

# Dynamics of Oxide Films using in-situ Analysis for Surface Properties of Steel Products

Kazuyuki KITAMURA\*      Takashi DOI  
Yoshitaka NISHIYAMA      Yasuyoshi HIDAKA  
Yasuto HIGASHIDA      Yasuhiro MASAKI  
Nobuo OTSUKA

## Abstract

*Dynamics of oxide films, such as initial stage, growth and fracture, reveal surface properties of steel by using in-situ analytical technique. In this article, we report O<sub>2</sub> adsorption and oxidation on Ni surface at initial stage of oxidation and the kinetics of low growth rate at growth stage. And at fracture stage, we also present the dynamics of stress and fracture and transformation of wüstite scale.*

## 1. Introduction

When exposed to the atmosphere or aqueous solutions, surfaces of steel, including stainless steel, are inevitably oxidized and covered with oxide films (scale). Oxide films are involved, therefore, in every reaction that takes place on the material surface, and play important roles in enhancing the properties of the material. Nippon Steel & Sumitomo Metal Corporation has conducted several R&D studies focusing on surface oxide films.

Such studies include those on the atmospheric corrosion of low-alloy steels envisaging better corrosion resistance by using oxide films forming at room temperature. The mechanisms of corrosion resistance improvement of alloy elements and surface treatment have been clarified through detailed analysis of steel surface scale using different analytical methods.<sup>1-4)</sup>

The corrosion resistance of stainless steel is due to a natural oxidation film called a passive film that forms at room temperature. For the improvement of corrosion resistance by the natural oxidation film, a technology was proposed whereby surface oxide films are formed at high temperature for the purpose of minimizing metal elution to high-temperature water or ultra-pure water as well as improving the resistance to corrosion due to corrosive gases. With respect to such protective oxide films, Matsuda studied the effects of their forming conditions on film properties using Raman scattering spectroscopy and other analysis methods.<sup>5)</sup> Stainless steel has long been used as the material resistant to corrosion at high temperature, and various products designed to withstand repetitive thermal history have been developed and put into use.<sup>6,7)</sup>

Since the reaction rate increases dramatically at high tempera-

ture, the roles of surface oxide films are even more important in such conditions. They insulate the base metal from the environment, and for this reason, when they are broken, the material is exposed directly to the hot environment, and it will undergo catastrophic reactions to a heavy thickness loss or burning out. To develop materials resistant to environmental attack, it is important to form and maintain a protective film on the surface, and the key to this is to know what kind of oxide film forms in different use conditions and how, and what roles the component elements play in the oxide film formation.

On the other hand, oxide films influence the surface properties of steel products during use as well as during the manufacturing processes, and there have been many reports on such events. Regarding scale defects at hot rolling, for example, Okada et al. studied the effects of the conditions of high-pressure water descaling on scale formation and the scale deformation during hot rolling.<sup>8,9)</sup> In addition to the above, Kondo et al. investigated the phenomenon of scale's spontaneous blistering and flaking off,<sup>10,11)</sup> and Hidaka et al. examined the high-temperature strength of different types of iron oxides, the main components of scale.<sup>12,13)</sup>

As those reports show, scale and other oxide films on steel surfaces play important roles at high temperature, but because of their high temperature and consequent high reaction rates, they keep on changing continuously and rapidly according to the changes in temperature and atmosphere. Because of this quick change, the stage of oxide film that must be focused upon to solve specific problems is unclear, and research activities are being conducted arbitrarily in most cases. It is therefore necessary to thoroughly understand the

\* Senior Researcher, Fundamental Metallurgy Research Lab., Advanced Technology Research Laboratories  
1-8 Fuso-cho, Amagasaki, Hyogo Pref. 660-0891

