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Preparation and characterization of thin oxides films formed at a brass surface oxidized by plasma treatment

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The surface of a 90Cu10Zn alloy exposed to a low pressure inductively coupled oxygen plasma gives rise to an oxide layer, the composition of which is determined by FTIR spectroscopy and X-ray diffraction techniques. The thickness of the oxide layer depends on the time of exposure to the plasma and on the distance between the sample and the first high voltage (HV) coil for given primary treatment parameters and on the preparation technique of the samples.

1. Introduction

The interaction of metals and alloys with oxidising agents induce the growth of surface films of oxidation products and 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]. In this study we report on the identification of the oxidation products of brass and its oxidation kinetics by an oxygen plasma.

The oxidising character of the species created in a low pressure oxygen rf plasma was investigated through previous studies: for example, treatments of copper and zinc foils lead to the formation of several oxides which were identified by means of optical and electrochemical methods [2, 3].

In a plasma, a number of processes take place (e.g., dissociation by electron impact, ionisation, molecular excitation). In the case of an oxygen plasma, these induce the formation of activated species [4–8] such as excited molecules ($O_2^1\Delta_g$ and $O_2^1\Sigma_g^+$), atomic oxygen (O^1D and O^3P), ozone O_3, molecular ions (O_2^+, O_2^-) and the relevant atomic ions (O^+, O^-) which may behave as reactive species. In addition, spectroscopy studies of electric discharges in oxygen show that the main path is the molecular dissociation from electronic impact of levels $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ [4]. The low pressure oxygen plasma analysis by optical emission spectroscopy in the 600–900 nm range shows only the presence of atomic oxygen as a reactive species [8–10]. The dissociation degree is around 10% [2]. Under our pressure and excitation conditions, no other oxygen species was detected within the spectral range investigated [2].

This paper is devoted to the identification of the oxides formed on 90Cu10Zn brass foils when exposed to an oxygen plasma gas produced by a classical 13.56 MHz inductively coupled plasma generator under reduced pressure (200 Pa). The excited particles formed in the oxygen plasma react at the alloy surface and lead to the formation of a thin oxide film. The characterisation of the oxides developed is carried out by non destructive methods such as the low angle X-ray diffraction for the determination of crystalline phases and the infrared reflectance spectroscopy.

2. Experimental

The treatment reactor is the classical low pressure inductively coupled plasma reactor previously used for the oxidation studies of copper and zinc [2, 3]. The oxygen plasma is produced by means of an rf (13.56 MHz) generator which is inductively coupled to a quartz tube reactor (10 cm in diameter, 30 cm in length). This work is performed at 800 W, a value of the input power selected in the available range 100–2200 W. Vacuum (200 Pa) is sustained by a primary pump. The oxygen gas is injected in the reactor at a fixed flow rate (i.e., 0.25 L·min^{-1} in standard conditions).

The metal samples are positioned on the holder normally to the gas flow at a distance d from the first high voltage (HV) coil. This holder is fitted with a water-cooled quenching head, so that the sample temperature stabilises in less than 10 min and never exceeds 50 °C. The sample temperature is measured by means of a K type chromel-alumel thermocouple.

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Brass disks (90Cu10Zn, 99.97%), with 1.1 cm^2 surface area, were cut out from 0.5 mm thick foils purchased from Trefimetaux. The samples were chemically cleaned in 15% H_2SO_4 for 10 s, washed in absolute ethanol and nitrogen dried before being exposed to the oxygen plasma.

The specular IR spectra were recorded on a Nicolet FTIR 710 (range analysed, 5000–225 cm^{-1}; angle of incidence, 80° : RS 80). The X-ray diffraction patterns were recorded at a near grazing incidence angle ($\alpha \cong 6^\circ$) with a cobalt anticathode ($\lambda_{k\alpha 1} = 0.1789$ nm).

The thickness of the oxide layers was determined from interferometry measurements.

