January, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 219—221 (1975) 219

An Analysis of the Surface Composition of Passive Film on Cu-Ni Alloys by means of Auger Electron Spectroscopy and X-Ray Photoelectron Specroscopy

Yoshio Takasu, Shun-ichi Maru, Yoshiharu Matsuda, and Hazime Shimizu*
Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755
**Electrotechnical Laboratory, Tanashi, Tokyo 188*

(Received August 20, 1974)

A potentiostatic polarization method, Auger electron spectroscopy (AES), and photoelectron spectroscopy (XPS) were used to examine the composition of the passive films formed on Cu–Ni alloys anodized in an acid. The Flade potential of pure nickel in 0.5 M $HClO_4$ at 25 °C was −0.085 V (*vs.* SCE), while those of the alloys varied linearly from 0.180 V at 95%Ni to 0.310 V at 47%Ni. Analysis by AES and XPS revealed that (a) the passive region contained nickel and copper in the same ratio as the alloy, and (b) the chemical species of the film were made of NiO and copper oxide (Cu_2O and/or CuO). The Flade potential was assumed to be governed by the mixed potential of the formation of such oxides.

Copper–nickel alloys find extensive use in saline water environments or in chemical instruments. Nickel-rich alloys in Cu–Ni are acid-resisting materials. Experimental studies have indicated that the presence of thin films on the surface of the alloys is primarily responsible for the excellent corrosion resistance of the nickel alloys,[1] but the composition of the initial films that form on the alloys on exposure to acid has not been experimentally determined. Coulometry should be applicable to an analysis of the composition of the passive films on Cu–Ni alloys, as attempted by Okuyama,[2] however, it has been difficult to obtain a clear E–Q curve.

Recently, Auger electron spectroscopy (AES) and photoelectron spectroscopy (XPS) techniques have become available for the investigation of very thin films on surfaces. Hulett and his co-workers[3] have studied the passive film on a Cu–Ni alloy which was formed in a NaCl solution by means of XPS; they found the passive film to be enriched with nickel.

On the other hand, one of the present authors has previously established a quantitative analysis of the surface alloy composition of the Cu–Ni alloy system by using AES.[4,5]

In this paper, an electrochemical observation of the passive films on Cu–Ni alloys in an acid and the direct analysis of the surface composition of the passive films by means of AES and XPS will be described.

Experimental

Polarization Measurements. An electronic potentiostat (Hokuto Denko Corp. HA-101) and a function generator (Kowa Electronics Ltd. FG-102) were used for polarization measurements. The corresponding current flow was drawn on a X-Y recorder.

Pure nickel and seven Cu-Ni alloys, 95, 86, 76, 67, 57, 47, and 42 at% nickel, were adopted in this study. The alloys were cast from 99.99% copper and 99.9% nickel, hot rolled, scalped, cold rolled to a thickness 0.01—0.005 cm, and annealed. The apparent surface area of each test electrode was 2.0 cm^2. It was abraded with emery paper (1500♯) and then rinsed in water and acetone.

The reference electrode was a saturated calomel electrode. The electrolyte was composed of 0.5 M $HClO_4$, through which purified nitrogen could be bubbled in order to remove any dissolved oxygen. The cell was located in a thermostat maintained at 25±0.1 °C.

Surface Analysis. Specimens were anodized potentiostatically in their passive region between 450—850 mV *versus* SCE for one hour. After anodization, the specimens were rinsed with distilled water and dried while being stored until examination. Auger analysis was carried out by using a CMA-type Auger spectrometer (NEVA AES-200). The X-ray photoelectron spectra were measured by the use of a Hitachi XPS E-507 analyzer.

Results

Anodic Polarization Behavior of Cu–Ni Alloys. Figure 1 shows a typical polarization curve for 86%Ni alloy in 0.5 M $HClO_4$ at 25 °C; the potential sweep rate was automatically set at 1 mV/s. The potential was moved anodically from the active region to the passive region. Potentials corresponding to P_1 were found to be affected only a little by the potential sweep rate. A slower potential sweep rate resulted in a higher corrosion rate of the electrode in the active region. In consideration of this high corrosion rate, the potential sweep rate was set at 1 mV/s. It might be previsionally possible to consider the P_1 potential as the Flade potential.