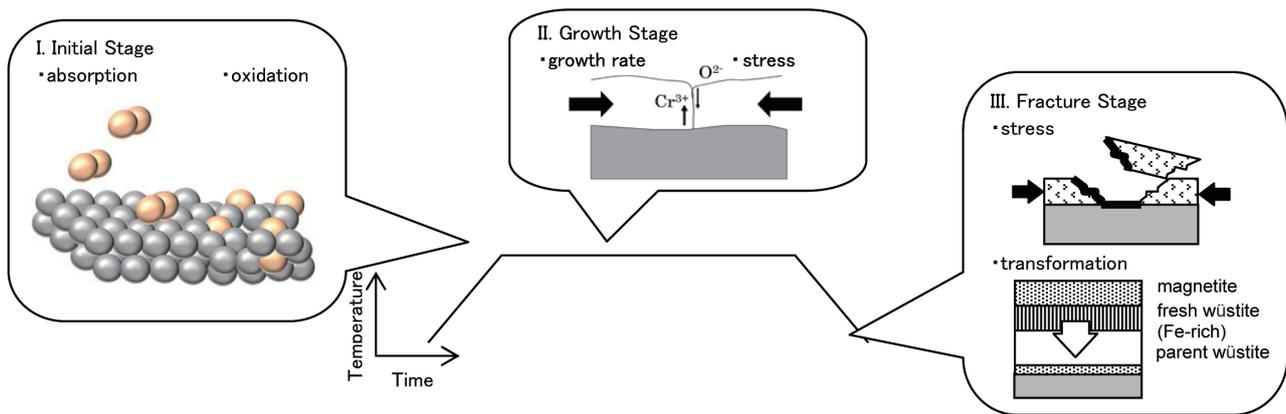


Fig. 1 Schematic illustration of key points about dynamics of oxide films

whole “life” of oxide film from its initial formation through growth to destruction during cooling. Only by this will it be possible to obtain guidelines for the development of new steels, such as the effects of added elements and optimum alloy design. **Figure 1** schematically illustrates the events that serve as the keys for understanding the behavior of the oxide film at different stages.

The methods for clarifying, or analyzing, surface oxide films at the stages of initial formation, growth and destruction during cooling have so advanced that the region of examination is becoming increasingly smaller, and smaller amounts of component elements are being detected. Thanks to this, combined with the advances of electronic and other devices, it is now possible to observe and analyze oxide films directly in corrosive or high-temperature oxidizing environments, where they actually form and grow. Such in situ observation technology has proved to be a powerful problem solving means since it allows direct viewing of the reactions and material behavior that take place at different life stages of oxide films.

This paper introduces some application examples of in situ observation technology and related analysis tools to clarify the dynamics of surface oxide films and the mechanisms of steel surface properties.

## 2. Initial Formation of Surface Oxide Films

The behavior of the atoms of the component elements and oxygen at steel surfaces has not yet been fully elucidated. According to Nii, as many as nine theories have been proposed regarding the formation of a thin oxide film at the initial stage of oxidation of metals,<sup>14)</sup> but there is no unified understanding yet. This is presumably because it can only be conjectured based on the observation of specimens after the event, and the film is so thin that new analysis techniques that can delve into nano regions and detect minimal matter are required. In spite of the difficulty, it is essential for evaluating the environmental resistance of steel materials to investigate the details of the reactions taking place between the metal and gases at the interface in high-temperature, oxidizing environments.

### 2.1 Initial processes of Ni oxidation

Oxidation of alloy materials for common use is a very complicated process because it involves surface segregation of alloy elements, the change in interface reactions due to the advance in internal oxidation, etc. To untangle the complex situation, it is necessary in the first place to understand the behavior of pure metal in an initial oxidation stage. Regarding the changes that take place at metal surfaces contacting high-temperature oxidizing gas, there have been various reports of detailed studies dealing with several pure met-

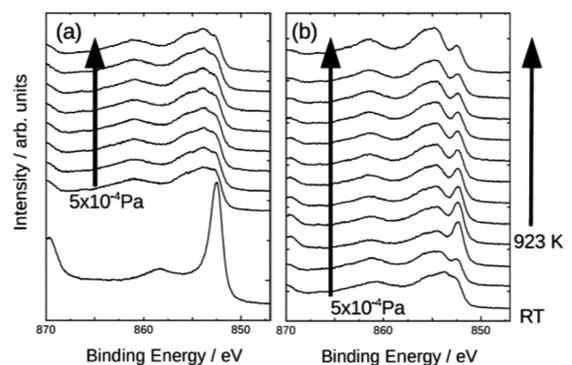


Fig. 2 Ni-2p<sub>3/2</sub> XPS spectra on Ni  
(a) O<sub>2</sub> adsorption and oxidation at room temperature  
(b) Oxidation at 650°C

als.<sup>15,16)</sup> Useful information on fundamental phenomena of metal oxidation such as chemical adsorption and dissociation of atmosphere gas, and the nucleation, two-dimensional growth and thickness increase of oxide are available in such reports. For the same purpose, we observed the initial surface oxidation phenomena of Ni in situ in a high sensitivity environment by X-ray photoelectron spectroscopy (XPS) using the high-intensity X-ray of the SPring-8 as the excitation light source.<sup>17)</sup>

The XPS is a typical surface structure analysis technology whereby an X-ray beam is irradiated onto a specimen as a probe to measure the kinetic energy and intensity of the electron discharged from it, and thus to obtain information on the composition of the oxide film on the surface, the binding mode of its component elements and their valences.

