaturated solid solution of carbon shows a remarkable increase in hardness by heat treatment (so-called aging) at low temperature. This is believed to be caused by the formation of a carbon cluster in the ferritic steel.¹¹⁾ Direct observation of carbon clusters using 3D atom probe tomography (3DAP) has been reported by many researchers.^{12–15)} However, 3DAP measurement is limited to observation of the aggregation of carbon, and the

mechanism of formation of the carbon cluster has not been clarified. Therefore, to explain the strengthening mechanism of the ferritic steel by carbon clusters, it is necessary to understand the dynamic change of the chemical state of carbon in the steel with aging, which is difficult to observe by microscopic method.

In X-ray absorption spectroscopy (XAS), the X-ray absorption fine structure (XAFS) spectrum is obtained by sweeping the energy of incident X-rays and measuring absorbance. XAFS spectra include information on only the target element, since the XAS method uses core level electronic transitions specific to the element. Therefore, it is useful as an analytical method for studying the chemical state and the local structure of carbon in the matrix of ferrite steel, which consists of multi-component.^{16,17)} Since the energy of the C *K* absorption edge is very low (284.3 eV), it is difficult to perform XAS measurements in the transmission mode.^{18,19)} Therefore, in order to measure the XAS spectrum of carbon in the steel, either the electron yield or fluorescence yield mode needs to be used.

The surface of steel undergoes chemical deterioration when it comes in contact with molten salt or oil during the production process. Furthermore, in the case of low-carbon

* Corresponding author: E-mail: nishibori.maiko.511@m.kyushu-u.ac.jp
DOI: <https://doi.org/10.2355/isijinternational.ISIJINT-2019-206>

steel, decarburization occurs from the surface of the steel during hot rolling and annealing, and an oxide layer is formed upon exposing it to the atmosphere.^{20–23)} Therefore, in the characterization of steel, it is important to distinguish between the surface and the bulk.

In this study, to clarify the aging mechanism of the low-carbon steel, we investigate the change in the chemical state of carbon in low-carbon steel by measuring the near-edge X-ray absorption fine structure (NEXAFS) spectrum. Additionally, in order to evaluate NEXAFS spectrum correctly, we measure the photoelectron spectrum for the surface by changing the energy of incident X-ray and evaluate the thickness of the impurity layer on the surface of the steel.

2. Experimental Details

Low-carbon steel, in which carbon is dissolved to form a supersaturated solution, was produced by vacuum melting, hot rolling, and cold rolling. The specimens of the low-carbon steel were subjected to solution treatment in a salt bath at 700°C for 20 min, followed by quenching into iced water. Following this, they were subjected to heat treatment in an oil bath at 50°C for a predetermined time. The sample, after the heat treatment, was kept in liquid nitrogen and was mirror-polished just before the measurement. **Table 1** shows the chemical composition of the low-carbon steel prepared in this study. The carbon content was set to 0.045 wt% based on Abe¹¹⁾ (hereinafter referred to as “0.045C steel”).

The chemical analysis of the sample surface was carried out using photoelectron spectroscopy (PES) with an Al $K\alpha$ and synchrotron radiation (SAGA-LS, BL10 and BL12) X-ray sources. In this study, PES measurement using synchrotron radiation was performed for the quantitative evaluation of the thickness of impurity layers by taking advantage of the dependence of probe depth on the energy of incident X-rays. Here, incident energies of 350, 600, 900 (synchrotron radiation), and 1 486.7 eV (Al $K\alpha$) were selected for the measurements.

NEXAFS spectra at the C K absorption edge (284.3 eV) were simultaneously measured using the total electron yield (TEY) and partial fluorescence yield (PFY) at BL27SU in SPring-8. TEY spectra were obtained by measuring the drain current from the sample. PFY spectra were obtained by using silicon drift detector. Full X-ray fluorescence spectrum was obtained at each excitation energy and extracting carbon $K\alpha$ fluorescence yield from a data set. These spectra were normalized by dividing each spectrum by a I_0 spectrum which obtained by measuring the drain current of fresh Au plate on the sample holder. The photon energy was scanned from 280 to 320 eV with an integration time of 7 s for every 0.1 eV. In order to suppress the progression of aging during the measurement, the sample temperature was maintained at –20°C using a Peltier device.

