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Ni-free alloys as final coatings: white bronze coatings on copper

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The problem of allergies arising from the presence of Ni in alloys used for decorative objects coming into contact with the skin has become increasingly important over the past five to ten years. As an alternative, "white bronze" has been shown to be an effective solution even from an aesthetic point of view. This work investigates the corrosion behaviour of copper treated with two different techniques: electroplating and ion beam mixing. To this end copper has been electroplated with a thin (0.3 and 0.04 μm) coating of white bronze (Cu 66, Sn 23, Zn 10, Pb 1 wt%), the high brightness (as a noble metal) and corrosion resistance of which allow it to be used in decorative industries for jewellery, watches, *etc.* The bronze coating was ion beam mixed through bombardment with an argon ion beam. The corrosion behaviour of the bronze coatings was compared with that of pure copper through two method of analysis: a) electrochemical analysis, aimed at measuring the corrosion rate in a alkaline solution (pH = 12.4); and b) surface analysis intended to verify the thickness, homogeneity and composition of coatings through Rutherford backscattering spectroscopy (RBS) and scanning electron microscopy (SEM). The implanted bronze electroplated copper showed the best corrosion behaviour. Electrochemical tests showed low corrosion rates and a corrosion mechanism similar to that of more noble coatings.

1. Introduction

Nickel is known to be the most frequent cause of contact allergy in Europe, where about 15–20% of the female population and 2–5% of males are afflicted by these allergies.[1,2] The adsorption of Ni ions released from certain Ni-containing materials coming into direct and prolonged contact with the skin generally causes irreversible sensitisation: further exposure to Ni salts results in allergies such as eczemas, dermatitis, *etc.*[3,4]

These Ni effects make it highly unlikely that coatings containing high percentages of Ni ($>$20 wt%) will continue to be used as a bright decorative substrates in objects coming into direct contact with the skin. As a result, the galvanic decorative industries producing such objects—as well as those making jewellery, watches, *etc.*—will have to substitute this metal in the final substrate. Among the various coatings alternative to Ni, certain Ni-free alloys (such as Cu–Sn and Cu–Sn–Zn bronzes) are known for their aesthetic effects and good corrosion resistance, especially when the layer employed is micrometers thick.[5,6]

This work aims to investigate the corrosion behaviour of copper treated with two different techniques: electroplating and ion beam mixing.

It is well known that the process known as "ion beam mixing" consists of atomic intermixing and that it can occur at the interface separating two different materials. A major driving force in the development of the ion beam mixing process is its ability to produce ion-modified materials with higher solute concentrations at lower irradiation doses.[7] Further, it can be observed that ion implantation (I.I.) of chemically active species on the substrate can be used as a surface alloying tool because the implanted elements exhibit their normal chemical and electrochemical properties when the surface alloy is exposed to the corrosive environment. For example, the I.I. of Cr, Ti or Ta on copper has significant beneficial effects on the passivation behaviour of Cu in deaerated alkaline sulfate solutions.[8] In contrast, the I.I. of Ar^+, considered an inert ion, does not seem to produce any significant effects on the passivation behaviour of Cu. In this work the principal aim of the Ar^+ I.I. was to obtain a "back-mixing" of the coating with the substrate, and to study the effect of this treatment on the corrosive performance of the final coating. To this end, copper has been electroplated with a coating of white bronze, the predominant characteristic of which is a brilliance (as a noble metal) that allows it to be used in the decorative industries. Its other important characteristics include 1) the high passivity of the layer, due to the high content of tin (23 wt%),[9,10] which should allow for good corrosion resistance, and 2) the absence of Ni which is an allergy-causing factor.

2. Experimental

The corrosion behaviour of bronze coatings was compared to that of pure copper, through the use of a) the usual electrochemical techniques, that allow one to measure the corrosion rates and study the corrosion mechanism in a alkaline solution (pH = 12.4), and b) surface analysis such as Rutherford backscattering spectroscopy (RBS) and scanning electron microscopy (SEM), to verify the thickness, homogeneity and composition of coatings.

2.1. Copper specimens

In all experimental tests the plates were cut from the same 0.5 mm thick commercial Cu (99.5% purity) sheet to a surface area of 10.5 cm × 10.5 cm.

The preliminary tests of specimens cut from the commercial copper plates (disks whose diameter was 11.3 mm) revealed the non-homogeneity of the material: in fact their use resulted in a

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great dispersion of the electrochemical data in the potential *vs.* time and potentiodynamic tests. For these reasons a coating (20 μm thick) of Cu was electro-deposited over the commercial plate before the bronze deposition.