The above-mentioned SPring-8 (Super Photon ring-8 GeV) is a large synchrotron radiation facility of the world's highest performance, located at Harima Science Garden City, Hyogo, Japan. When an electron is accelerated to near the speed of light and its travelling direction is changed in a magnetic field, a strong and thin beam of electromagnetic wave is emitted. The present study took advantage of this beam, which is herein referred to as X-ray.<sup>18)</sup>

The surface of a pure Ni specimen was cleaned in an ultrahigh vacuum, an oxide film was formed at the surface using a very small amount ( $5 \times 10^{-4}$  Pa) of oxygen at room temperature, and then the specimen was heated to 650°C (927K). All these processes were observed by XPS in real time at BL23SXU, a beam line of the SPring-8. Part (a) of **Fig. 2** shows the change of Ni2p<sub>3/2</sub> spectra

while the specimen was held at room temperature. Here, the process in which pure Ni adsorbed  $O_2$  and oxidized to NiO was observed. Part (b) shows the growth of the NiO layer in real time while the specimen was held at 650°C.

We are presently investigating the initial oxidation behavior of alloy steel containing a variety of elements by the same method.<sup>19)</sup> Such studies are expected to clarify the roles of alloy elements in the formation of oxide films and the reaction mechanisms, which will lead to new guidelines for developing new steel products.

### 3. Growth of Surface Oxide Film

The growth rate of a surface oxide film is an important and fundamental piece of information because it defines the service life of steel material.<sup>20)</sup> Wagner's theory of oxidation<sup>21)</sup> is a famous concept regarding the growth of the oxide film on steel surfaces,<sup>21)</sup> according to which the growth rate of an oxide film depends on the rate of element dispersion. However, Kofstad reported that the growth rate of  $Cr_2O_3$  fluctuates across three decimal orders.<sup>22)</sup> We believe that the key to the cause of this large fluctuation of the growth rate will be revealed by clarifying 'what diffuses and reacts with oxygen and how' through in situ analysis of steel surface.

#### 3.1 Growth stress of oxide film of stainless steel forming at high temperature and effect of rare-earth element addition

To clarify the above 'what and how', we observed by the Raman spectroscopic analysis (RSA) an oxide film on a stainless steel surface forming at high temperature.<sup>23)</sup>

The RSA is a crystal structure analysis method taking advantage of the fact that the frequency of Raman scattering light from a substance shifts from the incident light by the energy of the phonon (lattice vibration) of the substance, and that the spectrum of the scattering demonstrates a shape (the number of peaks and their positions) peculiar to the composition and structure of the substance. The result of the analysis yields information about the molecular structure of the substance in question. In appreciation of this, it is widely used for structural analysis even in compounds of low crystallinity such as oxides and hydroxides, which X-ray diffractometry (XRD) cannot deal with effectively. When a visible laser beam is used as the incident light source and the spectroscopy is done also in the band of visible light, transparent matter such as glass, water solutions or gas does not disturb the RSA analysis, and because of this advantage, when combined with optical microscopes, its spatial resolution becomes as high as several micrometers and it is effectively used for the structural analysis of objects in natural and controlled environments. Therefore, the method has been used for the structural analysis of corrosion products<sup>24,25)</sup> and their in situ analysis in aqueous solutions.<sup>26)</sup> In addition, because the peaks of Raman scattering are sensitive to stress, the method is also applicable to stress analysis of oxide films.<sup>5)</sup>

The growth of oxide films on the surfaces of 17 mass% Cr stainless steel and 25 mass% Cr-20 mass% Ni stainless steel (hereinafter called 25Cr-20Ni) were examined at 900°C, using an Ar-ion laser beam 514.5 nm in wavelength as the incident light source.<sup>23)</sup> The spectra thus obtained clarified that a single-layer film of  $\alpha$ - $Cr_2O_3$  had formed on the surface of each specimen. Then, standard spectra of  $\alpha$ - $Cr_2O_3$  were measured at high temperatures using a surface of sintered  $\alpha$ - $Cr_2O_3$ , and the peak-shift values of measured spectra from the standard spectra were obtained; Fig. 3 shows the change in the peak-shift values. Since the oxide layer after the oxidizing test was a single layer of  $Cr_2O_3$ , we consider that the peak shift exhibits the state of stress. The peak shift was converted into stress as given

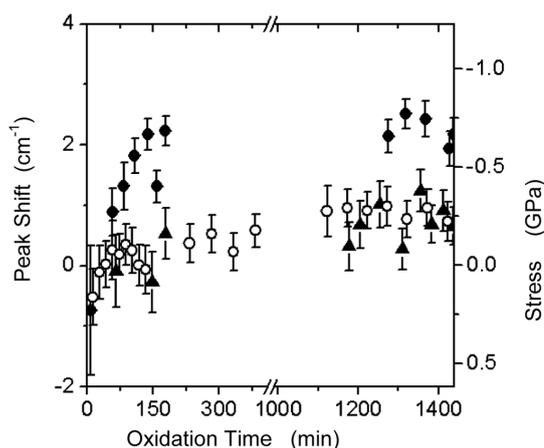


Fig. 3 Growth stress of stainless steels (negative values are compressive stress)  
Solid circle: 25Cr-20Ni 1.2 mm thick, Open circle: 25Cr-20Ni 0.1 mm thick, Solid triangle: 17Cr 1.2 mm thick

along the right-hand vertical axis; in the absence of stress measurement at high temperature, the value measured at room temperature by Mougín et al.<sup>27)</sup> was used for the conversion.