Table 1. Chemical composition of low-carbon steel.

	C	Si	Mn	P	S	Al	N
0.045C (wt%)	0.045	0.015	0.34	0.020	0.0170	0.038	0.0060

3. Results and Discussion

3.1. Quantitative Analysis of Impurity Layer Formed on the Sample Surface by Photoelectron Spectroscopy

Since the corrosion layer on the surface of the low-carbon steel formed during the heat treatment is removed on polishing, it has no effect on the NEXAFS spectrum. However, it is difficult to avoid the formation of a natural oxidation layer and a contamination layer on the outermost surface of the low-carbon steel. Therefore, the NEXAFS spectrum is expected to contain information on carbon present in the outermost surface in addition to information on interstitial carbon in the bulk Fe. In order to evaluate correctly the measured NEXAFS spectrum from the low-carbon steel, it is necessary to estimate the composition and thickness of the natural oxidation layer and the contamination layer. Therefore, we perform a depth analysis of the chemical constitution using the mean free path of photoelectrons in the material. The main peak of the photoelectron spectrum is attributed to photoelectrons emerging without energy loss by inelastic scattering. The probing depth can be estimated by calculating the inelastic scattering length of photoelectrons within the solid. When the electron moves a distance z , the probability $P(z)$ that no collision occurs at all can be expressed as

$$P(z) = \exp\left(-\frac{z}{\lambda}\right) \dots\dots\dots (1)$$

where λ is the average inelastic scattering length. The distribution function representing the probability of photoelectron generation ($\phi(z)$) and the detected photoelectron intensity (I) at a depth z from the solid surface can be written as

$$\phi(z) = c \exp\left(-\frac{z}{\lambda}\right) \dots\dots\dots (2)$$

$$I = \int_0^\infty \phi(z) dz. \dots\dots\dots (3)$$

In order to obtain λ , the following TPP-2M equation proposed by Tanuma, Powell, Penn *et al.* is generally used.²⁴⁾

$$\lambda = \frac{E_k}{E_p^2 [\beta \ln(\gamma E_k) - C / E_k + D / E_k^2]} \dots\dots\dots (4a)$$

$$\beta = -0.10 + 0.944(E_p^2 + E_p^2)^{-1/2} + 0.069 \rho^{0.1} \dots\dots\dots (4b)$$

$$\gamma = 0.191 \rho^{-0.50} \dots\dots\dots (4c)$$

$$C = 1.97 - 0.91 U \dots\dots\dots (4d)$$

$$D = 53.4 - 20.8 U \dots\dots\dots (4e)$$

$$U = N_V \rho / M = E_p^2 / 829.4 \dots\dots\dots (4f)$$

Here, N_V is the number of valence electrons per atom, ρ is the density (g/cm³), M is the atomic or molecular weight, and E_p is the plasmon energy (in eV). In many cases, λ is a downwardly convex curve in the low energy region where the kinetic energy of photoelectrons E_k is around 50 to 100 eV. Since λ is divergent at even lower energies, the

TPP-2M formula cannot be applied.