3. Results and discussions

The plasma oxidation mechanism [2] of pure copper begins with the growth of a precursor oxide Cu_xO ($x > 4$) which has the same crystallographic structure as Cu_2O but presents different UV spectra [11]. Cu_2O is identified by two bands around 650 cm^{-1} (LO mode) and 610 cm^{-1} (TO mode) [2, 12]. The IR reflectance spectra of the CuO/Cu system consist of many bands around 605, 530, 470 cm^{-1} (TO mode) and 620, 583, 550, 510 cm^{-1} (LO mode) [2, 12]. The treatment of zinc foils by an oxygen plasma has also been reported [9]. The FTIR spectrum of ZnO shows a band between 575 and 587 cm^{-1}, and two others at 410 and 370 cm^{-1} which are respectively attributed to the longitudinal (LO) and transverse (TO) optical vibrations [3].

In addition, the thermal oxidation kinetics of the CuZn alloys have been studied [13] over the whole composition range to identify the oxides formed at high temperature ($T = 873$ K): ZnO, Cu_2O and CuO were found in the surface layer.

3.1. Oxidation of 90Cu10Zn alloy by oxygen plasma

A (90Cu10Zn) sample exposed to the oxygen plasma for 6 min in fixed working conditions ($P = 800$ W, $p = 200$ Pa, $d = 20$ cm) was examined by FTIR spectroscopy. The spectrum (Fig. 1) shows an intense band at 645 cm^{-1} which is attributed to the longitudinal optical vibration (LO) of Cu_2O, and two minor bands at 605 and 575 cm^{-1} respectively assigned to CuO and ZnO. The occurrence of the three oxides is confirmed by X-ray diffraction analysis.

This shows that the FTIR spectroscopy and X-ray diffraction are suitable techniques to identify the different oxides formed by the plasma treatment of 90Cu10Zn alloy foils.

3.2. Influence of the working conditions

In this section the influence of the working parameters on the oxidation kinetics is examined with particular focus on the exposure time t and distance d between the brass sample and first HV coil. Another standard parameter used to characterise the plasma, is the energy density P/N, where P refers to the rf power and N to the number of gas moles present in the plasma volume [2, 3]. For given distance (e.g., $d = 5$ cm) and rf power (e. g., $P = 800$ W), that is for $P/N = 2.03\,10^7$ W·mol^{-1}, the oxidation kinetics and the nature of the oxides formed depend only on the exposure time.

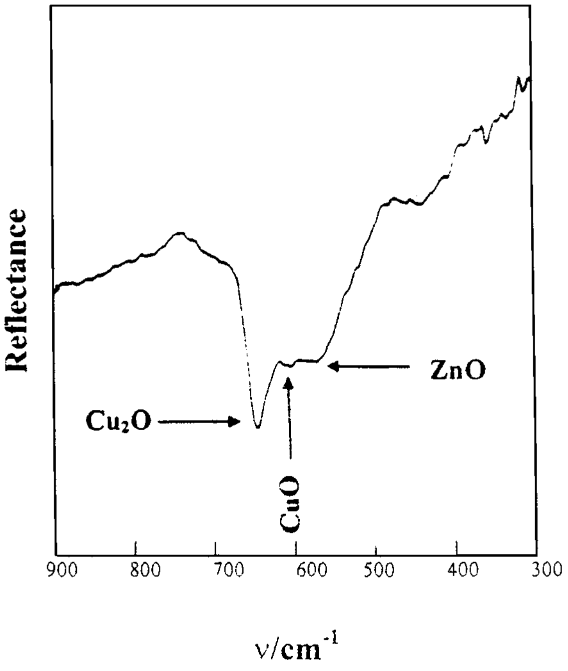

Figure 1 Experimental infrared reflectance spectrum (80° off-normal) of a 90Cu10Zn sample oxidized in oxygen plasma for 6 min ($P = 800$ W, $p = 200$ Pa, $d = 20$ cm).

The IR reflectance spectra (Fig. 2) of samples treated for at least 3 min were recorded under an incidence angle of 80°. They present an intense band at 645 cm^{-1} which characterises the longitudinal optical vibrations (LO) of Cu_2O. The band intensity decreases as t increases, and, correlatively the thickness of the oxide layer increases (Fig. 3). Layers thicker than 0.1 μm result from treatment times longer than 6 min in the given conditions: a new intense band appears at 590 cm^{-1} and is attributed to the longitudinal optical vibrations (LO) of ZnO. The copper oxide CuO is identified by a series of low intensity bands at 605 (shoulder), 475 and 323 cm^{-1} (TO) present on the spectra of samples treated for at least 6 min.