As seen in Fig. 3, whereas the compressive internal stress measured with the 1.2-mm thick 25Cr-20Ni test piece was approximately 0.7 GPa, it was as small as 0.2 to 0.3 GPa with the 1.2-mm thick 17 mass% Cr and the 0.1-mm thick 25Cr-20Ni test pieces. This demonstrates that the internal stress of the oxide film is mitigated by the deformation of the base metal when the material strength is low as in the case with ferritic stainless steel, or when the base metal is thin and not rigid enough, if the steel is of a high strength.

A similar test was conducted using specimens prepared by adding rare-earth elements (RE) by roughly 0.03% to 25Cr-20Ni stainless steel.<sup>6,7)</sup> As a result, the growth stress of the oxide film after heating for 24 h was as high as 1.2 GPa. We consider that the significant increase in the compressive stress from 0.7 GPa of the 25Cr-20Ni test piece without the RE addition is due to the RE atoms of large ionic radii segregating at grain boundaries of the oxide film and consequent large strain in the crystal structure. The state of stress in a material influences the ion diffusion in it: the higher the compressive stress, the more difficult it is for  $Cr^{3+}$  and  $O^{2-}$  to diffuse across grain boundaries of the oxide, which presumably accounts for the thickness decrease of the oxide film, or a decrease in the growth rate of  $Cr_2O_3$  after 24 h of heating.

As seen above, it is possible to decrease the growth rate of a  $Cr_2O_3$  film on stainless steel surfaces by controlling its local structure. Taking advantage of the finding, a new stainless steel thin sheet product suitable for long-term use in a gas environment of 800°C or higher has been developed.<sup>6)</sup>

### 4. Destruction of Surface Oxide Film

Destruction of surface scale at high temperature has a fatal effect on the material since environmental resistance of a material results from the scale insulating it from the surroundings. Once an oxide film is broken and the base material is exposed to the environment, its effective constituent elements are depleted through rapid oxidation, a protective oxide film does not form on the surface, and oxidation advances catastrophically.<sup>28)</sup> The fracture characteristics of an oxide film have direct influences on its flaking behavior, and thus, its destruction is closely related to the ease or otherwise of its re-

moval. As stated herein earlier, the ease of scale removal has been studied as a cause of scale defects, an important issue in steel manufacturing processes.

The destruction of surface oxide films significantly affects the service life of steel materials and their surface properties, but the destruction mechanism has not yet been elucidated.

**4.1 Destruction of surface oxide films during cooling and effect of RE addition**

Surface oxide films flake off during cooling as a result of compressive stress in the film layer due to the difference in the thermal expansion coefficients between it and the base metal, but the details of the flaking mechanism and the scale behavior are still unclear. To clarify them, we evaluated the stress inside the oxide film layer by Raman scattering spectroscopy and observed the course of scale destruction using acoustic emission (AE).<sup>7,29)</sup>

Test pieces of 25Cr-20Ni stainless steel, 1.2 and 0.1 mm in thickness, were held at 900°C for 3 h to have oxide films form on their surfaces, and then the Raman spectroscopic analysis and the AE observation were conducted in real time during cooling at a rate of -0.83 Ks<sup>-1</sup>. Note here that the AE observation was done continuously during the cooling, but the Raman spectroscopic analysis was conducted by suspending the cooling several times at prescribed temperatures and holding the specimen temperature there for 300 s each.

