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Depth Profile Chemical State Analysis of Oxide Films on High Temperature Treated Stainless Steel Using EPMA with a Soft X-ray Spectrometer at Variable Accelerating Voltage

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Stainless steel is an alloy of steel that contains 11% or more chromium (Cr) in iron (Fe) [1]. Since the Cr in stainless steel has a higher ionization tendency than Fe, the Cr binds to **o**xygen (O) before Fe and forms a thin oxide film called a "passive film" that inhibits the further oxidation of the Fe. The higher the Cr content, the stronger the passive film becomes and the better the corrosion resistance of stainless steel. In this paper, it is shown that the soft X-ray emission spectrometer (SXES) on the Electron Probe Microanalyzer (EPMA) can analyze the chemical state of the surface of the stainless steel**,** and the SXES can in addition analyze the depth profile of the surface of the stainless steel by changing the accelerating voltage. Furthermore, we report the comparison of these results with those of Auger electron spectroscopy (AES).

The major difference between a wavelength dispersive spectrometer (WDS) on the EPMA and an SXES is that WDS can detect only one element at a time per spectrometer, while the SXES can detect X-rays from multiple elements simultaneously. There are two SXES systems, the SXES-LR (Low-energy Range) and the SXES-ER (Extended Range), both of which can be attached to the JEOL's FE-SEMs or EPMAs.

In this study, the chemical state of Cr, Fe, and Ni, which are the main elements of stainless steel (SUS304), were analyzed using the SXES-ER attached to an EPMA (JXA-iHP200F). Two samples were prepared and were mechanically polished, one was heated for 2 hours at 300°C in the atmosphere (heated sample), and the other was kept in the atmosphere for one week (unheated sample). To analyze the surface oxidation state of sample SUS304, the accelerating voltage was varied between 1.0 to 3.0 kV in 0.1 kV steps. To obtain the X-ray counts, the beam current was set to 250 nA, and the measurement time was integrated 20 times for 30 seconds.

Figure 1 shows the L-line spectra of Cr, Fe, and Ni for the heated and unheated samples measured at accelerating voltages between 1.0 and 3.0 kV. The characteristic X-ray generation volume depends on the accelerating voltage. Thus, the surface-sensitive and bulk-sensitive spectra can be obtained with lower and higher accelerating voltages, respectively. The depth of the X-ray generation can be calculated using Monte Carlo modeling. The spectra measured at each accelerating voltage were compared with the metal and oxide reference standard spectra. The peak position of the Fe state spectra of the heated samples shifted toward Fe_2O_3 at accelerating voltages of between 1.0-1.2 kV, and at accelerating voltages higher than 1.5 kV, the peak position of the Fe state spectra was identical to pure Fe. In addition, the spectrum of Cr was observed to have a Cr_2O_3 peak shape at 1.3 kV for the unheated sample and at 1.4-1.5 kV for the heated sample. The lower the accelerating voltage, the more the measured information is about the surface suggesting that the oxide film on the surface of stainless steels is formed in the order of first Fe, and then Cr. For Cr, the spectral shape was a mixture of Cr_2O_3 and Cr at an accelerating voltage of 1.3 kV. For Fe, the spectral shape was Fe_2O_3 at an accelerating voltage of

1.0 kV. At higher accelerating voltages, such as between 2.0 kV and 3.0 kV, the spectral shape of each element is closer to metal. This implies that the chemical state of iron further inside the sample is metallic.

Figure 2 shows the results of an O, Fe, Cr, and Ni depth profile analysis of a heated and an unheated sample by AES (JAMP-9510F). The O depth profile analysis results confirmed that the thickness of the surface oxide film was about 4 nm for unheated samples and about 15 nm for heated samples. These results indicate that the surface of stainless steel is oxidized in the order of first Fe, and then Cr, which is consistent with the result measured by the SXES. The analytical conditions were changed to a high-energy resolution mode for the depth profile chemical state analysis by AES that was performed on the heated sample. From Fig. 3, the layer composition is estimated in the order of Fe_2O_3, FeO, Cr_2O_3, and Ni-rich layer from the top surface down.

As a result of evaluating the oxide film on the surface of stainless steel using the SXES, it was estimated that Cr had a Cr-rich oxide layer around 15 nm from the surface and Fe had a Fe-rich oxide layer around 8 nm, and similar results were obtained by AES. In the case of the unheated sample, the thickness of the oxide film is estimated to be less than 5 nm, but to analyze oxide films less than 5 nm with SXES, the accelerating voltage must be further lowered, and the analysis must be performed while taking into consideration the excitation voltage of each element. It is said that Cr, which has a greater ionization tendency than Fe, is generally oxidized first on the stainless steels surface, but in this study, it was confirmed that Fe was oxidized before Cr. This may be a result of the differences in the experimental conditions, such as air versus vacuum atmosphere.