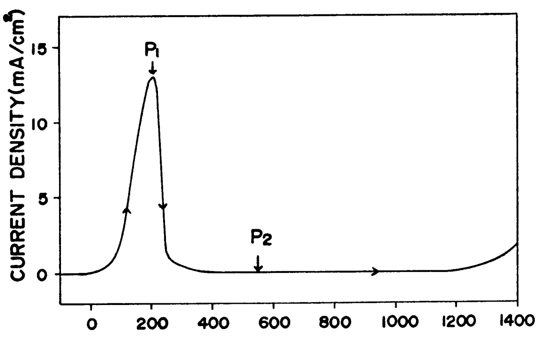

Fig. 1. Polarization curve for 86% Ni in dearated 0.5 M $HClO_4$ at 25 °C, 1 mV/s.

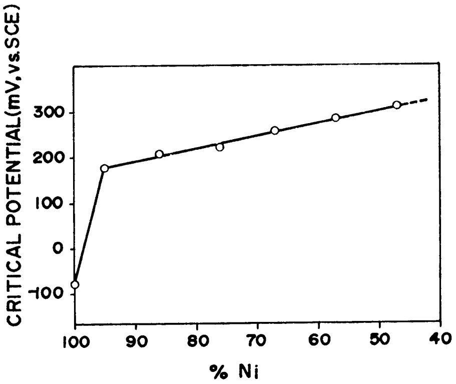

Fig. 2. Critical passivating potential (Flade potential) *versus* alloy composition.

The current density shows its minimum in the passive region at the P_2 potential. This was termed the passive current density. The Flade potential of Cu–Ni alloys in this experimental condition is shown in Fig. 2. Cu-rich alloys more than 42%Ni showed neither critical current at P_1 nor any minimum current at P_2. It is of interest that the Flade potential was changed almost linearly depending on the alloy composition.

Table 1. Surface content of nickel to copper in passive film by AES

Bulk content (at%Ni)	Surface content (at%Ni)
95	95—97
86	84—89
76	76—79
67	64—66
57	44—55

Surface-Alloy Composition of the Passive Films. The surface content of nickel in relation to copper in the passive films on Cu–Ni alloys, as measured by AES, are summarized in Table 1. It was reported that the surface alloy composition of the Cu–Ni system could be quantitatively analyzed by using a calibration curve.[4] As is shown in the table, the passive films contain nickel and copper in the same ratio as the alloys.

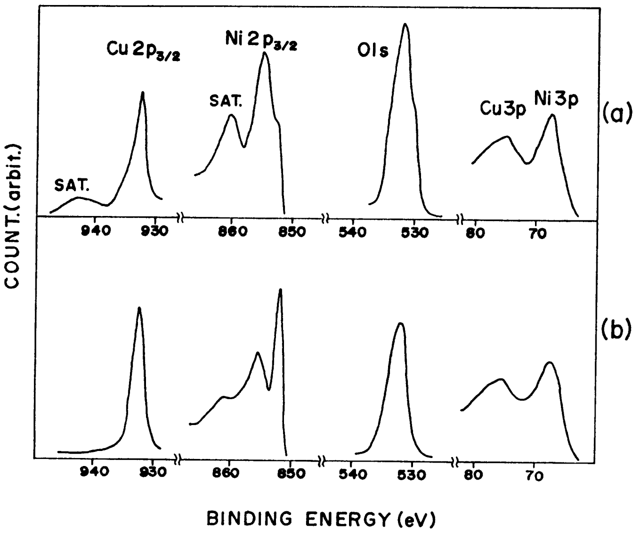

Fig. 3. Photoelectron spectra of (a) passive film and (b) abraded surface (76% Ni alloy).

