

# Analysis of oxide layers on stainless steel (304, and 316) by conversion electron Mössbauer spectrometry

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Stainless steels of type SUS304 and SUS316 were chemically treated and heated at various temperatures, and the oxide films formed on the surface were analysed by Auger electron spectrometry and conversion electron Mössbauer spectrometry. The outermost oxide layers of stainless steels were enriched with iron and chromium after heat treatment below 600°C and above 700°C, respectively. It was found that at least two magnetic components of iron species were present in the oxide layers of stainless steel heated below 600°C and that the fine particles of iron oxide are produced in the inner oxide layers of the samples prepared by heating at temperatures higher than 700°C. Only paramagnetic iron species were detected in the oxide layers of the stainless steel prepared by chemical treatment. The structures of the oxide layers produced by those heat and chemical treatments are proposed.

## 1. Introduction

Stainless steel is one of the most useful materials in industry, architecture, and daily use. It is known that the heat treatment and chemical oxidation of stainless steel at under certain conditions improve the corrosion resistance of the substrate by forming coloured films [1]. Coloured stainless steel of type SUS304 is known to become golden at 400°C, orange at 500°C, red to purple at 600°C, purple at 700°C, and blue above 700°C. X-ray photoelectron spectrometric (XPS) studies of the coloured films, which were formed by the immersion of stainless steel in chromic acid and sulphuric acid solution, have been reported by Ansell *et al.* [2]. Many researchers have studied passivating films of 1 to 5 nm thick on iron and stainless steel. Thick oxide films of  $^{57}\text{Fe}$  were initially studied by electroplating enriched  $^{57}\text{Fe}$  on the surface of non-enriched iron [3]. *In situ* study of passive oxide film on iron was undertaken by O'Grady [4]. Recently, Stewart *et al.* [5] applied conversion electron Mössbauer spectrometry (CEMS) to the analysis of the oxide layer on the enriched  $^{57}\text{Fe}$  thin foil of stainless steel (type 310) which was oxidized at high temperatures ( $> 700^\circ\text{C}$ ) and reported that  $\alpha\text{-Fe}_2\text{O}_3$  was detected in the chromium-depleted layers. However, very few Mössbauer spectrometric studies have been carried out on the formation of oxide films on stainless steel which was systematically oxidized by a heating and/or chemical procedure. We recognized experimentally that it takes too much time to measure CEM spectra of oxide films on stainless steel containing a natural abundance of  $^{57}\text{Fe}$ . Even a thin oxide film sometimes became charged while detecting conversion electrons. While improving the detector for CEMS, we have so far analysed the chemical structure of oxide layers [6], phosphate layers [7] and oxalate layers [8] of steels. We also

reported recently that an oxide film on stainless steel can be used as a pH sensor [9]. The pH response of this oxide film, however, depended on the preparation condition of oxide film. Oxide structures of stainless steel analysed by CEMS and Auger electron spectrometry (AES) are reported in this paper.

## 2. Experimental details

Sheets of stainless steel (type SUS304 and SUS316) were degreased in acetone, and heated in air for 1 h at 400, 500, 600, 700 and 800°C. SUS316 stainless steel contained 3 wt % Mo in addition to similar constituents of SUS304 stainless steel with 18 wt % Cr, 8 wt % Ni, and Fe balance. The other oxide films were also prepared by immersing stainless steel in 2.5 mol dm<sup>-3</sup> chromic acid and 5.0 mol dm<sup>-3</sup> sulphuric acid solution at 70°C. In order to analyse these oxide-coated samples by CEMS, 25 mCi  $^{57}\text{Co}$ (Rh) source and a gas flow counter [10] were used. Care was taken to prevent a sample from becoming electrically charged during the measurement by contact of the substrate with the counter wall when the sample was mounted in the detector. Distributions of a hyperfine field of partial data were calculated using Hesse's method [11]. The intensity ratio of magnetically split peaks was supposed to be 3:3:1:1:3:3 although this method is not really suited for the Mössbauer spectrum in which several kinds of iron oxides are included. Some data were fit to the sum of Lorentzian using the fitting program which was loaded on a personal computer. Depth profiles of some samples were measured by AES to support the analysis of Mössbauer data. The thickness of oxide films on stainless steel was roughly estimated by the weight change of stainless steel and by the AES peaks coupled with argon ion etching, presuming that the oxide films were composed of uniform  $\text{Fe}_2\text{O}_3$ .