Figure 1 shows the relationship between λ and E_k obtained by using the parameters for pure iron ($\rho = 7.874 \text{ g/cm}^3$, $E_p = 30.6 \text{ eV}$). Assuming that the criterion of the detection depth is up to 95% of the total signal strength ($I=0.95$), we can integrate $\phi(z)$ from 0 to d and write it as

$$\begin{aligned} I &= \int_0^d \phi(z) dz / \int_0^\infty \phi(z) dz \\ &= \int_0^d \exp\left(-\frac{z}{\lambda}\right) dz / \int_0^\infty \exp\left(-\frac{z}{\lambda}\right) dz \dots\dots\dots (5) \\ &= 1 - \exp\left(-\frac{d}{\lambda}\right) \end{aligned}$$

When Eq. (5) is solved for d , we obtain $d \approx 3\lambda$. Therefore, the detection depth can be estimated to be three times the average inelastic scattering length. The probing depth (Λ) as a function of the photoelectron take-off angle can be written as:

$$\Lambda = d \sin \theta = 3\lambda \sin \theta. \dots\dots\dots (6)$$

Figure 2(a) shows the Fe2p_{3/2} PES spectra of 0.045C steel after mirror polishing. The incident X-ray energy (E) in Fig. 2(a-1) is 900 eV and the binding energy (E_B) of Fe2p_{3/2} is 707 eV. Therefore, the kinetic energy of photoelectrons (E_k) is 193 eV since $E_k = E - E_B$. In this case, since the photoelectron take-off angle is set to 90°, the probing depth

can be estimated as 1.78 nm (from Eq. (6)). On the other hand, Fig. 2(a-2) shows the spectrum with incident X-ray energy of 1486.7 eV and a photoelectron take-off angle of 45°, having a probing depth of 2.90 nm.

It has been reported that the peak position of metallic iron (Fe⁰), Fe³⁺ oxide and Fe³⁺ oxyhydroxide are 707.0, 710.9 and 711.3–711.8 eV, respectively.²⁵⁾ In Fig. 2(a-1), no peak is seen at around 707 eV, but a broad peak is observed around 711 eV. It can be assumed that this broad peak appears due to the mixed chemical state of Fe²⁺ and Fe³⁺.

Fig. 1. Estimated inelastic mean free path of ferrite as a function of electron energy.

Fig. 2. XPS and Synchrotron Radiation Photoelectron Spectroscopy (SR-PES) spectra of 0.045C steel after polishing. (a-1) SR-PES Fe2p_{3/2} spectrum with probing depth of 1.78 nm. (a-2) XPS Fe2p_{3/2} spectrum with probing depth of 2.90 nm. (b-1) SR-PES O1s spectrum with probing depth of 1.65 nm. (b-2) SR-PES O1s spectrum with probing depth of 2.48 nm. (c-1) SR-PES Cls spectrum with probing depth of 1.65 nm. (c-2) SR-PES Cls spectrum with probing depth of 3.36 nm. (d) Schematic representation of the surface layer of 0.045C steel after polishing. (Online version in color.)

Therefore, the oxidation layer is expected to exist at least up to 1.8 nm from the surface. On the other hand, in Fig. 2(a-2), a broad peak around 711 eV and a weak peak near 707 eV are observed. Since the peak at 707 eV corresponds to Fe^0 , the layer from the surface to 2.9 nm contains both metallic iron and iron oxides. These results indicate that the thickness of the natural oxidation layer formed on the outermost surface of the low-carbon steel after mirror polishing is about 2–3 nm, in good agreement with the results of Isshiki *et al.*²¹⁾

Figure 2(b-1) shows the O1s spectrum at an incident X-ray energy of 600 eV and a photoelectron take-off angle of 90° . The probing depth can be estimated as 1.65 nm. Since the kinetic energy of the resultant photoelectrons is about 69 eV, which is outside the defined range shown in Fig. 1, we assume an average inelastic scattering length of 0.55 nm. On the other hand, Fig. 2(b-2) shows the O1s spectrum at incident X-ray energy of 900 eV and a photoelectron take-off angle of 90° . In this case, the probing depth is about 2.48 nm. It has been reported that the peak position of iron oxide (O-Fe^{n+}) and hydroxide (O-H) are 528–531 and 531.5 eV, respectively.²⁶⁾ In Fig. 2(b-1), two peaks are observed around 531.6 and 529.1 eV. On the other hand, in Fig. 2(b-2), the corresponding peaks are observed around 531.6 and 529.9 eV, respectively. The peak at 531.6 eV is ascribed to O-H , and therefore, the hydroxide is present at both layers. On the other hand, the peak corresponding to O-Fe^{n+} is observed in both depth conditions although the peak positions were different. These peaks are shifted to the higher energy side with increasing probing depth, indicating that the valence of iron and its mixing ratio depends strongly on the depth.

