

SURFACE COMPOSITION OF THE SCALE ON Ni-Cu ALLOY FORMED IN
NITRIC OXIDE

Yoshio TAKASU,^{*} Yoshiharu MATSUDA,^{*} Shun-ichi MARU,^{*}
Setsuaki YOKOTA,^{**} and Yoshio MORONUKI^{**}

^{*} Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755

^{**} Analytical Instrument Division, ULVAC Corporation, 2500 Hagazono,
Chigasaki, Kanagawa 253

X-ray photoelectron spectroscopy(ESCA) and Auger electron spectroscopy(AES) were adopted for an examination of the surface composition of scale on Ni-Cu alloy(64%Ni) formed in nitric oxide at 700°C. The surface layer of the scale was mainly composed of NiO caused by preferential oxidation of nickel in the alloy by nitric oxide.

Some of the authors previously reported¹⁾ that nickel in Ni-Cu alloy was found to be selectively oxidized by nitric oxide, using X-ray diffractometry and Ion-Micro-Analysis(IMA). However, it has been difficult to reveal the depth profile of the chemical species of a thin oxide scale with such techniques.

In this study, ESCA and AES spectroscopic techniques were adopted for analyzing a thin oxide scale on Ni-Cu alloy formed in nitric oxide at high temperature. The alloy used was 64%Ni one. After annealing and rolling, the specimens(ca.0.2mm in thickness) were electropolished in a mixed acid($\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$)²⁾, and rinsed in distilled water. Oxidation of them was carried out in a high vacuum apparatus under 10Torr of nitric oxide or oxygen at 700°C for 5.0 minutes. The test specimens prepared by above procedure were set into an ESCA-AES apparatus(ESCA-AES Electron Spectrometer PHI Model 548) equipped with an argon ion-etching system. The apparatus could be evacuated under a pressure of 10^{-10} Torr. The X-ray from $\text{MgK}\alpha$ was used for the ESCA. The beam voltage of the argon ions for etching was set at 2kV with current densities of $65 \mu\text{A}/\text{cm}^2$. The rate of etching was about $1 \times 10^2 \text{ \AA}/\text{min}$.

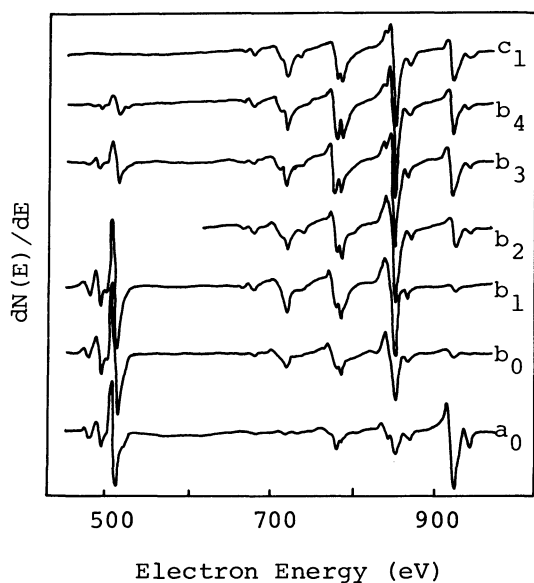


Fig.1. Auger spectra of the scale on Ni-Cu alloy formed in nitric oxide or oxygen.

a_0 : surface of the scale formed in oxygen,

b_0 : surface of the scale formed in nitric oxide,

b_1 -- b_4 : ion-etched surfaces of the scale formed in nitric oxide (etching time of each surface was as follows : b_1 -- 5 min., b_2 -- 13 min., b_3 -- 28 min., b_4 -- 66 min.),

c_1 : surface of the non-oxidized Ni-Cu alloy ion-etched for 10 min.

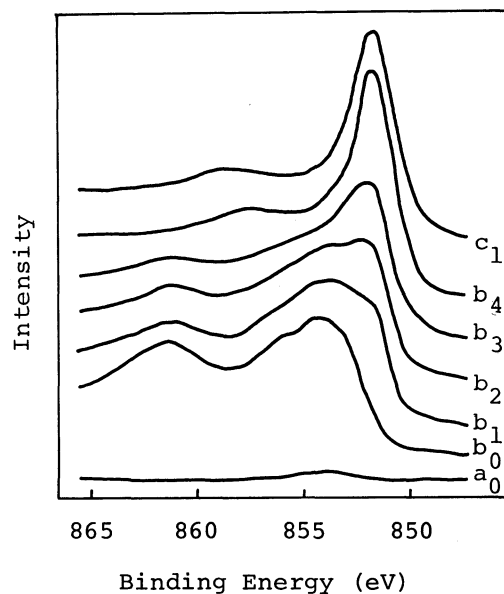


Fig.2. ESCA spectra of the scale on Ni-Cu alloy formed in nitric oxide or oxygen, ($Ni2p_{3/2}$).