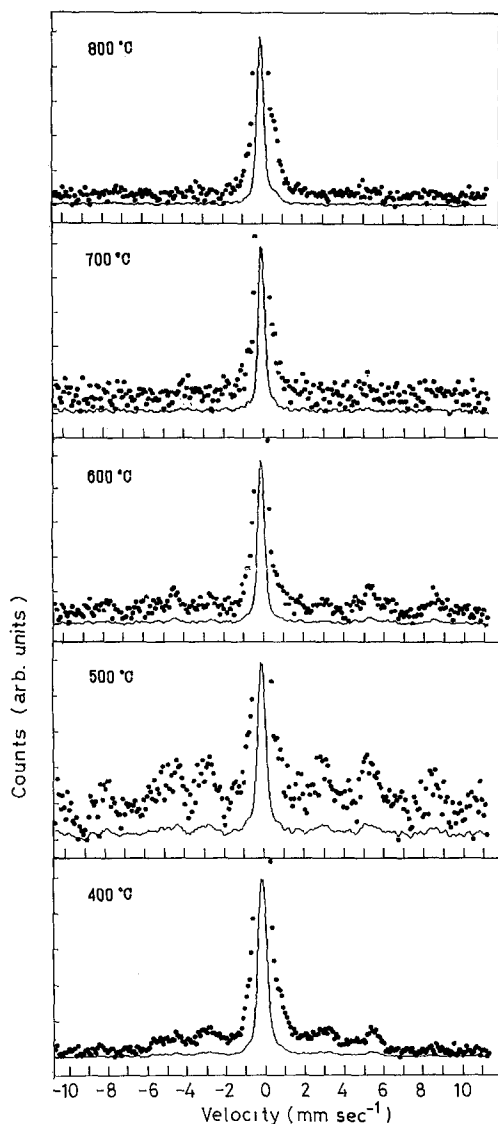


Figure 1 CEM spectra of oxide films on SUS304 stainless steel heated for 1 h at 400, 500, 600, 700 and 800°C.

### 3. Results and discussion

#### 3.1. Oxidation in dry air

##### 3.1.1. Oxide films on SUS304

Conversion electron Mössbauer (CEM) spectra of SUS304 sheets, which were heated at 400, 500, 600, 700 and 800°C for 1 h, are shown in Fig. 1. The thickness of the oxide films was estimated to be 20 to 50 nm on increasing the heating temperature to 700°C. The intensity of a singlet of austenitic stainless steel was extremely high compared with that of iron oxide peaks, because the iron content in the oxide layer was far less than that in the bulk, and the oxide film was thin compared with the range of 7.3 keV electrons in iron (ca. 300 nm). Data were plotted by the expansion to five times higher than the smoothing line of the whole peaks.

In the samples heated below 600°C, magnetically split peaks were clearly observed. The magnetic hyperfine field of iron compounds produced in the oxide films increased with increasing heating temperature as shown in Fig. 1. However, the intensity of the internal magnetic hyperfine field did not always increase in accordance with the increase in heating temperature. This suggested that the iron content changed in the oxide films. From the AES depth profile of the sample heated at 500°C as shown in Fig. 2, it was found that iron was concentrated on the outermost surface, and that iron, chromium and nickel were present in the inner oxide layers. Furthermore there was a smooth transition between these layers and the bulk. The sample heated at 500°C was measured at dry ice temperature and the CEM spectrum was analysed by Lorentzian fitting as shown in Fig. 3b. At least two iron species of isomer shift (IS) = 0.37 mm sec<sup>-1</sup>, quadrupole splitting (QS) = 0.02 mm sec<sup>-1</sup>, hyperfine field ( $H_{in}$ ) = 530 kOe and of IS = 0.2 mm sec<sup>-1</sup>,  $H_{in}$  = 350 kOe were found. The former species was