Figure 3 compares the XPS spectrum from a surface of a 76%Ni specimen anodized at 500 mV *versus* SCE with that of an abraded specimen. The assignments of the peaks are marked in the figure. The intensity and the shape of the Cu3p peak and the peaks of the anodized surface and those of the abraded surface are almost identical. The O1s peak of the former is larger than that of the latter. It is noted that the peak with the binding energy of 852 eV almost disappears upon the anodization, while the peak with a binding energy about 3 eV higher grows stronger. This finding gives evidence of the formation of NiO in the passive film. The $\mathrm{Cu2p_{3/2}}$ peak of the passive film is almost unchanged by the anodic polarization, but a weak peak at 943 eV was produced. This peak corresponds to the satellite peak from Cu_2O or CuO.[6] The XPS spectra from the $\mathrm{Cu2p_{3/2}}$ and $\mathrm{Ni2p_{3/2}}$ peaks for the other specimens are shown in Figs. 4 and 5 respectively. These spectra also show that NiO and copper oxide (Cu_2O and/or CuO) were formed on the surface by the anodic polarization.

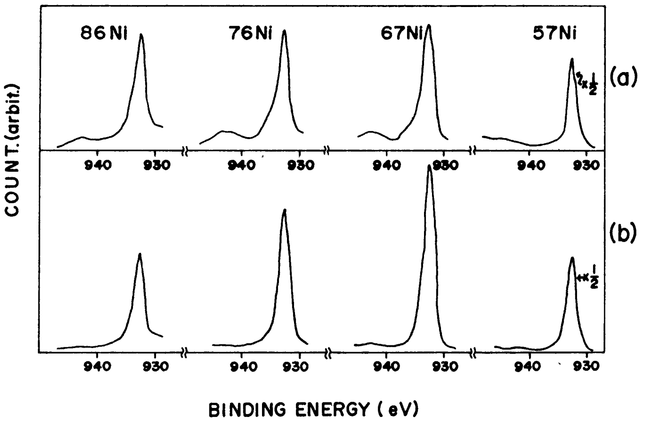

Fig. 4. Photoelectron spectra of (a) passive film and (b) abraded surface ($\mathrm{Cu2p_{3/2}}$).

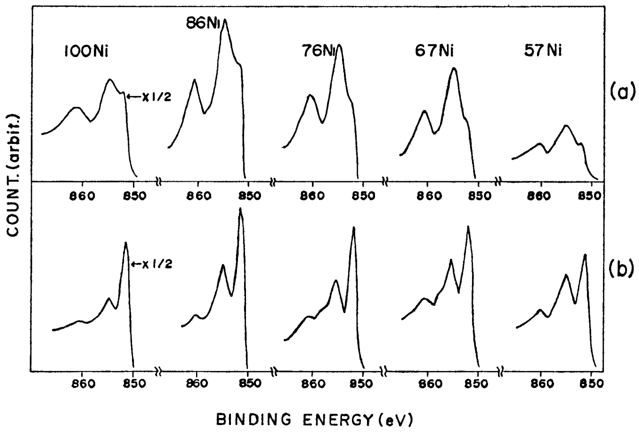

Fig. 5. Photoelectron spectra of (a) passive film and (b) abraded surface ($\mathrm{Ni2p_{3/2}}$).

Discussion

Osterwald and Uhlig[1] insisted that a passive film of Cu–Ni alloy in 0.5 M H_2SO_4 at 25 °C was almost identical with that on pure nickel; this phenomenon was observed on the alloy whose nickel content was over 30%Ni. However, they did not discuss copper oxide, although their data showed that the values of the Flade potential changed from 0.13 V (*vs.* SHE) at pure nickel to 0.38 V (*vs.* SHE) at 30.4%Ni.

As has been described above, Hulett and his coworkers[3] reported that the X-ray photoelectron spectrum of the passive films on 70%Ni alloy in a NaCl solution at 100 °C indicated primarily nickel oxide and was very similar to the spectrum obtained from pure nickel made passive in the same environment.

On the other hand, Okuyama[2] examined the composition of the passive film on the Cu–Ni alloy which was formed in a boric acid–sodium borate buffer solution (pH=8.39) by means of coulometry; he found that NiO, Ni_3O_4, and Cu_2O were formed in the film on the alloy whose nickel content was over 50%Ni.

