

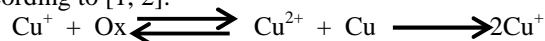
Thin surface films over copper–nickel alloys: Corrosion behavior in neutral and acidic medium in presence of chloride ions

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Copper resists corrosion under the influence of atmosphere and many chemicals. However, it is known that in aggressive media, it is susceptible to corrosion, such as in presence of chloride ions. On the other hand, Cu-Ni alloys are characterized by their corrosion resistance through a protective layer consisting mainly of a thin, strongly adherent inner barrier Cu₂O-layer that is followed by a porous and thick outer Cu(II) hydroxide/oxide-layer which is in contact with the electrolyte. The nickel content in Cu-Ni alloys affects the barrier properties of the surface film, spontaneously formed on Cu-Ni alloys through a segregation of Ni from the alloy into the Cu₂O layer.

In this work, we present the results obtained from a systematic study of the surface of (90-10) Cu-Ni alloy by X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscopy (FE-SEM) electrochemically polarized under different conditions and exposed to neutral and acidic sulfate solutions in presence and absence of chloride ions. The data obtained from the electrochemical dc and ac-measurements were also related to those obtained from monitoring the metallic species content in the electrolyte phase by inductively-coupled plasma (ICP).

Thus, it is important to relate the “extent” of protection of the Cu₂O layer-containing Ni to the nature of electrolytic medium, applied potential and polarization time. The charge transfer process is mainly activation controlled upon the maturity of the inner Cu₂O barrier layer growth. The temperature dependence of the dissolution-precipitation mechanism of both Cu- and Ni-species should be related to “post” equilibrium between the metal-surface species and the counter-ions in the solution phase. The suggested mechanism of dissolution in acid media is based on the formation of Cu(I) ions in the vicinity of the electrode surface where a “first-stage” equilibrium is established between the unstable Cu(I) ions and Cu(II) ions. The amount of Cu(II) ions is related to the extent of Cu(I) oxidation in the aerated electrolyte according to [1, 2]:



This indicates the promotion of self-catalyzed formation of Cu(I)-sulfate (or chloride, in presence of sodium chloride) complex that dissolves in solution. The results we obtained from the electrochemical polarization curves showed that the barrier layer is stabilized by the formation of the Ni-sulfate (or chloride) upon Ni-diffusion from the alloy towards the surface. XPS data confirmed this finding by comparing the amount of Cu(II) (originated by the stabilized Cu(II)-oxide, sulfate or chloride) and Ni(II) (originated from the formation of Ni(II)-oxide, sulfate or chloride). Table (1) shows the relative atomic percentages of Cu(II)-species and Ni(II)-species on the surface of the Cu-Ni alloy from the XPS experiments when the alloy was subjected to a polarization applied potential of 0.150 mV (vs. Ag/AgCl) for 30s, 30 minutes, and 60 minutes, in 0.1 M H₂SO₄, 0.1 M Na₂SO₄ and 3.58% NaCl solutions, respectively.

The relative atomic percentages of Cu and Ni on a “clean” unexposed surface are 6.68 and 0.27, respectively. Thus, in H₂SO₄ the amount of Cu increases substantially during the first relatively short time interval of the polarization with a fast kinetics for the dissolution process. The depleted Ni amount from the bulk of the alloy compensates further by an apparent slow step leading to a substitution for the Cu in the lattice of the surface layer. This allows a relatively more stabilized layer that is relatively compensating the amount of Cu. In chloride, we observed that both metals in the alloy deplete with Ni rate relatively higher compared to Cu. This result confirmed that Ni was sacrificed in the pitting process for Cu that showed almost a stable surface concentration. Neutral media such as Na₂SO₄ showed moderate to slow kinetics for the dissolution process for both Cu and Ni. These findings were confirmed by the data obtained from ICP-measurements in solutions after exposure.

The electronic/ionic nature of the surface films were discussed in reference to the data obtained from the electrochemical impedance spectroscopy (EIS) tests.

	(0.1 M) H ₂ SO ₄			(0.1 M) Na ₂ SO ₄			(0.58) M NaCl		
	30 s	30 min	60 min	30 s	30 min	60 min	30 s	30 min	60 min
Cu(II) %	10.66	4.67	9.32	-	-	4.75	22.41	19.95	18.96
Ni(II) %	0.26	2.03	1.85	-	-	0.67	2.43	1.54	0.92

Table 1. XPS Cu(II)/Ni(II) % in oxide layer after polarization with E = 0.150 V (vs. Ag/AgCl) in different electrolytes.

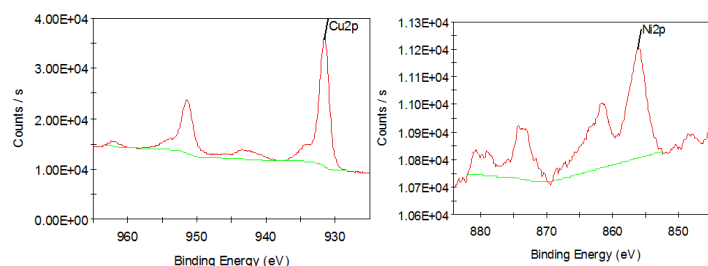


Figure 1. XPS of Cu(II) and Ni(II) spectra of Cu-Ni (90-10) alloy after exposure to 0.58 M NaCl under E_{app} = 0150 V vs. Ag/AgCl for 60 minutes.

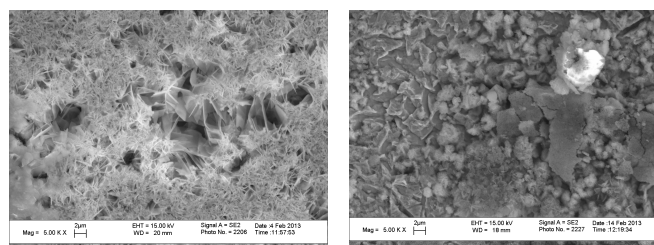


Figure 2. FE-SEM Cu-Ni (90-10) alloy after exposure to 0.58 M NaCl, 0.1 M H₂SO₄, 0.1 M Na₂SO₄, and 0.1 M H₂SO₄ + 0.58 M NaCl, under E_{app} = 0150 V vs. Ag/AgCl for 60 minutes

[1] M. Metikoš-Huković, I. R. Babić, I. Škugor, Z. Grubač, Corrosion Science 53 (2011) 347 – 352.

[2] J. M. Maciel, R. F. V. Villamil Jaimes, P. Corio, J. C. Rubim, P. L. Volpe, A. A. Neto, S. M. Leite Agostinho, Corrosion Science 50 (2008) 879–886.