X-ray analysis of samples exposed to the plasma for at least 6 min confirm the spectroscopically provided results. Fig. 4 shows several lines, and their number depends on the treatment time. Only the Cu_2O lines are detected on the spectra of 6 min treated samples (Fig. 4a). The spectrum of the 15 min treated sample (Fig. 4b) is much richer and shows that Cu_2O ([1 1 0], [1 1 1]), CuO ([1 1 1], [2 0 0]) and ZnO ([1 0 0], [0 0 2], [1 0 1]) are present in the layer.

Both the IR reflectance and the X ray analysis spectra show that the signals relevant to ZnO are of limited intensity compared to those of the copper oxides. Such a result is unexpected as the oxidation potentials of Cu and Zn favour the oxidation of Zn. In addition, it shows that the oxidation of Zn by copper oxide

$$\text{Zn (in alloy)} + Cu_2O = 2Cu + ZnO$$

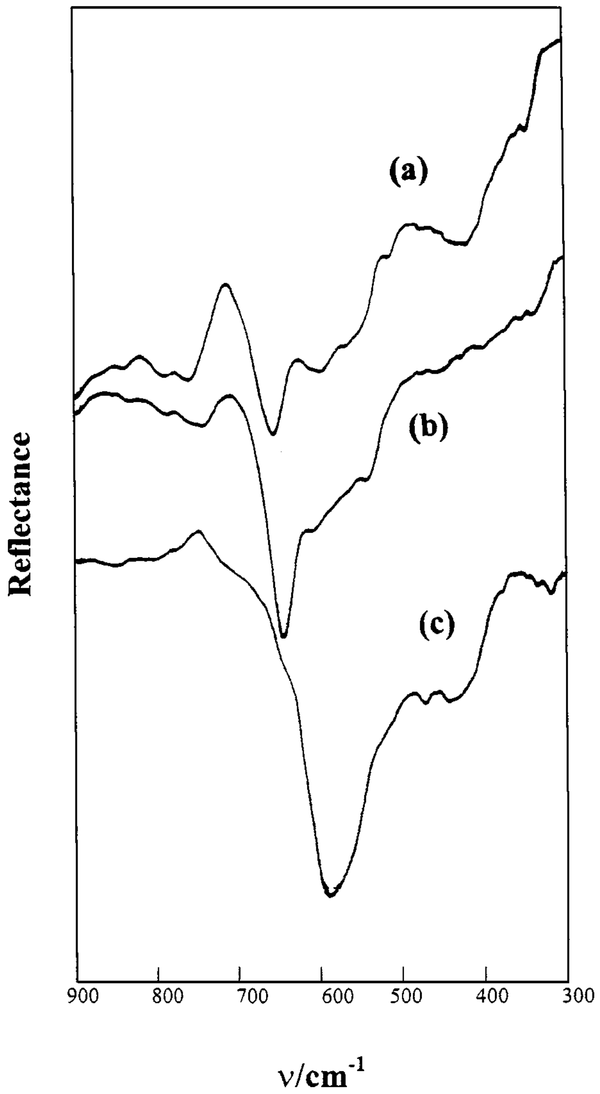

Figure 2 Experimental infrared reflectance spectra (80° off-normal) of 90Cu10Zn samples exposed to the oxygen plasma ($P = 800$ W, $p = 200$ Pa, $d = 5$ cm) for (a) 3 min, (b) 6 min, (c) 15 min.