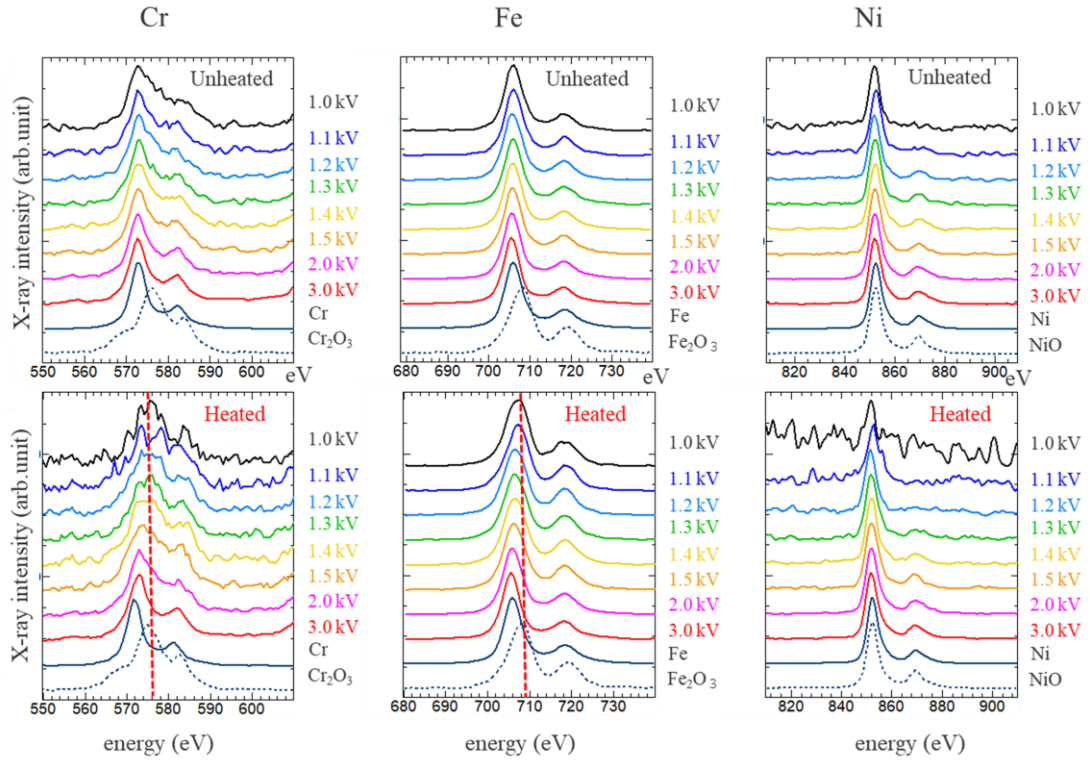

Fig. 1 Comparison of standard reference spectra with those of the samples at each accelerating voltage.

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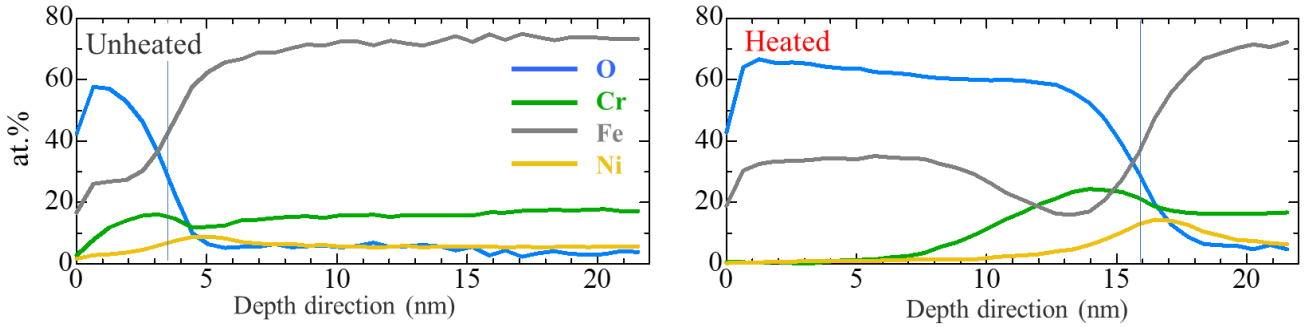

Fig. 2 Depth profile of the heated and unheated sample using an AES (JAMP-9510F Auger).

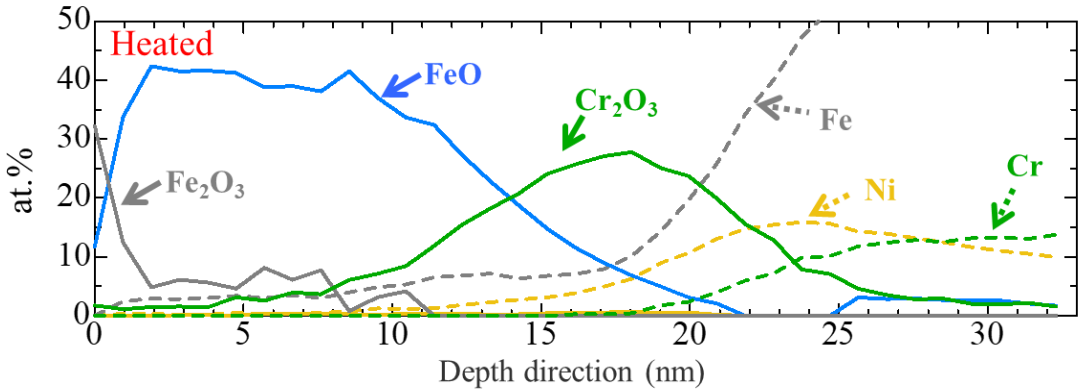

Fig. 3 Depth profile of state analysis using an AES (JAMP-9510F Auger).

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