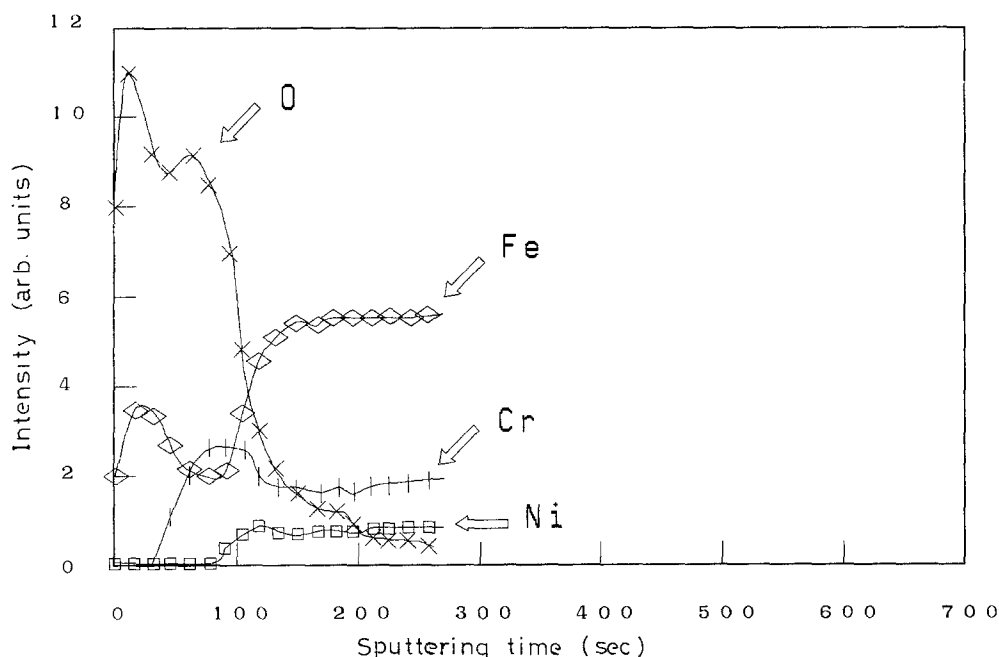


Figure 2 AES in-depth profiles of SUS304 stainless steel heated at 500°C for 1 h. Thickness/sputtering time  $\approx$  10 nm/60 sec.

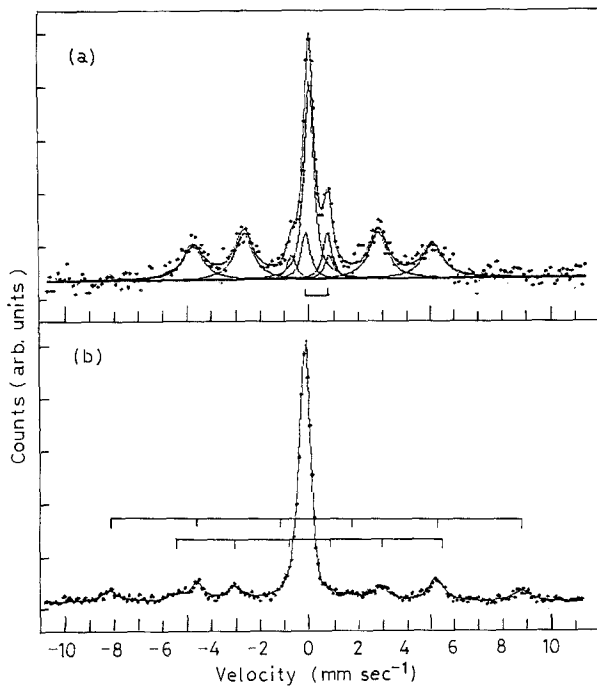


Figure 3 Dry-ice temperature CEM spectra of oxide films on SUS304 stainless steel heated for 1 h at (a) 900°C and (b) 500°C.