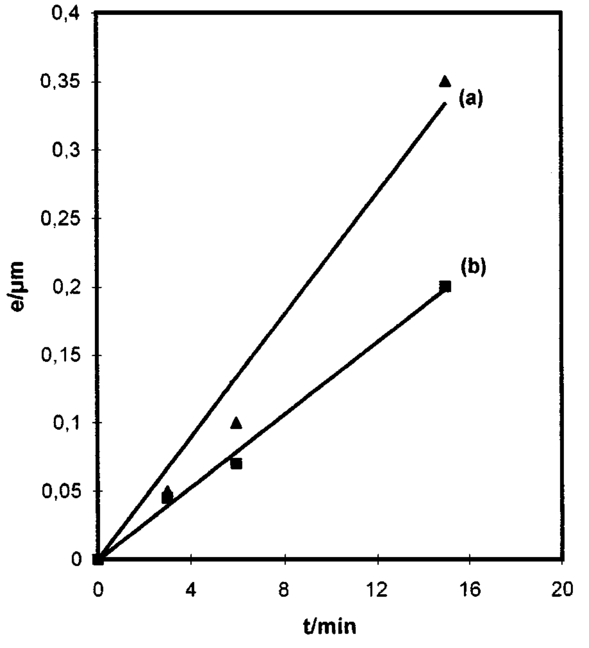

Figure 3 Film thickness $e(\mu$m) of the oxide layer versus the treatment time ($P = 800$ W, $p = 200$ Pa). for various distances (a) $d = 5$ cm, (b) $d = 20$ cm.

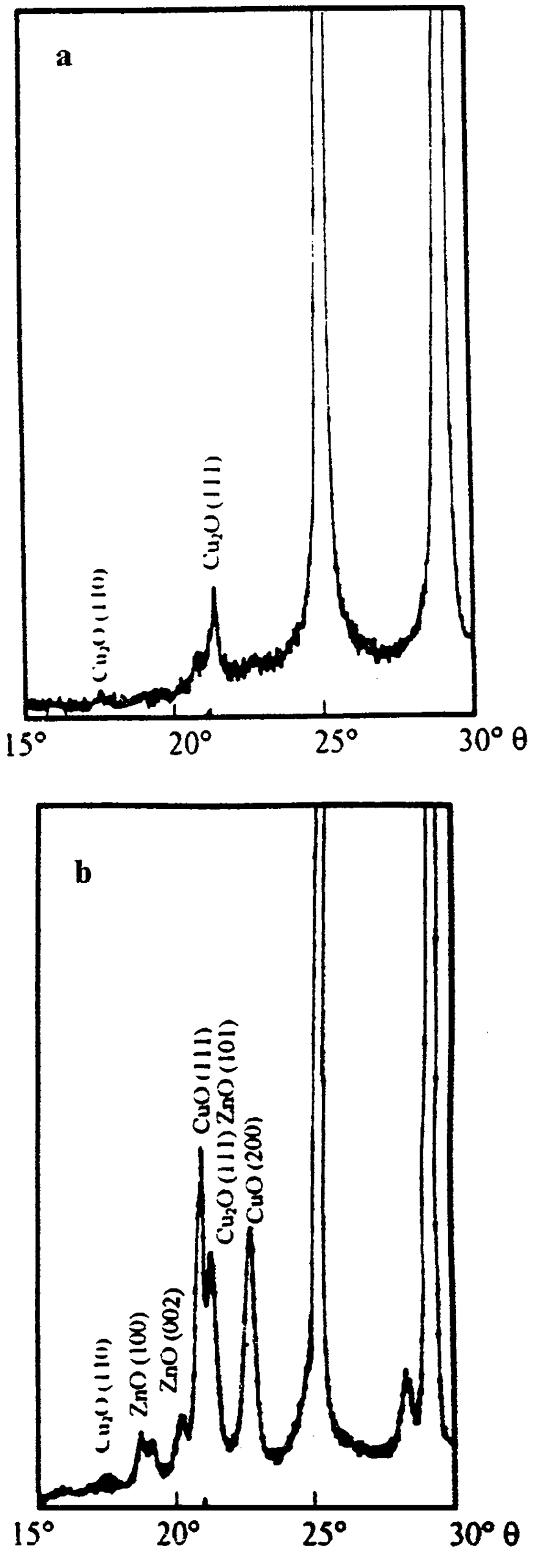

Figure 4 Experimental XRD spectra of 90Cu10Zn samples oxidized in oxygen plasma ($P = 800$ W, $p = 200$ Pa, $d = 5$ cm) for (a) 6 min, (b) 15 min.

reported [14] for long conventional thermal treatments does not take place for a plasma treatment. The feature of an apparent preferential oxidation of Cu compared to Zn may be related to the technique used to prepare the sample surfaces. Sulphuric acid dissolves more easily Zn than Cu, so that the surface is enriched with copper.