The AE observation was conducted by connecting the test piece in the furnace to a sensor with a Pt wire and detecting the vibration caused by the destruction (cracking, flaking, etc.) of the scale. In usual practice of AE measurement, the number of signals of a prescribed intensity or higher is counted as the number of events, and in the present study, the events corresponded to the fracture of scale, but no information as to the size of the destruction was given. For simplicity's sake, the AE energy was assumed to be the square of the maximum amplitude *V<sub>p</sub>* of the AE waveform, and the cumulative AE energy after the first signal was plotted as seen in Fig. 4. This AE energy corresponds to the energy released from the inside of the oxide film. In the case of the 1.2-mm thick specimen (solid curve), the cumulative energy increased drastically from -Δ*T*=500 K, and it increased further as the cooling continued. As seen here, it is possible to follow the process of oxide film fracture by tracing in real time the cumulative change of AE energy, which corresponds to the

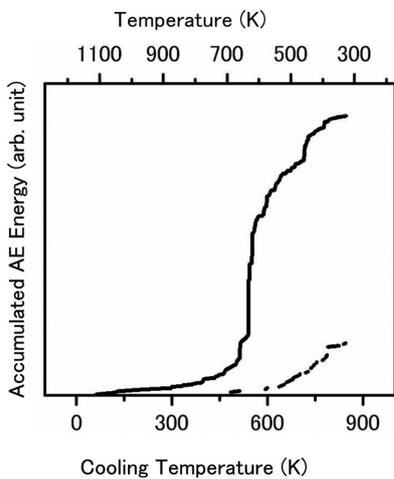


Fig. 4 Temperature dependence of AE energy of stainless steel (solid line: 1.2 mm thick, broken line: 0.1 mm thick)

released energy. Table 1 shows the temperature -Δ*T<sub>AE</sub>* at which the cumulative energy curves began to rise rapidly.

Figure 5 shows the peak shift values of the measured spectra from the standard spectra at different temperatures during the cooling from 900°C (1 173 K) and the oxidizing temperature; the measured spectra were obtained through Raman scattering spectroscopy. The stress  $\sigma_{th}$  (hereinafter called thermal stress) arising in the oxide layer owing to the difference in the thermal expansion coefficients between the oxide layer and the base metal is calculated according to Equation (1) given below.

$$\sigma_{th} = \frac{E_{ox} \cdot \Delta T \cdot (\alpha_{Me} - \alpha_{ox})}{(1 - \nu) \cdot \{1 + 2 (E_{ox}/E_{Me}) (h_{ox}/h_{Me})\}} \quad (1)$$

where *E* is Young's modulus,  $\alpha$  linear coefficient of expansion,  $\nu$  Poisson ratio, *h* the suffix for thickness, *Me* the same for the base metal and *Ox* the same for the oxide layer.

The right-hand vertical axis of the graph is the stress value converted using the coefficient proposed by Mougín et al.<sup>21)</sup> as shown in Fig. 3. In the case of the 1.2-mm thick specimen (open circles), the compressive stress increased according to Equation (1) up to -Δ*T*=400 K, then deviated from the equation and remained constant. In the case of the 0.1-mm thick specimen (solid circles), the compressive stress increased according to Equation (1) up to -Δ*T*=200 K, remained at the level temporarily, then increased again to -Δ*T*=600 K and stayed there. We understand that the thermal stress was relaxed at those temperatures. These peculiar temperatures of stress relaxation are those listed in Table 1 as -Δ*T<sub>AE</sub>*.

The stress inside the scale layer and its fracture behavior are examined below based on the above measurement results. As the Raman analysis was conducted at intervals of 200°C, -Δ*T<sub>R</sub>*=400 K and -Δ*T<sub>AE</sub>*=500 K of the 1.2-mm thick specimen are substantially

Table 1 Critical temperatures from AE and Raman measurements (-Δ*T<sub>AE</sub>*, -Δ*T<sub>R</sub>*)

Specimen thickness (mm)	-Δ <i>T<sub>AE</sub></i> (K)	-Δ <i>T<sub>R</sub></i> (K)
1.2	500	400
0.1	600	200, 600

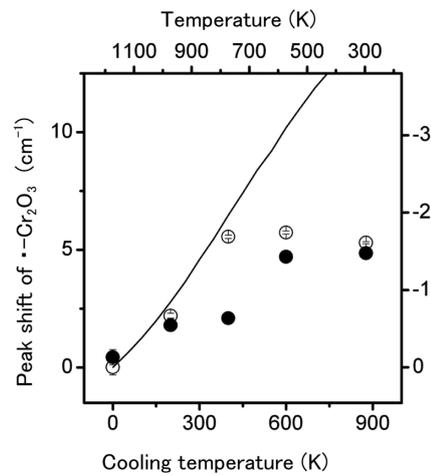


Fig. 5 Temperature dependence of stress of stainless steel (negative values are compressive stress) Solid circle: 25Cr-20Ni 1.2 mm thick, Open circle: 25Cr-20Ni 0.1 mm thick, Solid line: calculation of Eq. (1)

equivalent to  $-\Delta T_R = 600$  K and  $-\Delta T_{AE} = 600$  K of the 0.1-mm thick specimen. This means that the measurement captured the phenomena wherein the surface oxide film was broken by thermal stress at these temperatures, and the stress was relaxed as a result. Here, as for the stress value at which the oxide film broke, we presume that it is determined by the adhesion strength of the oxide film to the base metal at the temperature range ( $-\Delta T_{AE} = 600$  K or below,  $300^\circ\text{C}$  or below), the composition of the film and mode of fracture, and think that, if the composition and the mode of fracture are the same, it can be used as an indicator for quantitatively evaluating the adhesion strength. They also think that by using this indicator, it is possible to quantitatively evaluate the effects of alloy elements, which will serve as effective guidelines for the development of new steel materials.