attributed to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the latter to a poor crystalline spinel compound such as NiO(Cr, Fe)<sub>2</sub>O<sub>3</sub>. Only paramagnetic peaks were observed at room temperature in samples heated above 700°C as shown in Fig. 1. The chromium content tended to increase in the outermost surface and the iron content to decrease in the sample heated at 700°C, as shown in the AES profile of Fig. 4. Although the CEM spectra of oxide film of SUS304 sample heated at 900°C gave a doublet at room temperature, a broad sextet ( $IS = 0.025 \text{ mm sec}^{-1}$ ,  $QS = 0.08 \text{ mm sec}^{-1}$ , and average  $H_m = 300 \text{ kOe}$ ) and a doublet ( $IS = 0.27 \text{ mm sec}^{-1}$ ,  $QS = 0.86 \text{ mm sec}^{-1}$ ) were observed at dry-ice temperature as shown in Fig. 3a. The doublet observed at room temperature was considered to be due to super-

paramagnetism of fine iron oxide beneath the Cr<sub>2</sub>O<sub>3</sub> layer. It may also be mixed with chromium, nickel and iron to form as (Fe, Cr)<sub>2</sub>O<sub>3</sub> and NiO (Fe, Cr)<sub>2</sub>O<sub>3</sub> at the initial oxidation. When the sample heated at 400°C for 1 h was further heated at 700°C, large particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, haematite, were observed on the chromium oxide layer by scanning electron microscopy.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is formed as a result of decomposition of these intermediate mixed compounds when the stainless steel is further heated for a long time. It is considered that the growth of iron oxide beneath the chromium-oxide layer destroys the stacking and uniformity of chromium oxide layers at high temperature.

### 3.1.2. Oxide films on SUS316

CEM spectra of heated SUS316 between 400 and 900°C are shown in Figs 5 and 6. The peak intensity of iron products was higher than that of SUS304 although the oxide layers on SUS316 were a little thicker than oxide layers on SUS304. The surface colour of SUS316 was not as shiny as that of heated SUS304. Three iron species, which had hyperfine fields of 280, 340, and 530 kOe, were found in the sample heated at 400°C. These were considered to be due to Fe(III)/(Fe(II) pairs in octahedral sites and Fe(III) in tetrahedral sites of spinel compounds such as (Fe, Ni)O(Fe, Cr)<sub>2</sub>O<sub>3</sub>, and Fe(III) in columbom structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (Fe, Cr)<sub>2</sub>O<sub>3</sub>. The distribution of the internal magnetic field of iron oxide produced on SUS316 is shown in Fig. 7. The hyperfine fields of the intermediate iron compounds increased and the intensity decreased with increasing heating temperature. The schematic changes of oxide films on SUS316 as a function of heating temperature were similar to those of SUS304. However, a larger amount of iron remained at the outermost surface on SUS316 than on SUS304 heated below 600°C. Because molybdenum is easily oxidized, the oxidation of the SUS316 surface is considered to proceed while the diffusion of iron into the bulk and of chromium into the surface is

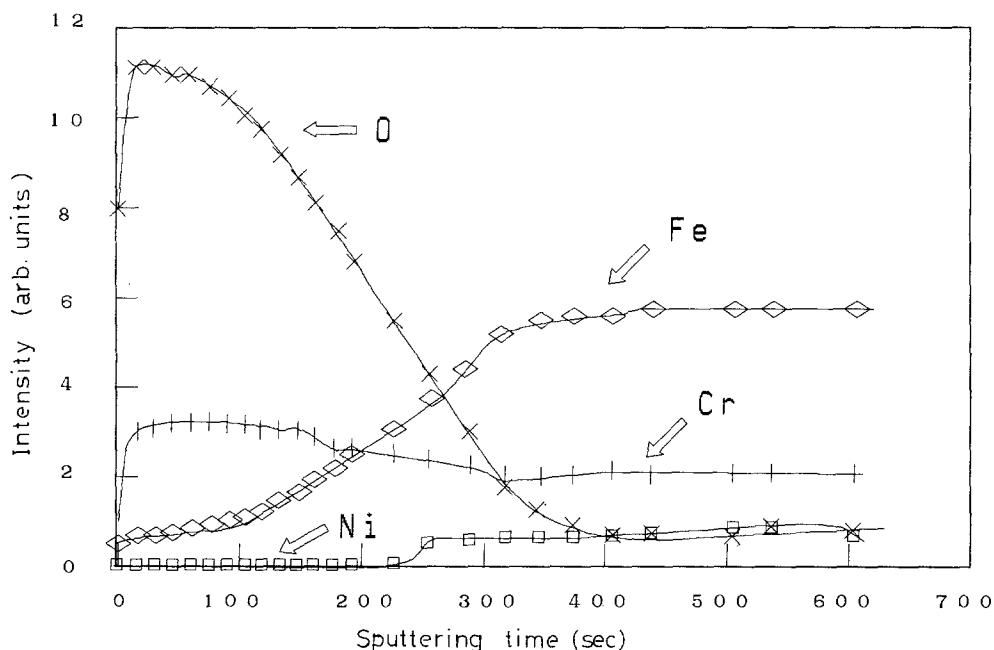


Figure 4 AES in-depth profiles of SUS304 stainless steel heated at 700°C for 1 h. Thickness/sputtering time  $\approx 10 \text{ nm}/60 \text{ sec}$ .