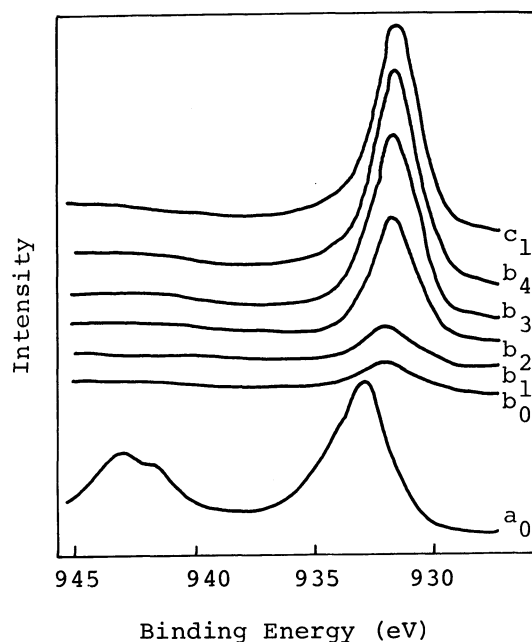


Fig.3. ESCA spectra of the scale on Ni-Cu alloy formed in nitric oxide or oxygen, ($Cu2p_{3/2}$).

Figure 1 shows the AES spectra of the surface and inner layers of the scale on the Ni-Cu alloys formed in nitric oxide or oxygen. In the figure, a_0 denotes the spectrum of the surface of the scale formed in oxygen, and b_0 denotes that in nitric oxide. The spectra of the ion-etched surfaces of the scale formed in nitric oxide were denoted with b_1 -- b_4 , and that of a non-oxidized one was denoted with c_1 . As is well known, the Auger peak at 921eV is due to copper, and that at 720eV is due to nickel. According to the estimation by Chang³⁾, the escape depth of the Auger electron having a energy between 720--921eV is about 15 \AA . On comparison of these spectra(a_0 and b_0), it was apparent that the surface of the scale formed in nitric oxide was occupied mainly by nickel and oxygen, while that formed in oxygen atmosphere was occupied mainly by copper and oxygen. The content ratio of nickel to copper decreased in duration of the ion-etching(b_0 , b_1 , b_2 , b_3), and it gave minimum at 28 minutes(b_3). Chemical species of the scale were examined with ESCA, and the spectra were shown in Figs.2 and 3. The escape depth of the photoelectrons from $\text{Ni}2p_{3/2}$ or $\text{Cu}2p_{3/2}$ level is about 12 \AA ³⁾. The spectra of the surface oxidized in oxygen(a_0) showed that the surface was covered mainly with CuO (or CuO and Cu_2O) and a small amount of NiO . Because the $\text{Ni}2p_{3/2}$ peak at 854.2eV(NiO)⁴⁾ was not only very weak, but also $\text{Cu}2p_{3/2}$ peak at 933.1eV was very strong with a strong satellite peak at 943eV(CuO)⁵⁾. On the other hand, the spectra of the surface oxidized in nitric oxide(b_0) were characterized by the strong $\text{Ni}2p_{3/2}$ peak at 854.2eV and the weak $\text{Cu}2p_{3/2}$ peak at 931.8eV(Cu_2O)⁶⁾. This suggests that the surface was composed of NiO and a small amount of Cu_2O . The $\text{Ni}2p_{3/2}$ peak at 851.7eV(metallic nickel) and the $\text{Cu}2p_{3/2}$ at 931.5eV(metallic copper) grew strongly in duration of the ion-etching. Then, no peak of nitrogen or sulfur and very weak peak of carbon were observed in the spectra of AES of these scales.

These findings should signify that nickel in the alloy was preferentially oxidized in nitric oxide and it formed the scale, and the content of it decreased gradually in the direction of its depth. Copper in the alloy was slightly oxidized into Cu_2O and it existed near the surface of the scale with much less content ratio of nickel to copper than that in the bulk. This conclusion does not contradict with the previous results by use of IMA¹⁾. There have been generally reported⁷⁾ that the scales on Ni-Cu alloys formed in oxygen consisted of two distinct layers; i.e. the component of the outer layer was copper oxide and that of

the inner was nickel oxide. It is noteworthy, as shown in this study, that the scale on the Ni-Cu alloy formed in nitric oxide should mainly consisted on nickel oxide.

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