In contrast, the oxide film of the 0.1-mm thick specimen did not fracture as a result of the stress relaxation at  $-\Delta T_R = 200$  K. The strength of the material measured at high temperature and the roughly estimated force imposed on the base metal are of the same order of magnitude, and for this reason, the stress relaxation is presumably due to the deformation of the base metal. Thin-sheet test pieces are often seen to wave in an oxidation test at high temperature; this is considered to result, like the above, from stress relaxation due to thermal stress of cooling and consequent deformation of the base metal.

As stated above, the combination of two in situ analysis methods makes it possible to closely follow the behavior of internal stress of surface oxide films and that of their fracture, which will be instrumental in clarifying the mechanism of oxide film fracture and in obtaining guidelines for the development of new steels capable of preventing it.

#### 4.2 Transformation of surface oxide film during temperature change

Oxide films on steel surfaces undergo phase transformation as the temperature changes during cooling. While the transformation is considered to affect the fracture of the oxide films directly, and indirectly via consequent structural change, various details of the transformation have not yet been elucidated. Regarding ferrous oxide films, for example, FeO is stable at  $570^\circ\text{C}$  or above, but it becomes unstable below the temperature, and undergoes eutectoid transformation into Fe and  $\text{Fe}_3\text{O}_4$  during cooling (wüstite transformation).<sup>26)</sup>

The structure resulting from the wüstite transformation differs depending on the chemical composition of the steel and the cooling pattern. In view of this, we examined the transformation process of oxide films in situ by XRD.<sup>30)</sup>

Since steel materials and most oxide corrosion products on their surfaces are aggregates of polycrystalline bodies, when a monochromatic X-ray beam is irradiated to such an object, it is diffracted at the lattice planes of crystal grains, forming diffraction lines that satisfy the Bragg condition,  $2d\sin\theta = n\lambda$  (where  $d$  is the lattice spacing,  $\theta$  the angle of the incident beam relative to the lattice plane, and  $\lambda$  the wavelength of the X-ray). The XRD is a method of crystal structure analysis making use of the fact that the pattern of the diffraction lines is different depending on the composition and structure of the object material. Since X-ray is highly penetrant and is not severely affected by aqueous solutions, gases, etc. in the environment, it is employed widely for in situ structural analysis. Angular resolved XRD using practically monochromatic X-rays such as  $\text{CrK}\alpha$ ,  $\text{CoK}\alpha$ ,  $\text{CuK}\alpha$ ,  $\text{MoK}\alpha$  is widely used. Its time resolution is so enhanced by using a multidimensional pixel detector that it is now able to trace transient phenomena during oxidation at high temperature.

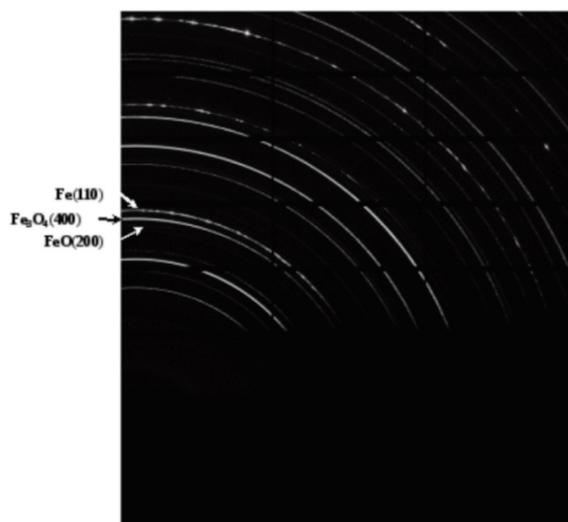


Fig. 6 Quarter circle of the Debye-Scherrer diffraction rings obtained for the wüstite scale transformed at  $450^\circ\text{C}$  for 6.6 ks in laboratory air

Specimens of 0.048 mass% C-Fe were heated at  $670^\circ\text{C}$  for 180 s, then held at 400, 450 and  $500^\circ\text{C}$ , and their isothermal transformation was examined at these temperatures by XRD. For in situ observation of the change in the structure and composition of the surface oxide films growing to a thickness of several micrometers or more and the base metal immediately beneath, combined use of a high-intensity radiation source and a high-speed and high-sensitivity detector is suitable. Accordingly, for the test at BL19 B2, another beam line of SPring-8, an X-ray source of 28 keV and a two-dimensional pixel detector Pilatus were used.<sup>31)</sup>

Figure 6 shows the Debye-Scherrer diffraction rings thus obtained. The crystal structures of the specimens were evaluated by obtaining such images at intervals of 30 s and converting them one-dimensionally. Figure 7 shows an example of the structural change during isothermal transformation of FeO at  $400^\circ\text{C}$ .