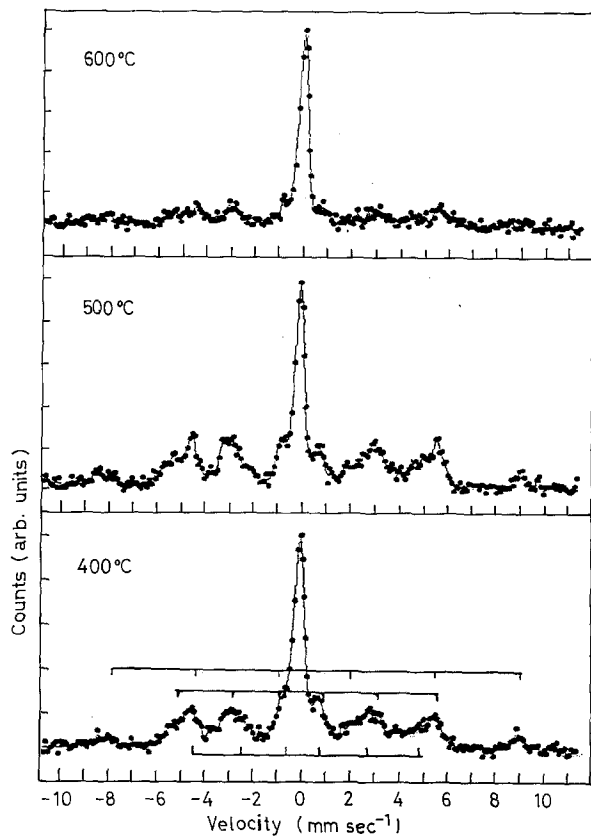


Figure 5 CEM spectra of oxide films on SUS316 stainless steel heated at 400, 500 and 600°C.

retarded by the formation of molybdenum oxide. A superparamagnetic doublet was observed in the room-temperature CEM spectra of the samples heated at a temperature higher than 700°C. The doublet indicated that iron species existed almost in the same fine

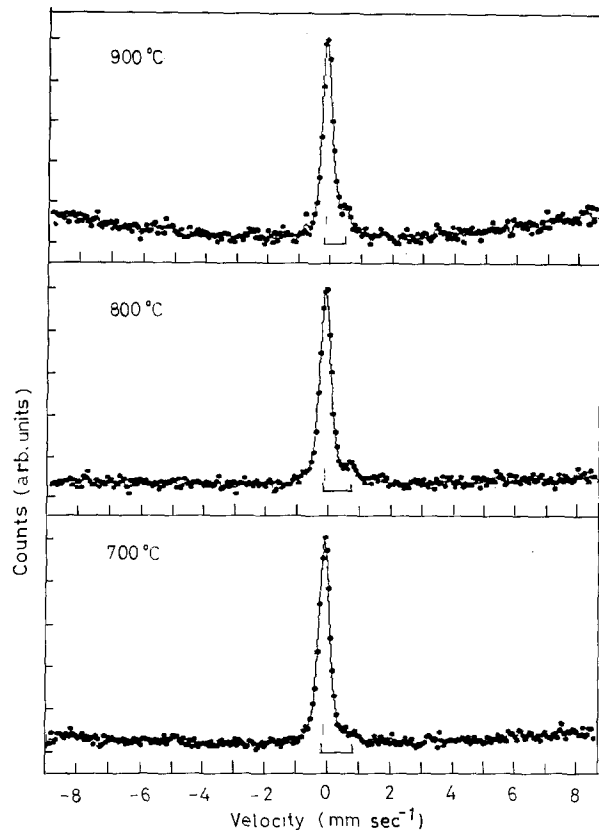


Figure 6 CEM spectra of oxide films on SUS316 stainless steel heated at 700, 800 and 900°C.