The coppered Cu plate was then electro-coated with the white bronze alloy layers. The specimens were painted with a strippable varnish to preserve them from wear during the cutting and handling. Discs of 11.3 mm of diameter were then cut from the plates and used in electrochemical and other tests.

2.2. Galvanic deposition

2.2.1. Pre-treatment. Before galvanic treatments, all plates of commercial Cu were degreased in an ultrasonic bath at 60 °C (30–120 s). After being rinsed in deionized water, the plates were electrolytically etched to remove the oxides, using a solution containing K_2CO_3, NaOH, silicates, phosphates, ionic and non-ionic biodegradable surfactants (operating conditions: $T = 30$–$60\,^\circ C$; immersion time = 30–120 s; current density = 1–4 A dm^{-2}, voltage = 3–5 V). They were then rinsed again in deionized water and activated in acid salts to remove every basic residual product of the electrolytic etching from the metal surface.

2.2.2. Acid coppering. As previously mentioned, an electrolytic copper coating (20 μm thick) was deposited to eliminate surface irregularities and obtain a good substrate before alloy deposition. The galvanic bath was composed of inorganic salts and some additives (see Table 1). The operating conditions were as follows: temperature = 24–26 °C; cathodic current density = 1–4 A dm^{-2}; voltage = 1–4 V; deposition rate = 0.7 μm min^{-1} at 3 A dm^{-2}; air flow rate = 12–20 $m^3\,h^{-1}$ per meter of cathodic bar; anodes = copper/phosphorus 0.03–0.06%; anodic sacks = Meraklon; filtration = continuous 2–3 volumes per hour; filters = polypropylene 5 μm; efficiency = *ca.* 100%.

2.2.3. White bronze electroplating. White bronze alloy (theoretical: Cu 55, Sn 35, Zn 10 wt%, Pb traces) electrodeposition was performed in a bath, the composition of which is reported in Table 2. The bath also contains brighteners, biodegradable surfactants and conductive salts.

The operating conditions were as follows: temperature = 40 °C; voltage = 2 V; cathodic agitation = 2–5 m s^{-1}; filtration = continuous, PP filters 1 or 5 μm; anodes = graphite; deposition rate = 1 μm every 5.5 min; current density = 0.2 A dm^{-2}; bath density = 1.45 kg l^{-1}; deposit density = 8.0 g cm^{-3}.

The homogeneity and composition of the alloys obtained in these experimental conditions were tested by scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS) (see below) and chemical analyses. Two kinds of samples of different thickness were prepared (0.3 and 0.04 μm). The effective percentage of the elements in the alloy, tested by atomic absorption spectroscopy (A.A.), gave Cu: 66; Sn: 23; Zn: 10; Pb: 1 wt%.

2.3. Electrochemical tests

All the electrochemical tests were carried out in alkaline medium [borate/boric acid led to pH = 12.4 with NaOH (10%)], a test solution commonly used in the literature to evaluate the corrosion behaviour of copper and other metallic materials.[11,12] All solutions were obtained using "pure for analysis" chemicals. The working electrode—a reference saturated calomel electrode (sce, to which all the potentials reported hereafter refer), inside a Haber–Luggin's capillary probe—and two platinum counter electrodes were placed inside a Pyrex glass ASTM cell.

Table 1 Composition of bath for acid coppering

Copper sulfate pentahydrate/g l^{-1}	175–210
Sulfuric acid ($\rho = 1.84$ g ml^{-1})/$cm^3\,l^{-1}$	32–38
Chlorides/mg l^{-1}	60–110
Brighteners/$cm^3\,l^{-1}$	0.5
Levelling/$cm^3\,l^{-1}$	0.5
Anti-dot compounds/$cm^3\,l^{-1}$	10

Table 2 Composition of the bath for depositing bronze alloys

Cu (as metal)/g l^{-1}	8
Sn (as metal)/g l^{-1}	16
Zn (as metal)/g l^{-1}	1.5
Pb/g l^{-1}	0.045
KOH/g l^{-1}	10
KCN/g l^{-1}	25
pH (ammoniac)	7.5–8.5
Density/kg l^{-1}	0.97

After free corrosion potential (E_{corr}) *vs.* time tests (30 min), potentiodynamic tests were carried out ("Tafel curves") in the range greater than ($E_{corr} \pm 250$ mV) to obtain further electrochemical data.[12] From these curves it is possible to obtain E_{corr}, the free corrosion potential; i_L, the limiting current density of the O_2 diffusion; i_{corr}, the corrosion current density (directly correlated to the corrosion rate, R_{corr}); and i_p, the passivation current density.