In general, the rust on the surface of the steel produced by atmospheric corrosion consists of crystalline corrosion products such as iron oxyhydroxide (FeOOH) and iron oxide (Fe_3O_4), along with other amorphous rust.²⁷⁾ Since the intensity of the iron oxide peak (O-Fe^{n+}) at 528–531 eV increases with probing depth, it indicates that iron oxyhydroxide is present on the outermost surface of the sample and iron oxide is present further beneath it.

Figure 2(c-1) shows the C1s spectrum at an incident X-ray energy of 350 eV and a photoelectron take-off angle of 90° . The probing depth under these conditions can be estimated as 1.65 nm. Figure 2(c-2) shows C1s spectrum at an incident X-ray energy of 900 eV and a photoelectron take-off angle of 90° . In this case, the probing depth is about 3.36 nm. Only a single peak at 285 eV is observed in Fig. 2(c-1). However, three peaks (285.0, 286.7 and 288.9 eV) are observed in Fig. 2(c-2). The peak at 285 eV can be ascribed to C–H, C–C and C=C bonds, which are most probably caused by the carbon contamination generated by an adhesion of organic matter. In other words, there is a considerable amount of carbon contamination on the surface of the sample. The peaks at 286.7 and 288.9 eV can be ascribed to C–O and O=C–O bonds, respectively. Considering the results of $\text{Fe}2p_{3/2}$ and O1s spectra, it can be concluded that these peaks originate from the carbon atoms present in the oxidized surface layer.

From the above results, it can be seen that an impurity layer with a thickness of about 3 nm exists on the surface of 0.045 C steel after the mirror polishing. This impurity layer forms a three layered structure: contaminated carbon, iron oxyhydroxide, and iron oxide (Fig. 2(d)). Since carbon atoms are present not only in bulk iron but also in the iron oxyhydroxide and oxide layers, it is difficult to selectively obtain information on carbon atoms existing in the bulk iron. Therefore, in XAS measurements on low-carbon steel, the C K NEXAFS spectrum includes information on carbon atoms present on the surface and in the bulk.

3.2. Chemical State Analysis of Carbon in Steel by C K NEXAFS Spectrum Measurement

The depth-resolved XAS measurement for 0.045C steel was performed by the simultaneous measurement of the TEY with an analytical depth of several nm, and the PFY with an analytical depth of about 50 nm. **Figure 3** shows the C K NEXAFS spectrum of 0.045C steel after heat treatment at 50°C for 16 days (a-1), and as-quenched 0.045C before any heat treatment (a-2). TEY and PFY spectra are similar in shape, and several absorption peaks are observed. Peaks (I),

Fig. 3. C K NEXAFS and q_3 spectra of 0.045C steel: (a-1) post aging treatment for 16 days, (a-2) as-quenched sample. (b) C K q_3 spectra of 0.045C steel (TEY: total electron yield. PFY: partial fluorescence yield).

Fig. 4. Variation in C K NEXAFS and q_3 spectra by PFY during isothermal aging at 50°C.

(II) and (III) are closed to the typical energy region where π^* , C–C or C–O, and σ^* peaks appear, respectively.²⁸⁾ From PES spectra, NEXAFS spectra include contributions not only from the carbon in the bulk iron but also from carbon present in the contamination, the iron oxyhydroxide, and the iron oxide layers. The chemical composition and the thickness of the impurity layer on the sample surface after the mirror polishing hardly change in spite of the time for the heat treatment if the sample composition is constant. Therefore, we have evaluated the spectral change and tried to extract the contribution of the carbon atoms present in the bulk iron.