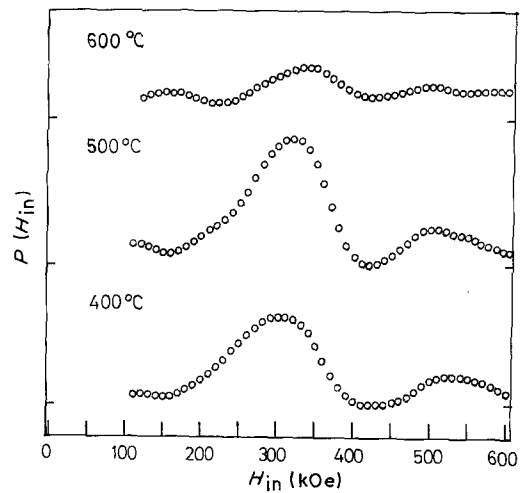


Figure 7 Distribution of hyperfine field of oxide films on SUS316 stainless steel heated for 1 h at 400, 500 and 600°C.

particles of chromium and iron mixed oxides as on SUS304. Magnetic splitting was observed in CEM spectra of the samples heated at 900°C for 2 h.  $\alpha$ - $\text{Fe}_2\text{O}_3$  is formed as the final product of the corrosion. Schematic structures of oxide films on SUS304 and SUS316 stainless steels are considered to be as shown in Fig. 8. There is no inherent difference of oxide structures between SUS304 and SUS316, although the outermost oxide layer of SUS316 contained more iron than that of SUS304. Molybdenum oxide was distributed throughout the whole oxide layers of SUS316. The transient oxidation of these Fe-Cr-Ni-(Mo) stainless steels was similar to that of Fe-Cr alloys reviewed by Homma [12].

### 3.2. Wet oxidation of stainless steel

Stainless steels were treated in a solution of  $2.5 \text{ mol dm}^{-3} \text{CrO}_3$  and  $5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$  for several tens of minutes. Ansell *et al.* [2] reported, from the results of their X-ray photoelectron spectroscopic study, that the coloured film on stainless steel, prepared by immersion in a chromate solution, is composed principally of iron, chromium and oxygen and the species

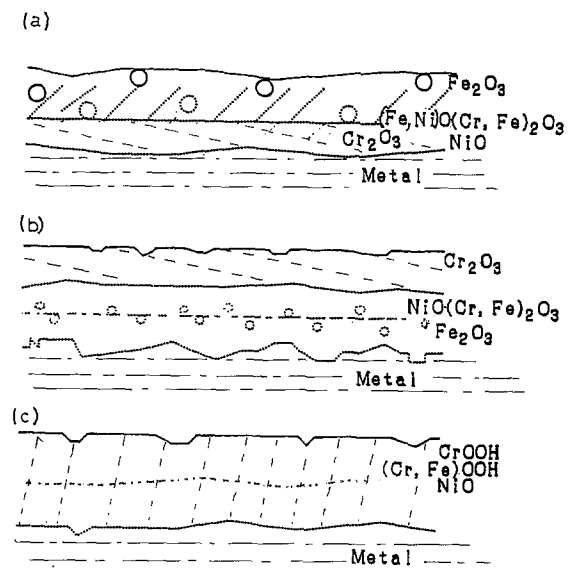


Figure 8 Schematic structure of oxide films on stainless steel heated at (a) lower temperature and (b) higher temperature than 700°C, and (c) oxide films formed in a chromate solution.

