OPTICAL STUDY OF LAYER OXIDES FORMED AFTER A LOW PRESSURE RF OXYGEN PLASMA TREATMENT OF A COPPER NICKEL ALLOY

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Abstract:

The surface of 90Cu10Ni alloy exposed to a low pressure inductively coupled oxygen plasma gives rise to an oxide layer. The oxides formed at the surface samples were identified by FTIR spectroscopy and X-ray diffraction techniques. The oxygen plasma treatment confirms the formation of copper and nickel oxides (i.e., Cu₂O, CuO and NiO). The thickness of the oxides layer depends on the time of exposure to the plasma for given fixed working conditions.

1. Introduction

The interaction of metals and alloys with oxidizing agents induce the growth of surface films oxidation products which have important technological consequences. The formation of thin oxide films on electrical and electronic contacts, which result from the occurrence of an arc, may influence the electrical and magnetic properties of the components [1].

This work is developed in the scope of aging studies in order to identify the oxidation products, to understand the nature of the different oxidation processes, and to optimize them in view of limiting the relevant negative effects. The oxidizing character of the species created in a low pressure oxygen RF plasma was investigated through previous studies: for example, treatments of copper, zinc and brass foils lead to the formation of several oxides which were identified by means of optical and electrochemical methods [2-4].

The various processes induced in oxygen plasma (e.g., ionization, dissociation by electron impact and attachment phenomena) induce the formation of activated species such excited molecules, oxygen atoms, ozone, molecular ions, which may behave as reactive species. Analysis of low-pressure oxygen plasma by optical emission spectroscopy in the range 600-900 nm shows only the presence of atomic oxygen as a reactive species [5]. The dissociation degree is around 10% [5].

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This paper is devoted to the identification of the oxide thin film formed on 90Cu10Ni alloy foils when exposed to an oxygen plasma gas produced by a classical RF inductively coupled plasma generator under reduced pressure (p = 2300 Pa). Characterization of the oxides is carried out by non-destructive methods, such as low angle X-ray diffraction, to determine the crystalline phases, and infrared reflectance spectroscopy.

2. Experimental details

The treatment reactor is a classical low-pressure inductively coupled plasma reactor. It was previously used for oxidation studies of metals and alloys [2-5]. The oxygen plasma is produced by means of a RF generator (13.56 MHz) which was inductively coupled to the reactor by a 7-turn coil. This work is performed at 900 and 1100 W. Vacuum (2300 Pa) is sustained by a primary pump. Oxygen was injected into the reactor at a fixed flow rate (0.25 N.L. min⁻¹) in standard conditions. The sample was positioned normally to the gas flow on a stainless steel quenching head at a distance d from the first high voltage (HV) coil.

The 90Cu10Ni (99.7 %) alloy and nickel (99.98 %) foils used in this study were purchased from Goodfellow. All the samples (1 cm² surface area) were mechanically polished with different grinding papers (400, 800, 1000 and 1200 grade) and finally with a 6 μm grade diamond lap. They were rinsed in absolute ethanol and dried immediately with nitrogen before being exposed to the oxygen plasma.

The specular reflectance infrared spectra were recorded with a Nicolet FTIR 710 (analyzed range: 225 to 5000 cm⁻¹, incidence angle: 80°). The X-ray diffraction patterns were recorded at near grazing incidence (θ ~ 6°) with a cobalt anti-cathode (λₐ = 0.1789 nm). The thickness of the oxide layers was determined from interferometry measurements.

3. Results and discussions

3. 1. Oxidation of copper by oxygen plasma [2, 5]

Plasma oxidation mechanism of pure copper has been studied. The oxygen plasma treatment begins with the growth of a precursor oxide Cu₂O (x>4) which has the same crystallographic structure as Cu₂O but presents different UV spectra. Cu₂O is identified by two bands around 650 cm⁻¹ (LO mode) and 610 cm⁻¹ (TO mode). The IR reflectance spectra of the CuO shows a many bands around 605, 530, 470 cm⁻¹ (TO mode) and 620, 583, 550 and 510 cm⁻¹ (LO mode).

3. 2. Oxidation of nickel foils by oxygen plasma

A nickel sample exposed to the oxygen plasma for 15 min in fixed working conditions (P = 1100 W, p = 2300 Pa, d = 5 cm) was examined by FTIR spectroscopy. The spectrum (Fig. 1) shows two bands near 610 cm⁻¹ and 385 cm⁻¹, which are respectively attributed to the longitudinal and transverse optical vibrations of NiO [6]. The presence of NiO oxide was confirmed by X-ray diffraction method. The spectrum presents three peaks at θ =21.79°, θ =25.37° and θ =37.31° which correspond respectively to NiO [111], NiO [200] and NiO [220].