The spectral change was calculated as the difference spectrum between the reference spectrum (from an as-quenched sample) and the measured spectrum (from the heat treated sample) on the basis of Eq. (7). In this study, since S/N ratio of the measured spectra is low, the cube of the difference spectrum is shown (hereinafter referred to as q_3 spectrum).

$$q_3 = (f_{\text{heat}} - f_{\text{as-quench}})^3 \dots\dots\dots (7)$$

Here, f_{heat} and $f_{\text{as-quench}}$ are the spectra of the heat treated sample and the as-quenched steel, respectively. Figure 3(b) shows the q_3 spectra calculated from C K NEXAFS spectrum of 0.045C steel after heat treatment at 50°C for 16 days. The shape of the q_3 spectra measured by TEY and PFY are nearly identical, and its spectral modulations occurring at 284.5, 287.5, and 290–294 eV in the positive direction. It can be assumed that these spectral modulations originate from the chemical state of carbon present in bulk iron.

Here, if the chemical state of carbon in bulk iron is modified with the heat treatment, q_3 spectra should change according to the heat treatment time. **Figures 4(a) and 4(b)** show the C K NEXAFS spectra and q_3 spectra of

0.045C steel post heat treatment at 50°C for predetermined time, respectively measured by PFY method. For the C K NEXAFS spectra, since the shape of each spectrum is similar, it is difficult to determine the change in the chemical state of carbon depending on the heat treatment time. On the other hand, it was found that these q_3 spectra change depending on the heat treatment time and can be classified into 3 groups, (i) 20 m and 6 h, (ii) 16 h and 4 d, and (iii) 16 d.

This suggests that the change in the chemical state of carbon in bulk iron is observed since the features of the q_3 spectra have a tendency to change depending on the heat treatment time. On the other hand, if the change of q_3 spectra is randomly change without the dependency of the heat treatment time, it can be assumed that the observed change is not related to the carbon in bulk iron. Therefore, we considered that q_3 spectra calculated from C K NEXAFS spectra in this study succeeded to observe the chemical state change of only carbon in the bulk iron with aging. The q_3 spectrum for 16d heat treatment shows the increase of peak (I) region and the decrease of peak (II) region. The decrease of peak (II) region and the increase of peak (I) region suggest the rearrangement of carbon atoms and the formation of graphitic (sp^2) carbon components which may be considered as carbon clusters or carbides, respectively. However, it is not clear whether the carbon cluster shows sp^2 orbital since the structure of carbon cluster has not been elucidated. Therefore, to clarify the formation mechanism of carbon clusters, further experiments are needed.

4. Conclusions

In this study, C K NEXAFS has been measured to observe changes in the chemical state of carbon in low-carbon steel.

Additionally, in order to evaluate NEXAFS spectra correctly, photoelectron spectrum was measured by changing the wavelength of incident X-ray, and the thickness of the impurity layer on the surface of the steel was estimated. It was found that a three layered impurity structure with a thickness of about 3 nm, consisting of contaminated carbon, iron oxyhydroxide, and iron oxide, exists on the surface of 0.045C steel after mirror polishing. Furthermore, the effect of aging on the chemical state of carbon could be observed by analyzing the difference spectra between the reference spectra obtained from the as-quenched sample and the NEXAFS spectra obtained from the heat treated sample, the chemical state change of only carbon in the bulk iron with aging could be observed.

As a future course of action, a detailed analysis of the spectral change depending on the heat treatment time is required to understand the dynamics of the chemical state of carbon in the steel. This will lead to a new and fundamental understanding of the aging phenomenon in low-carbon steel.

Acknowledgements

We would like to thank Professor Atsushi Takahara and Associate Professor Tomoyasu Hirai for useful comments and discussions. The synchrotron radiation photoelectron spectroscopy measurements were performed at Kyushu Synchrotron Light Research Center (SAGA-LS) BL10 and BL12 (Proposal No. 1411110G, 1601149S, 1705026Pi, 1707068F). The C K NEXAFS spectrum measurements were performed at SPring-8 BL27SU (Proposal No. 2015B1434, 2016A1428).