The details of the following processes were observed in real time at the present analysis: while  $\text{Fe}_3\text{O}_4$  formed as a result of the isothermal transformation at  $500^\circ\text{C}$  from  $\text{Fe}_{1-x}\text{O}$ , which had formed at  $670^\circ\text{C}$ , at those at 400 and  $450^\circ\text{C}$ ,  $\text{Fe}_{1-y}\text{O}$  ( $y < x$ ) of a higher Fe content formed in the first place, and  $\text{Fe}_3\text{O}_4$  and Fe formed later.

As stated earlier, scale plays important roles in steel manufacturing processes. The present study has created better understanding of scale transformation at different holding temperatures, and the techniques employed therefor proved capable of clarifying the mechanisms of scale flaking, which will provide hints for process improvement and guidelines for the development of new steels.

## 5. Conclusion

Some examples of studies on the behavior of oxide films on steel surfaces and the mechanisms of steel surface properties employing in situ observation techniques have been reported herein.

The combination of XPS and SPring-8 has proved effective at observing  $\text{O}_2$  adsorption and the growth of oxide films in the initial stage of oxidation. At their growth stage, internal stress of scale was evaluated by the Raman scattering spectroscopy, and then the effects of alloy elements to retard the growth of oxide films were clarified. Combined use of AE analysis and Raman scattering spectroscopy proved effective at clarifying the mechanisms of stress and film

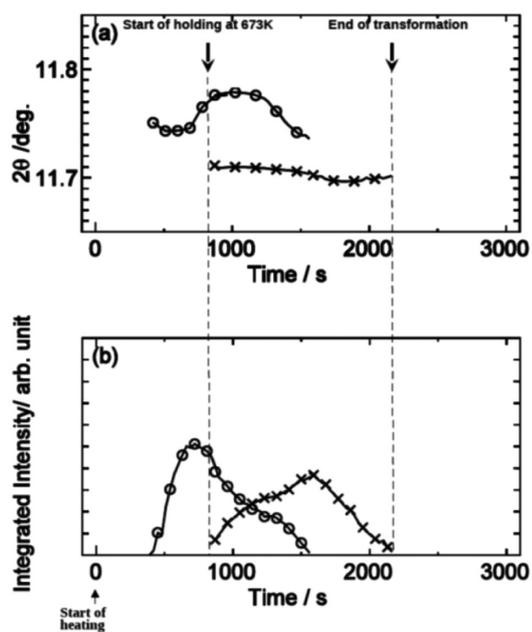


Fig. 7 Changes over isothermal transformation at 400°C in laboratory air (a) Diffraction angle  $2\theta$ , (b) Integrated intensity of wüstite (200) peaks

fracture in the film destruction stage. In addition, the combination of XRD and SPring-8 has clarified the process of wüstite transformation, which is believed to influence the flaking characteristics of surface oxide films. These findings will lead to better knowledge of the corrosion resistant effects of alloy elements.

As has been reported herein above, the technologies for in situ observation are extremely useful for clarifying the dynamics and the behavior of surface oxide films, which change from moment to moment during the stages of initial formation, growth and destruction during cooling, according to temperature, atmosphere and other environmental conditions. We intend to expand the effective use of these technologies beyond mere understanding of the phenomena to surface metallurgy, or elaboration of new steel chemistry and the structure and creation of new steel material excellent in surface properties in response to the diverse requirements of customers.