These discrepancies among the data obtained by different investigators seem to be caused not only by the difference in the experimental conditions (the composition, the pH, and the temperature of the electrolyte), but also by the differing accuracies of the methods of surface analysis.

Therefore, this study makes it clear that (a) passive films formed in 0.5 M $HClO_4$ contain nickel and copper in the same ratio as the alloy, (b) and the chemical species of the film are composed of NiO and copper oxide (Cu_2O and/or CuO).

If one assumes NiO formation during the passivation of nickel at P_1, the reaction is as follows:[7]

$$Ni + H_2O = NiO + 2H^+ + 2e^- \qquad (1)$$

$$E_{NiO} = -0.131\ V\ (vs.\ SCE, 25°C)$$

Moreover, the formation of Cu_2O or CuO during the passivation of copper at P_1 is shown by the following reactions:[7]

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \qquad (2)$$

$$E_{Cu_2O} = 0.230\ V\ (vs.\ SCE, 25°C)$$

$$Cu + H_2O = CuO + 2H^+ + 2e^- \qquad (3)$$

$$E_{CuO} = 0.329\ V\ (vs.\ SCE, 25°C)$$

As is shown in Fig. 2, the experimental datum on the pure nickel was −0.085 V, while those on the alloys varied linearly from 0.180 V at 95%Ni to 0.310 V at 47%Ni. The experimental data were somewhat different from the thermodynamical data shown in Eqs. (1), (2), and (3). However, some differences are usually observed between the results of thermodynamical calculation and the experimental data, depending on the variation in the activities of the species on the electrode and the measuring conditions, whether at equilibrium or at non-equilibrium. Therefore, it can be assumed that NiO and Cu_2O and/or CuO were formed in the passive film of the alloy, and that their Flade potential was governed by the mixed potential by the upper reactions. This estimation corresponds also to the findings obtained by AES and XPS. However, more precise data for the potentials at P_1 for several temperatures and pH would be needed for a more fruitful correlation.

Uhlig explained a critical composition for passivity in Cu–Ni alloys at about 30%Ni with a critical electronic configuration which is based on the "rigid band model."[8] However, recent experimental results on the electronic structure of the Cu–Ni alloy system support a "coherent potential approximation model,"[9,10] not such a "rigid band model"; that is, Cu-rich alloys in the Cu–Ni alloy system should also have holes in the 3d band. Accordingly, the reason why the Cu-rich alloy in Cu–Ni does not form passive films in acid must not include the idea of the "filled d-band."

The authors are grateful to professor Toshiro Yamashina of the Faculty of Engineering, Hokkaido University, for giving them the alloy samples; they also wish to thank Professor Shiichiro Teranishi, Assistant Professor Toshinobu Imanaka, and Dr. Yasuyuki Okamoto of the Faculty of Engineering Science, Osaka University, for their kindness and advice in using the photoelectron spectrometer.

References

1) J. Osterwald and H. H. Uhlig, *J. Electrochem. Soc.*, **108**, 515, (1961).

2) S. Okuyama, The 41st Conference of the Electrochem. Soc. of Japan, Chiba, 1974.

3) L. D. Hulett, A. L. Bacarella, L. Lidonnici, and J. C. Griess, *J. Electron Spectrosc.*, **1**, 169, (1972/73).

4) K. Nakayama, M. Ono, and H. Shimizu, *J. Vacuum Sci. Technol.*, **9**, 749, (1972).

5) Y. Takasu and H. Shimizu, *J. Catal.*, **29**, (1973), 473.

6) G. Schön, *Surface Sci.*, **35**, 96, (1973).

7) M. Pourbaix, "Atras of Electrochemical equilibria in Aqueous Solutions," Gauthier-Villars (1963); trans. by J. A. Franklin.

8) N. F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys," Dover Publications Inc., New York (1958).

9) P. Soven, *Phys. Rev.*, **156**, 809, (1967) and **178**, 1136, (1969).

10) Y. Takasu and T. Yamashina, *Japan. J. Appl. Phys.*, (in press).