REFERENCES

- 1) M. Takahashi: *Tetsu-to-Hagané*, **100** (2014), 1 (in Japanese).
- 2) T. Senuma: *ISIJ Int.*, **41** (2001), 520.
- 3) O. R. Terrazas, K. O. Findley and C. J. Van Tyne: *ISIJ Int.*, **57** (2017), 937.
- 4) I. Tamura, T. Maki and H. Hato: *Trans. Iron Steel Inst. Jpn.*, **10** (1970), 163.
- 5) K. Sugimoto, N. Usui, M. Kobayashi and S. Hashimoto: *ISIJ Int.*, **32** (1992), 1311.
- 6) O. Grassel and G. Frommeyer: *J. Mater. Sci. Technol.*, **14** (1998), 1213.
- 7) J. G. Speer, E. De Moor, K. O. Findley, D. K. Matlock, B. C. De Cooman and D. V. Edmonds: *Metall. Mater. Trans. A*, **42** (2011), 3591.
- 8) Y. Z. Shen, S. H. Kim, H. D. Cho, C. H. Han and W. S. Ryu: *Nucl. Eng. Des.*, **239** (2009), 648.
- 9) J. W. Morris, Jr., Z. Guo, C. R. Krenn and Y. H. Kim: *ISIJ Int.*, **41** (2001), 599.
- 10) J. W. Morris, Jr.: *ISIJ Int.*, **51** (2011), 1569.
- 11) H. Abe: *Scand. J. Metall.*, **13** (1984), 226.
- 12) C. Zhu, A. Cerezo and G. D. W. Smith: *Ultramicroscopy*, **109** (2009), 545.
- 13) Y. Kobayashi, J. Takahashi and K. Kawakami: *CAMP-ISIJ*, **28** (2015), 307, CD-ROM (in Japanese).
- 14) S. Sampath, R. Rementeria, X. Huang, J. D. Poplawsky, C. Garcia-Mateo, F. G. Caballero and R. Janisch: *J. Alloy. Compd.*, **673** (2016), 289.
- 15) F. G. Caballero, M. K. Miller and C. Garcia-Mateo: *Acta Mater.*, **58** (2010), 2338.
- 16) X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, ed. by D. C. Koningsberger and R. Prins, Wiley, New York, (1988), 573.
- 17) D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen and D. E. Ramaker: *Top. Catal.*, **10** (2000), 143.
- 18) J. Stöhr: *NEXAFS Spectroscopy*, Springer, Berlin, (1992), 154.
- 19) S. Turchini, R. Delaunay, P. Lagarde, J. Vogel and M. Sacchi: *J. Electron Spectrosc. Relat. Phenom.*, **71** (1995), 31.
- 20) A. Ichihara and Y. Nuri: *Sanyo Tech. Rep.*, **8** (2001), 43.
- 21) M. Isshiki, K. Mimura and S. Suzuki: *J. Vac. Soc. Jpn.*, **45** (2002), 5.
- 22) S. Suzuki, T. Kosaka, H. Inoue and Y. Waseda: *ISIJ Int.*, **36** (1996), 433.
- 23) S. Suzuki, T. Nakazawa and Y. Waseda: *ISIJ Int.*, **36** (1996), 1273.
- 24) S. Tanuma, C. J. Powell and D. R. Penn: *Surf. Interface Anal.*, **17** (1991), 911.
- 25) S. Suzuki, K. Yanagihara and K. Hirokawa: *Surf. Interface Anal.*, **30** (2000), 372.
- 26) XPS (X-ray Photoelectron Spectroscopy) Database, <http://techdb.podzone.net/eindex.html>, (accessed 2018-01-15).
- 27) T. Misawa: *Corros. Eng.*, **32** (1983), 657 (in Japanese).
- 28) J. G. Chen: *Surf. Sci. Rep.*, **30** (1997), 1.