## References

- 1) Kihira, H., Ito, S., Mizoguchi, T., Murata, T., Usami, A., Tanabe, K.: *Zairyo-to-Kankyo*. 49, (2000)
- 2) Okada, H.: *J. of Soc. of Materials Science Japan*. 17, 705 (1968)
- 3) Yamashita, M., Miyuki, H., Nagano, H., Misawa, T.: *Zairyo-to-Kankyo*. 43, 26–32 (1994)
- 4) Doi, T. et al.: *J. Japan Inst. Met. Mater.* 74 (1), 10–18 (2010)
- 5) Matsuda, K.: *Materia Japan*. 38, 633 (1999)
- 6) Nishiyama, Y. et al.: *Materia Japan*. 49, 72 (2010)
- 7) Nishiyama, Y. et al.: *J. Japan Inst. Met. Mater.* 71, 55 (2007)
- 8) Okada, H. et al.: *Tetsu-to-Hagané*. 80 (11), 849–854 (1994)
- 9) Okada, H.: *Shinnittetsu Sumikin Giho*. (401), 75 (2015)
- 10) Kondoh, Y. et al.: *Tetsu-to-Hagané*. 100 (3), 352–358 (2014)
- 11) Kondoh, Y. et al.: *Shinnittetsu Sumikin Giho*. (401), 82 (2015)
- 12) Hidaka, Y. et al.: *J. Japan Inst. Met. Mater.* 64 (5), 291–294 (2000)
- 13) Hidaka, Y. et al.: *Current Advances in Materials and Processes*. Report of ISIJ Meeting. 13 (6), 1099–1102 (2000)
- 14) Nii, K.: *Oxidation and Corrosion of Metal Materials at High Temperature*, edited by Jpn. Soc. Corr. Eng. Maruzen, 1984, p. 41
- 15) Fehlner, F.P., Mott, N.F.: *Oxidation of Metals*. 2, 52 (1970)
- 16) Holloway, P.H.: *J. Vac. Sci. Technol.* 18, 653 (1981)
- 17) Doi, T. et al.: *Zairyo-to-Kankyo (Materials and Environment)*. 64 (8), 348 (2015)
- 18) SPring-8 homepage. <http://www.spring8.or.jp/ja/>
- 19) Doi, T., Nishiyama, Y., Yoshigoe, A., Teraoka, Y.: *Surf. Interface Anal.* 48 (7), 685–688 (2016)
- 20) Otsuka, N., Nishiyama, Y., Kudo, T.: *Oxid. Met.* 62, 121–139 (2004)
- 21) Wagner, C.: *Z. Phys. Chem.* B21, 25 (1933)
- 22) Kofstad, P.: *High Temperature Corrosion*. London, Elsevier, 1988
- 23) Kitamura, K. et al.: *Mat.Sci.Forum*. 522–523, 489 (2006)
- 24) Doi, T., Kitamura, K., Nakanishi, K., Kashima, K., Kamimura, T., Miyuki, H., Ohta, T., Yamashita, M.: *J. Japan Inst. Metals*. 74, 10 (2010)
- 25) Kamimura, T., Doi, T., Kashima, K., Wagure, N., Hara, S., Nakahara, K., Ando, R., Miyuki, H.: *J. Soc. Mater. Sci., Japan*. 56, 1035 (2007)
- 26) Ohtsuka, T., Guo, J., Sato, N.: *J. Electrochem. Soc.* 133, 2473 (1986)
- 27) Mougín, J., Rosman, N., Lucazeau, G., Galerie, A.: *J. Raman Spectrosc.* 32, 739 (2001)
- 28) Schütze, M.: *Protective Oxide Scales and Their Breakdown*. Chichester, Institute of Corrosion and Wiley, 1997
- 29) Kitamura, K., Nishiyama, Y., Otsuka, N., Kudo, T.: *Corrosion/2007*. No. 7466, Houston, TX: NACE, 2007
- 30) Darken, L.S., Gurry, R.W., Bever, M.B.: *Physical Chemistry of Metals*. New York, McGraw-Hill Company, 1953, p.351
- 31) Otsuka, N., Doi, T., Hidaka, Y., Higashida, Y., Masaki, Y., Mizui, N., Sato, M.: *ISIJ International*. 53, 286 (2013)

NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 114 MARCH 2017



Kazuyuki KITAMURA  
Senior Researcher  
Fundamental Metallurgy Research Lab.  
Advanced Technology Research Laboratories  
1-8 Fuso-cho, Amagasaki, Hyogo Pref. 660-0891



Yasuto HIGASHIDA  
Senior Researcher  
Pipe Manufacturing Process Research Lab.  
Process Research Laboratories



Takashi DOI  
Senior Researcher, Dr. Eng.  
Fundamental Metallurgy Research Lab.  
Advanced Technology Research Laboratories



Yasuhiro MASAKI  
Chief Researcher, Dr. Eng.  
Pipe & Tube Research Lab.  
Steel Research Laboratories



Yoshitaka NISHIYAMA  
General Manager, Head of Div., Dr. Eng.  
Hydrogen & Energy Materials Research Lab.  
Steel Research Laboratories



Nobuo OTSUKA  
Dr. Eng.  
Amagasaki Division  
Nippon Steel & Sumikin Technology Co., Ltd.



Yasuyoshi HIDAKA  
Senior Researcher, Dr. Eng.  
Pipe Manufacturing Process Research Lab.  
Process Research Laboratories