Anodic Dissolution of Cu-Ni Alloys in Perchloric Acid

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Cu-Ni alloys were firstly anodized, and then the alloy surfaces were examined by means of Auger electron spectroscopy and the metallic ions dissolved into the bulk solution were analyzed through atomic absorption analysis. Some corrosion behaviors of Cu-Ni alloys were clarified in the potential ranges of anodic corrosion and passivation.

1. Introduction
Anodic dissolution of alloys have been investigated in view of its application, but a few studies have been found in the basic field. Pickering and his co-workers1-6 investigated on anodic dissolution of Cu-Au and Cu-Zn systems, and they found that Cu was dissolved alone from Cu-Au alloys through the measurement by means of X-ray diffraction analysis. In the case of Cu-Zn alloys, selective dissolution of Zn and simultaneous dissolution of Cu and Zn were observed in the wide potential range. The dissolution of Ag-Au system was reported by Tischer and Gerischer.7 Also, Feller and Uhlig8 studied on the passivation of Cu-Ni alloy, but they did not investigated on the surface condition. As to the experimental techniques for the examination of the surface condition and composition of solid, X-ray diffraction method, X-ray fluorescence analysis, X-ray micro-prove analysis, ellipsometry and electron microscopy have been adopted. Recently, photoelectron spectroscopy (UPS, XPS), Auger electron spectroscopy (AES), low energy electron diffraction method (LEED) and others have been introduced. Among them, AES was adopted to examine alloy surfaces which were of 2 to 4 atomic layers.

In this study, Cu-Ni alloy was firstly anodized, and then this alloy surface was examined by means of AES and the metallic ions dissolved into the bulk solution were analyzed through atomic absorption analysis. Consequently, some corrosion behaviors of Cu-Ni alloys were clarified in the potential ranges of anodic corrosion and passivation.

2. Experimental Technique
Cu-Ni alloys—The composition of Cu-Ni alloys used were 95, 86, 76, 67, 47, 35, 26, 11, and 5.4 atomic percent of nickel respectively. After annealing and rolling, these piece were about 0.3 mm in thickness and then polished with an emery paper No. 2000. The dimension of the test pieces was 1×1 cm for the electrochemical measurement and 1×0.3 cm for the AES.

Electrolytic cell—The electrolytic cell was a beaker type one and 10 cm in height and 5 cm in diameter. The counter electrode was a platinum plate with large apparent surface area and the reference electrode was S.C.E. connected with a Luggin capillary through a salt bridge. The electrolyte was 0.5 N HClO4 whose volume was 80 ml and pure nitrogen gas was bubbled into the electrolyte before electrolysis.

Electrochemical treatment—The potentiostatic electrolysis was made with a potentiostat, model HA-101 by Hokuto Denko, Ltd. and the potential sweep voltammetric measurement was made with the potentiostat and a function generator, model FC-102 by Kowa Electronics, Ltd. The amount of electricity passed was measured by means of a coulomb meter, model CLM-2 A by Hokuto Denko, Ltd. The electrochemical measurement was normally performed at 25°C.

Auger electron spectroscopy—The AES measurement was practiced in the same method reported in previous reports.9,10

Analysis of metallic ions in the electrolyte—Copper and nickel ions in the bulk solution were analysed through atomic absorption analysis.

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3. Results and Discussion

3.1 Anodic Dissolution in Active Region

The passivation phenomena were observed on the samples whose nickel content was over 47 at % Ni. Between the composition of the alloys and their Flade potential \((E_F)\) which was measured by means of potential sweep voltammetry (1 mV/sec), a linear relationship was observed in the range of the alloy composition from 95 to 47% Ni, as reported elsewhere. The relations between the alloy composition, and the Flade potential and the critical current density \((i_c)\) were shown in Fig. 1. The critical current density increased sharply from the pure nickel to the Cu–rich alloys.

To clarify the dissolution behavior of the alloys, copper and nickel ions went into the bulk electrolyte solution were estimated by means of atomic absorption analysis after anodic dissolution of the test electrode (57% Ni) with the passage of anodic current at 125 mV vs. S. C. E. Moreover, the surface composition of the alloy was examined by AES after the dissolution treatment. This examination usually gives information about the composition of 3 or 4 atomic layers in the surface. These data are represented in Table 1. In the initial stages of the anodic dissolution, the ratio of nickel to copper in the bulk electrolyte solution was larger than that in the bulk alloy. The ratio in the solution became equal to that in the bulk alloy after passage of 4.0 coulombs.

On the other hand, surface alloy composition of the electrode became rich in copper as the amount of electricity passed was increased. These findings signify that slightly preferential dissolution of nickel occurred from a very thin layer on the surface. The composition of the bulk electrolyte solution and the surface alloy composition of the electrode after the anodic dissolution with passage of 4.0 coulomb at 125 mV for the various specimens are summarized in Table 2. The amount of ions dissolved corresponded nearly to the composition of the alloys except 26 and 37% Ni specimens, while the surface alloy composition of the electrode became rich in copper after the anodization. Therefore, it was concluded that dissolution rates of copper and nickel from the alloys in the potential range of the active corrosion were almost same, but slightly preferential dissolution of nickel occurs in the very thin layer of the surface, and it results in the enrichment of copper over the surface of the alloys.

3.2 Anodic Dissolution in Passive Region

The corresponded experiments were made on the Cu–Ni alloys in the passive potential region. The findings are shown in Fig. 2 and Table 3. As shown in Fig. 2, logarithm of the passive current density \((i_p)\) of Cu–Ni alloys changed linearly from pure nickel to 47% Ni alloy which was the critical composition of the passivation behavior. This linear relation corresponds to the fact that the atomic ratio of nickel to copper in the passive film

![Fig. 1. Critical current density \((i_c)\) and Flade potential \((E_F)\) against alloy composition.](image-url)
Table 3. Compositions of alloy surface and bulk electrolyte solution after the anodic dissolution at potentials in passive region (350–570 mV vs. S. C. E., 25°C).

<table>
<thead>
<tr>
<th>Sample (% Ni)</th>
<th>Anodizing potential (mV vs. S.C.E.)</th>
<th>Solution (% Ni)</th>
<th>Amount of electricity passed (coul./cm²)</th>
<th>Surface (% Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>350</td>
<td>93</td>
<td>0.74</td>
<td>96</td>
</tr>
<tr>
<td>86</td>
<td>410</td>
<td>83</td>
<td>0.16</td>
<td>87</td>
</tr>
<tr>
<td>67</td>
<td>506</td>
<td>61</td>
<td>0.21</td>
<td>65</td>
</tr>
<tr>
<td>57</td>
<td>570</td>
<td>52</td>
<td>0.20</td>
<td>57</td>
</tr>
</tbody>
</table>

Fig. 2. Relationship between composition of the alloy and passive current density (i_p).

was almost same as that of the bulk alloy (Table 3). However, copper atoms were dissolved more than nickel atoms from alloys as represented in Table 3. The faster dissolution of copper must be caused by faster diffusion of copper atoms than that of nickel atoms through the passivated layer which is consisted of oxides of them.\textsuperscript{11)}

The authors are grateful to professor Toshiro Yamashina of the Faculty of Engineering, Hokkaido University for giving them the alloy samples, and they also wish to thank Mr. Hazime Shimizu of the Electro-technical Laboratory, Tanashi for measurement of the surface alloy composition of Cu–Ni alloy by means of AES.

(Received September 13, 1974)

References