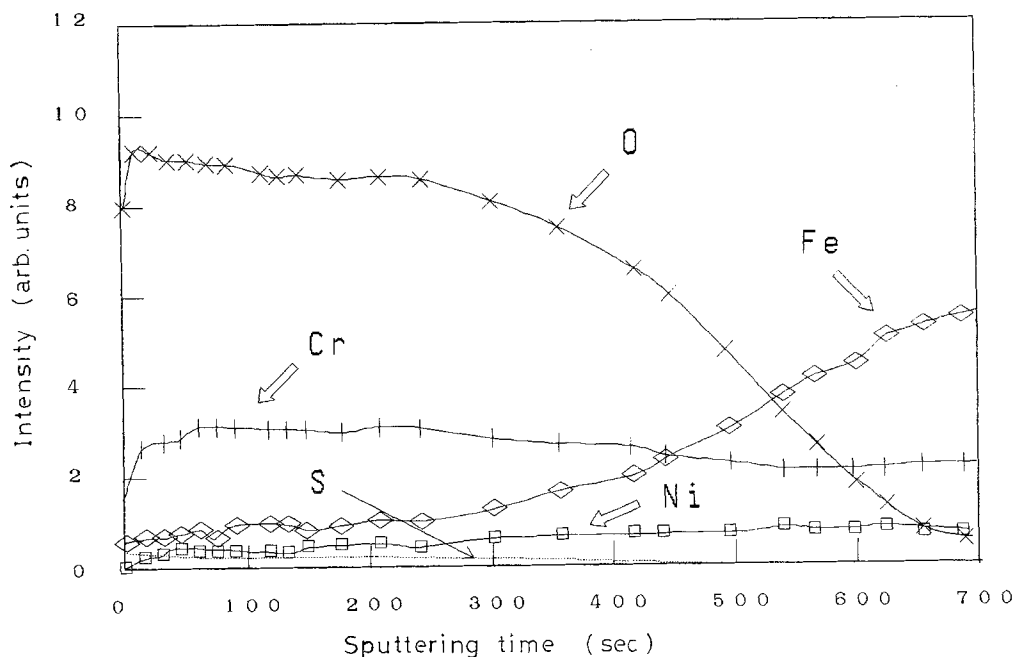


Figure 9 AES in-depth profiles of SUS304 stainless steel treated in a chromate solution at 70°C for 25 min. Thickness/sputtering time  $\approx 10$  nm/60 sec.

present in the film are invariant with thickness. That is, in the coloured region, the intensity ratio of Fe/Cr remained reasonably constant although the ratio decreased on ageing from the heated coloured specimens. It was found from AES results as shown in Fig. 9 that chromium was slightly enriched and iron decreased slightly on the outermost oxide films and that nickel existed uniformly in the oxide films. Sulphur was detected in the oxide layers because a treatment solution contained many sulphate ion. In the chemical state of iron in these films, only a doublet (IS = 0.4 mm sec<sup>-1</sup>, QS = 1.0 mm sec<sup>-1</sup>) appeared in the CEM spectra both at room and dry-ice tem-

peratures as shown in Fig. 10. This iron product was considered to be iron oxyhydroxide containing chromium and nickel. The intensity of the doublet decreased from 20% to 10% with increasing immersion time although the chemical state of iron in the oxide films remained the same.

The oxide films on SUS316 treated in a chromate solution gave the same CEM spectra as those on SUS304 as shown in Fig. 11. The IS and QS of the doublet were 0.34 and 1.10 mm sec<sup>-1</sup> respectively. The intensity of the doublet tended to decrease with the temperature of the chromate solution. More iron was included in oxide films of SUS316 than in those of SUS304. Molybdenum was detected uniformly in the

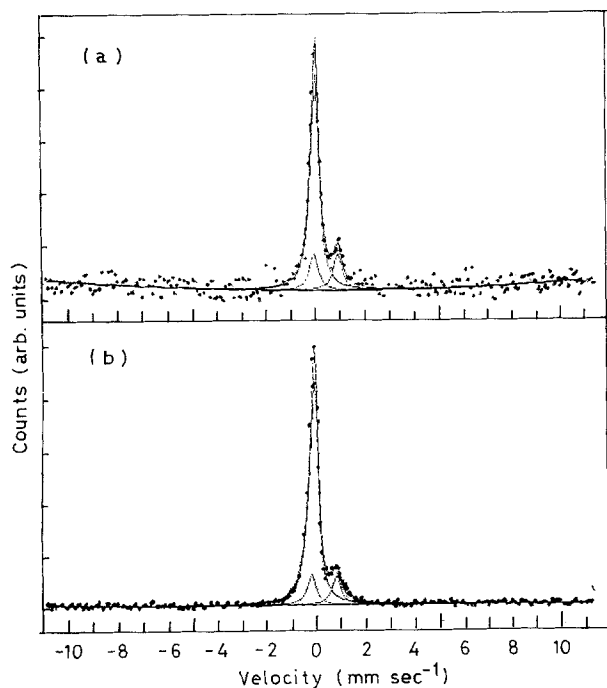


Figure 10 CEM spectra of oxide films on SUS304 stainless steel treated in a chromate solution at 70°C for 15 min. Measuring temperature: (a) room temperature and (b) dry-ice temperature.