The specimens cut from the treated plates (11.3 mm diameter) were used as working electrodes inside a Teflon holder that left a 0.50 cm^2 surface exposed. Anodic and cathodic polarisation curves were carried out at 25 °C. The temperature was adjusted to $\pm 0.1\,^\circ C$ of the required value using a thermostatically controlled water bath. The corrosion cell was always filled with a known amount (700 ml) of solution, aerated by prolonged bubbling with pure air (12 h).

Potentiodynamic tests were carried out according to the following procedure. The specimen was immersed for about 30 min; when the E_{corr} was reached, the scan was started from around E_{corr} until a potential around $E = -1000$ mV. The potential scanning rate was 500 μV s^{-1}. The sample in the Teflon holder was then taken out, substituted with a homologous one, washed and degreased with methanol, and then re-immersed inside the electrochemical cell in the same solution. After E_{corr} was reached (30 min), the anodic scan was started from E_{corr} until a potential around $E = +600$ mV. Each test was repeated at least three times on different specimens in different solutions at the same concentration.

3. Results and discussion

3.1. Ion implantation

The ion implantation (I.I.) technique has been identified as a way of improving the wear and corrosion resistance of a metal. It is well known that I.I. produces a modified surface by embedding appropriate atoms by way of a beam of ionised particles.[13] At the same time, it is possible to "back-mix" the metallic material, especially if the implanted ions are inert from the point of view of the passivation behaviour of the metallic substrate.[8] This is why the samples of bronze coatings on copper (0.04 μm) were also implanted with Ar^+ at an energy of 110 KeV and a dose of 6×10^{15} at cm^{-2} and at an energy of 95 KeV and a dose of 6×10^{15} at cm^{-2} respectively. The implantation was done at room temperature.

The implantation energy was chosen to place the maximum of the Ar profile at the interface of the films and was evaluated with a Monte Carlo simulation program (SRIM98).[14] In Fig. 1 it is possible to see that the maximum of the Ar^+ profile (at cm^{-3}) is placed around the interface between the white bronze coating and the copper substrate (at around 450 Å).

RBS measurements, used to measure the film composition, were performed with a 3 MeV $^4He^+$ beam with a detector

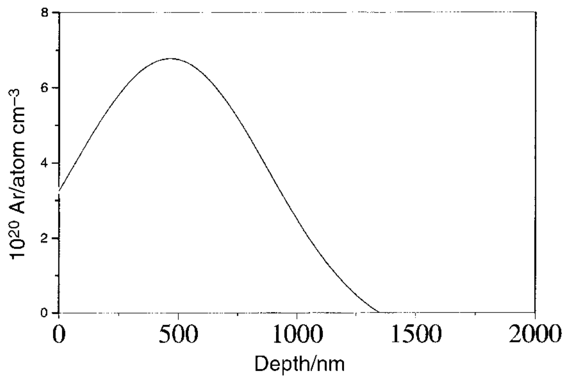

Fig. 1 The profile of the Ar$^+$implant [95 keV RT in 450 Å of white bronze–Cu].

scattering angle of 160°. This technique is usually considered non-destructive in that the interaction of the probe beam and the sample is so weak no changes are induced by the beam itself.

Fig. 2 shows the RBS spectra of the bronze: the film composition is Cu 66; Sn 23; Zn 10; Pb 1 wt%; the thickness of the film is 450 Å.

3.2. Electrochemical tests

All the electrochemical tests carried out on the bronze samples were aimed at verifying the duration of the very thin layers of bronze in the standard solution.

3.2.1. Potential *vs.* time tests. Fig. 3 reports the *E vs.* time curves obtained with bronze coatings compared with that of electrolytic copper. The results are in Table 3. The trend of the curves obtained with the bronze samples showed that only the 0.3 μm thick bronze seemed to exhibit behaviour similar to the Cu specimens even if the E_{corr} is more negative (-286/-288 mV$_{sce}$ for 0.3 μm, -217 mV$_{sce}$ for Cu). In fact, both 0.04 μm thick bronzes showed a very negative initial E_{corr} (around -560 mV$_{sce}$ for 0.04 μm compared with -480 mV$_{sce}$ for 0.04 μm I.I.). The potentials stabilised after around 10 min but only the I.I. samples reached values slightly more positive than copper.

This could mean that the 0.04 μm specimens initially had a similar trend due to the difficulty of showing an almost steady state. The 0.04 μm I.I. specimen behaved like that of 0.04 μm, but with a potential that was always 60–70 mV more positive.