In this section the influence of the working parameters on the oxidation kinetics is considered with particular emphasis on the exposure time (t). The thickness of the oxide films formed on the treated metal foils, was measured by means of interferometry method for exposure times between 15 and 120 min (Fig. 2). The layer thickness ε of the NiO oxide layer increases with the treatment time for given working conditions.

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Fig. 1: IR reflectance spectra of Ni foil oxidized in oxygen plasma (P = 1100 W, \( p = 2300 \text{ Pa} \), \( d = 5 \text{ cm} \)) at 80° off normal: (a): 15 min; (b): 30 min; (c): 60 min; (d): 120 min

Fig. 2: Variation of the thickness of NiO oxide layer for a given treatment time.
3.3. Oxidation of 90Cu10Ni alloy by oxygen plasma

The basic key parameters to vary the plasma treatment conditions are the exposure time \( t \), the injected electric power \( P \) and the distance between the sample and the first high voltage (HV) coil. For given distance \( d = 10 \text{ cm} \), a pressure \( p = 2300 \text{ Pa} \) and an electric power \( P = 900 \text{ W} \), the oxidation kinetic of 90Cu10Ni alloy samples depends only on the exposure time.

![Graph showing IR reflectance spectra of 90Cu10Ni oxidized in oxygen plasma](image)

**Fig. 3:** IR reflectance spectra of 90Cu10Ni oxidized in oxygen plasma \((P = 900 \text{ W}, p = 2300 \text{ Pa}, d = 10 \text{ cm})\) at 80° off normal: (a): 15 min; (b): 30 min; (c): 60 min

The IR reflectance spectra (Fig. 3) of samples treated for at least 10 min were recorded under an incidence angle of 80°. They present many bands attributed to the copper and nickel oxides. The IR spectrum of the sample treated during 15 minutes shows three bands at 650, 600 and 580 \text{ cm}^{-1} \) which are respectively attributed to Cu$_2$O, NiO and CuO oxides. The intensity of the Cu$_2$O band decreases and of the NiO and CuO increases with the treatment time. Cu$_2$O oxide was oxidized to CuO. All the IR and X-ray diffraction analysis are gathered in table 1.

<table>
<thead>
<tr>
<th>Analysis method</th>
<th>15</th>
<th>Treatment time (min)</th>
<th>30</th>
<th>60</th>
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</thead>
<tbody>
<tr>
<td>FTIR spectroscopy (s)</td>
<td>650 cm$^{-1}$: Cu$_2$O (s)</td>
<td>Cu$_2$O (w)</td>
<td>--</td>
<td>NiO</td>
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<tr>
<td></td>
<td>600 cm$^{-1}$: NiO (w)</td>
<td>NiO (m)</td>
<td>NiO</td>
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<tr>
<td>X-ray diffraction</td>
<td>580 cm$^{-1}$: CuO (w)</td>
<td>CuO (m)</td>
<td>CuO (s)</td>
<td>NiO, CuO</td>
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<tr>
<td></td>
<td>Cu$_2$O, CuO, NiO</td>
<td>NiO, CuO</td>
<td>NiO, CuO</td>
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</tbody>
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(s): strong, (m): medium, (w): weak
The thickness of the oxide film was measured by interferometry method. The film thickness increases as a function of the exposure time for given treatment conditions (Fig. 4). Also, it depends on the distance d between the sample and the first high voltage (HV) coil and decreases as d increases, for fixed treatment time. For example, an oxide layer 0.45 μm thick results from a treatment of 15 minutes at a distance of 10 cm, or 40 minutes at 20 cm. Both effects are interpreted in terms of plasma efficiency, since the smaller is d and the longer is the time exposure, the higher is the plasma efficiency.

Fig. 4: Variation of the thickness of the oxide layer formed at the 90Cu10Ni surface for a given treatment time.

4. Conclusions

The low-pressure RF oxygen plasma can be used as an efficient tool to oxidize metallic surfaces and in particular 90Cu10Ni foils. The association of FTIR spectroscopy and X-ray diffraction techniques allows the identification of the various oxides formed on the surface of 90Cu10Ni alloy when it is exposed to an oxygen plasma with excellent agreement to pertinent literature [6] relevant to the thermal treatment of alloy samples. The oxide film thickness depends strongly on the working conditions of the oxygen plasma. The nature of the metal oxides formed depends on the treatment time. For short treatments (i.e., t<30 min), we obtained a mixture of Cu$_2$O, CuO and NiO oxides where Cu$_2$O is the major species formed. For longer exposure time (i.e., t >30 min), Cu$_2$O is oxidized to CuO, which becomes the major product with NiO.

References