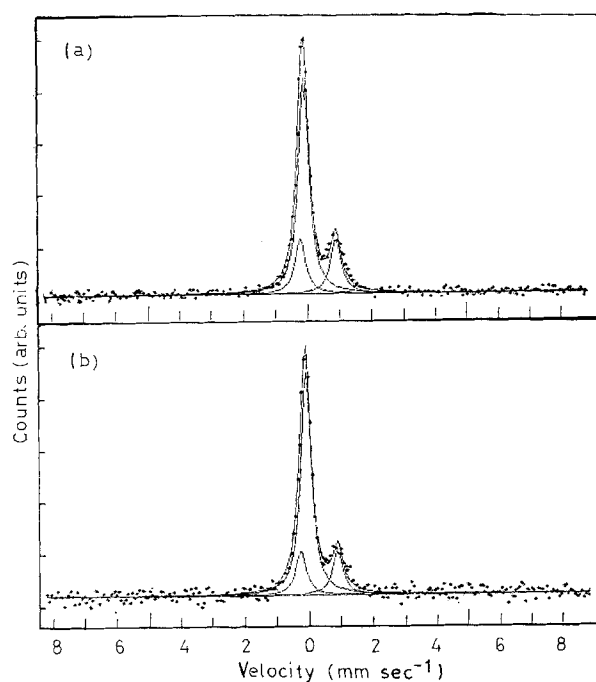


Figure 11 CEM spectra of oxide films on SUS316 stainless steel treated in a chromate solution for 20 min at (a) 60°C and (b) 70°C.

oxide layers of SUS316, although the intensity of fluorescent molybdenum X-ray tended to decrease with increasing immersion time.

Ensling *et al.* [13] studied the oxide layers produced on austenitic and martensitic steels after treatment under boiler conditions by CEMS and reported that  $\text{Fe}_{3-x}\text{O}_4$  formed on Fe-20Cr-10Ni steel and  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  on Incoloy 800 (Fe-20Cr-33Ni) with increasing immersing time. The three different iron species, namely  $\text{Fe}^{3+}$  in octahedral sites ( $H_{\text{in}} = 532$  kOe),  $\text{Fe}^{3+}$  in tetrahedral sites ( $H_{\text{in}} = 493$  kOe),  $\text{Fe}^{2+}/\text{Fe}^{3+}$  pairs in octahedral sites ( $H_{\text{in}} = 471$  kOe), were detected in the oxide spectrum of Incoloy. Chromium was depleted in the outer zone of the oxide layer. These oxide layers were different from our samples treated in a chromate solution.

#### 4. Conclusions

Oxide films formed on stainless steels, which were heated below  $700^\circ\text{C}$  or treated in a chromate solution, produced various shiny colours. Oxide films produced by the two preparation methods described above could be distinguished simply by detecting the iron state in the films using CEMS. The iron oxide on heated stainless steel showed magnetic hyperfine fields while the other showed paramagnetic peaks. The structure of the oxide layers differed with the preparation techniques. At least two oxide layers were observed on the thermally treated stainless steels, while multi-oxide layers could not be formed clearly by chemical treatment. The thick oxide films, prepared by heating below  $500^\circ\text{C}$ , were similar to the passive thin film observed by ESCA, because in the passive layer the air-formed film had a somewhat thicker iron oxide layer at the top surface [14].

The films on stainless steel, heated above  $800^\circ\text{C}$  were not so protective against inner corrosion. It is easily understood by observation of the CEM spectra that fine oxide particles produced in the oxide

layers grew with increasing oxidation time and heating temperature, and the large oxide particles destroyed the protective stacked oxide films.

The elements included in the bulk of the stainless steel are known to be segregated in deep layers by heating. The structure of the oxide layers formed on stainless steel by heating in air is considered to be determined as a result of the competitive oxidation and segregation rates of each element and the orientation of the crystalline oxides.

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