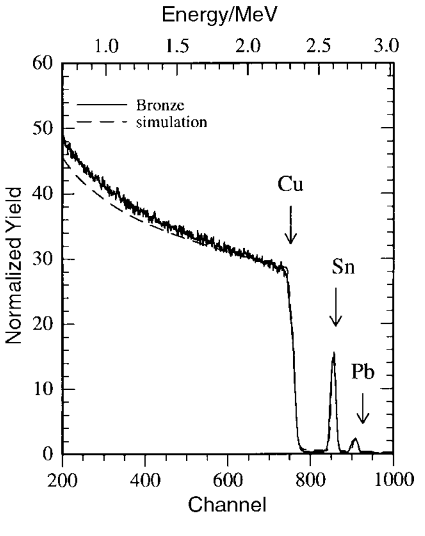

Fig. 2 RBS spectrum of white bronze sample obtained with 3 MeV of ^{4}He$^+$ particles. The simulation spectrum using a RUMP code[15] is also shown. The film composition is Cu 66; Sn 23; Zn 10; Pb 1 wt%.

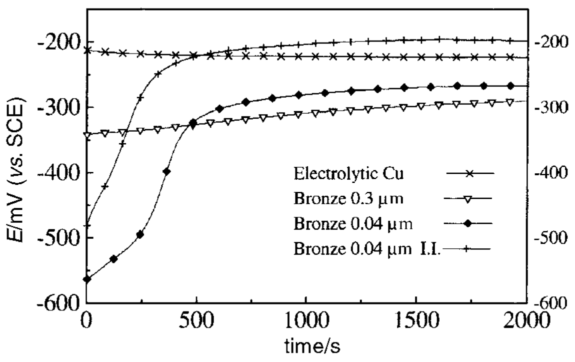

Fig. 3 Some typical *E*–time curves obtained with bronze coatings compared with that of electrolytic copper (pH = 12.4, *T* 25 °C, aerated solution).

Table 3 Comparison between the average E_{corr} obtained with the different samples (from *E*–time and potentiodynamic tests)

	E_{corr}–time/mV$_{sce}$	E_{corr} (Tafel)/mV$_{sce}$
Electrolytic Cu	-217 ± 3	-217 ± 5
Bronze 0.3 μm	-288 ± 7	-286 ± 6
Bronze 0.04 μm	-274 ± 8	-274 ± 8
Bronze 0.04 μm I.I.	-206 ± 7	-206 ± 6

3.2.2. Potentiodynamic tests. Potentiodynamic tests make it possible to draw out different electrochemical data, in particular the corrosion current density, i_{corr}, directly correlated with the corrosion rate (R_{corr}) of the different surface treatments.

Fig. 4 reports some typical potentiodynamic curves obtained with the different bronze coatings, compared with a typical curve of electrolytic Cu in the same experimental conditions.

Table 4 reports the more significant electrochemical data.

Trends of the 0.3 μm and 0.04 μm bronze potentiodynamic curves were similar, but differed substantially from that obtained with pure Cu. In bronze-coated specimens the passivation capacity of the surface treatments increased and the corrosion rate, R_{corr}, reached values one order of magnitude lower than that of Cu. The passivation capacity is due to the presence of Sn. This element gives (Fig. 4) a good passivation performance of the bronze in addition to other specific properties.[9,10,16]

From comparison with Cu, one can point out that the R_{corr} of bronze coatings were significantly lower than that of copper even at a thickness of 0.04 μm.

The I.I. specimen showed a similar trend. Even if the passivation current density, i_p, is equal to that of Cu, the R_{corr} is even lower than those obtained with the other bronze coatings. This signifies that the I.I. treatment had a global positive

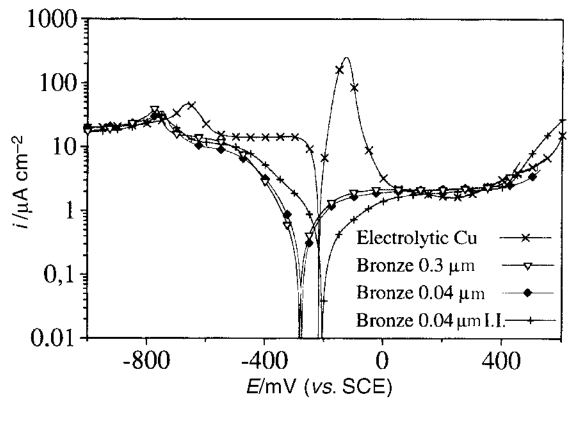

Fig. 4 Some typical potentiodynamic curves obtained with different bronze coatings compared with that of electrolytic copper (pH = 12.4, *T* = 25 °C, aerated solution).