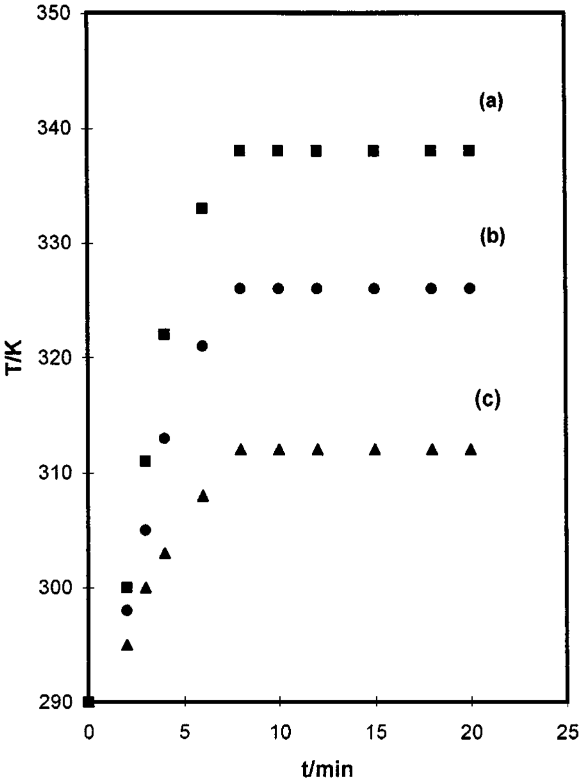

Figure 5 Variation of the sample temperature for various exposure time ($P = 800$ W, $p = 200$ Pa). (a) $d = 5$ cm, (b) $d = 10$ cm, (c) $d = 20$ cm.

Arguments supporting this assumption are provided by a comparison of these results with the spectral analysis of plasma treated samples with grounded surfaces which shows an increased contribution of the Zn bands with respect to the Cu bands. Such a feature is confirmed by the Zn/Cu ratio from XPS analysis performed of thermally oxidised samples [13].

Fig. 3 shows that the thickness e of the oxide layer varies with the exposure time to the plasma. e is a linear increasing function of t for given working conditions. The thickness also depends on the distance d and decreases with d for given treatments times. For example, a 0.15 μm thick oxide layer results from either a treatment time of $\cong$7 min at a distance $d = 5$ cm or $\cong$11 min at $d = 20$ cm.

Since the experiments are achieved with a constant flow of the input gas, the results may be related to the living time of the activated gaseous species which takes the values 0.20 and 0.69 s respectively for $d = 5$ and 20 cm.

The mean growing rate de/dt also depends on the plasma density P/N, since this parameter involves the reactor length d and varies in the same direction as P/N.

The question of the temperature has not been considered in the above discussion. The influence of the temperature on the oxidation of brass was considered [14] for the thermal oxidation of the alloys, but no information is available in the case of a non-equilibrium plasma treatment. Fig. 5 illustrates the variations of the sample temperature T with the exposure time for various positions of the sample. T increases when the distance decreases, so that the smaller is the distance d, the higher is the energy transferred from the plasma to the sample. Hence the temperature effect on the growing rate of the oxide layer is also improved by shortening the distance between the sample and the 1st coil while the nature of the oxides formed is obviously unaffected by the temperature variations.

4. Conclusions

The low-pressure rf oxygen plasma can be used as an efficient tool to oxidise metallic surfaces and in particular brass foils. The association of FTIR spectroscopy and X-ray diffraction techniques allows the identification of the various oxides formed on the surface of a 90Cu10Zn alloy foil when it is exposed to an oxygen plasma with excellent agreement to pertinent literature [13] relevant to the thermal treatment of brass samples. The oxide film thickness depends strongly on the working conditions of the plasma.

The nature of the metal oxides formed by the plasma treatment are the same as those resulting from a low thermal ($T < 673$ K) treatment, except that the precursor oxide Cu$_x$O was not identified in the plasma process. For short treatments (i.e., for $t < 6$ min), Cu$_2$O is the major species formed. For longer exposure time ($t = 15$ min), Cu$_2$O oxidises to CuO which becomes the major product. Severe oxygen plasma treatments lead to the formation of CuO which is the only thermodynamically stable phase, as illustrated by long exposures to the oxygen reactive species. The zinc oxide cannot be largely developed because its formation depends on the initial surface preparation. Indeed, the sulphuric acid cleaning leads to a copper enriched surface resulting from a preferential attack of zinc.

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