Table 4 Electrochemical data obtained from the potentiodynamic curves with different surface treatments. i_{L} = limit current density of oxygen diffusion. i_{p} = passivation current density. R_{corr} is in mg dm^{-2} day^{-1} (pH = 12.4, T 25 °C, aerated solution)

	i_{L}/µA cm^{-2}	i_{p}/µA cm^{-2}	i_{corr}/µA cm^{-2}	R_{corr}/mg dm^{-2} day^{-1}
Electrolytic Cu	15.7 ± 1.9	1.8 ± 0.1	1.80 ± 0.20	5.0 ± 0.6
Bronze 0.3 µm	17.9 ± 0.8	2.3 ± 0.1	0.19 ± 0.05	0.5 ± 0.1
Bronze 0.04 µm	17.4 ± 0.5	2.3 ± 0.1	0.30 ± 0.07	0.8 ± 0.1
Bronze 0.04 µm I.I.	19.0 ± 1.1	1.8 ± 0.1	0.15 ± 0.05	0.4 ± 0.1

influence on the corrosion behaviour of the I.I. coating, thus indicating that the surface "bombardment" also had a partial long-range effect, with the formation of a defective structure or a change in the structure of 450–550 Å, which is as thick as, or slightly thicker than, the surface coating layer.[17]

Some potentiokinetic polarization data reported in the literature for Ar-implanted copper seem to demonstrate that this I.I. produces no significant effects on the passivation behaviour of Cu in alkaline sulfate solution.[8] On the contrary, in the alkaline solution used by us the ion beam mixing effect really existed as can be seen in Table 4.

The average limiting current density of the O_2 diffusion (i_{L}) of bronze layers was higher than that of Cu (18–19 *vs.* 16 µA cm^{-2}). The passivation current densities, i_{p}, of non-implanted specimens were appreciably higher than that of Cu, even if the anodic characteristics of the bronzes compared with those of Cu tend to a significantly more rapid passivation of the metallic surface.

In any case the I.I. specimens showed behaviour similar to that of the bronze (0.3 µm) coatings ($R_{\mathrm{corr}} = 0.4$ and 0.5 mg dm^{-2} day^{-1} respectively), while the R_{corr} of bronze 0.04 µm is 0.8 mg dm^{-2} day^{-1}.

It is accepted that Ar-implantation on copper produces no significant effect on the passivation behaviour of copper in a similar environment (Ar^+ is considered as an inert ion in alkaline solution, pH = 12.4, 0.01 M Na_2SO_4[8]). In spite of this assumption, one can observe that, in this case, probably because of the thinness of the layers, the I.I. treatment could seem to provoke at least a partial amorphization of the coated surface; this resulted in a general decrease of R_{corr}. It was impossible to test the degree of amorphization because of the thinness of the coating (0.04 µm): in fact the usual X-ray techniques did not reveal differences between the 0.04 and the I.I. 0.04 µm layers.

However, in the case of the bronze layer, where the Cu content is 66 wt%, the Sn (23 wt%) seems to play an important role. It is well known that the elevated corrosion resistance of bronzes at high Sn content ($>20\%$) is due to the great influence of this element on the alloy's physical properties: in particular, it favours the layer's passivation capacity.[16] Further, I.I. R_{corr} was significantly lower than that of copper and the other bronze specimens, thus demonstrating the effectiveness of the adopted I.I. treatment.

4. Conclusions

Seeing that the European law 1811 (June 1998) fixes the limit of Ni release at 0.5 µg cm^{-2} week^{-1}, the galvanic industries will have to substitute the coatings containing this metal. "Ni-free" coatings are a good alternative. This paper demonstrates the good corrosion performance of Cu 66, Sn 23, Zn 10, Pb 1 wt% white bronze thin layers and of the I.I. treatments. One can conclude that:

(1) it is possible to deposit an alloy of white bronze (Cu 66; Sn 23; Zn 10; Pb 1 wt%) with high efficiency: the coatings are homogeneous and brilliant;

(2) electrochemical tests carried out in a standard solution [pH = 12.4 (borate–boric acid + NaOH (10%)); T 25 °C; aerated solution] showed that thin galvanic coatings (0.04–0.3 µm) of white bronze reduced the R_{corr} by more than one order of magnitude;

(3) the ion implanted 0.04 µm bronze specimens behaved like the 0.3 µm bronze ones, showing that after the I.I. treatment the I.I. R_{corr} was around half of that of the un-implanted 0.04 µm bronze;

(4) implanted bronze-electroplated copper showed the best corrosion behaviour. The electrochemical tests showed low corrosion rates and a corrosion mechanism similar to that of more noble coatings.

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