

## Bronze as alternative for replacement of nickel in intermediate layers underneath gold coatings



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### ABSTRACT

The aim of this work is to characterize the corrosion resistance of bronze used as an intermediate layer, underneath gold plate, and also that of an intermediate layer of palladium on bronze to improve the corrosion resistance of the system substrate-intermediate layer-thin gold layer. The corrosion resistance was characterized by electrochemical techniques, mainly, electrochemical impedance spectroscopy and potentiodynamic polarization tests. The surface after immersion and electrochemical tests was observed by scanning electron microscopy. The results of this work showed that the addition of an intermediate layer of palladium between bronze and gold layers showed that the resistances related to the specimens with palladium undercoat, either related to the coating-electrolyte interface (R<sub>2</sub>) or to the substrate exposed to the electrolyte underneath the coating defects (R<sub>3</sub>) were twice as that of bronze as the gold undercoat. Besides, the palladium undercoat to gold finish increased the resistance to tarnishing comparatively to the bronze undercoat. Tarnishing is a common problem associated to bronze corrosion. The introduction of palladium as an intermediate layer avoided the breakdown of passivity that occurred for the bronze gold coated material at potentials around 0.5 V<sub>Ag/AgCl(3M)</sub>.

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### 1. Introduction

Decorative and technical industry has a tendency to use gold layers for plating surfaces. For costume jewelry, gold plating is usually applied on steel, brass or zamack, all with an intermediate layer of copper and nickel to increase the quality of leveling and brightness of a thin top gold layer. The copper layer, however, can diffuse through the gold plating to the surface, losing the esthetic appearance [1]. The nickel layer has an important role in the quality of this thin gold layer which is to provide a smooth and bright surface for gold plating. However, the spread used of gold plated jewelry and the high cost of gold has led to increasingly thinner gold coatings.

It must be kept in mind is that gold for jewelry is measured in karats, which represents the amount of gold in the alloy. For instance, 24 karat represents 99.9% of gold, or pure gold, whereas 18 karat means 75% gold, 12 karat is 50% gold and 9 karat is 37.5%

gold. Concerning gold plated jewelry, a hypoallergenic type must be made of at least 18 karat gold. Depending on the metal the gold in the jewelry is alloyed with, for instance, white gold is usually alloyed with nickel, the gold coating must lead to jewelry allergy [2].

Nickel, however, is related to skin allergy problems while gold and platinum usually poses no risk of allergic contact dermatitis [3]. The literature reported studies carried out in USA confirming that 8–15% of the female population presented skin allergy problems [3] and 15.6% of males and 35.8% of females under the age of 18 are affected with nickel contact allergy [4]. In France, it is 27% of women and 11% of men [5]. The exposure of the substrates to the body fluids leads to corrosion, nickel dissolution and consequently, allergic reactions, such as dermatitis, which is a common type of allergic contact eczema. Due to corrosion by sweat, nickel chloride is produced on the skin beneath nickel plated articles, which is a source of nickel ions [3] bound to carrier proteins, forming a nickel-protein complex that activates immune reactions. Due to this, nickel for jewelry or any application that involves skin contact has been eliminated from many countries and prohibited in the European Community [6].

In order to avoid the problem of contact allergies, other types of intermediate layers have been proposed in the last years as potential replacements for nickel [5,7–9]. Moreover, the gold coatings

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underneath the nickel should be dense and adherent to the intermediate layer to avoid the corrosion of the substrate. However, it is difficult to preserve the substrate from contacting body fluids due to the increasingly thinner gold coatings and their regularly found defective areas [9–11]. Some industries have decided to eliminate nickel as leveling agents preserving copper as the substrate for gold plating, whereas others searched for additional alternatives.

Vicenzo et al. studied electrodeposited Au–Sn alloys to replace Ni in the jewelry industry [12]. Suitable alternatives are noble metals such as palladium and silver; however, they are not usually considered economically viable. Other alternatives have also been tried [9,13]; for instance, yellow and white bronze are being largely used, but have not been acutely characterized. Hovestad et al. [13] investigated nanocrystalline white bronze electroplated from a strongly acidic solution as alternative to Ni plating as undercoat for noble metals in jewelry application and found that it shows improved tarnishing resistance and similar corrosion and wear resistance as undercoat for gold compared to nickel. Ping et al. [14] studied the corrosion resistance of mild steel samples and samples copper and bronze plated. They concluded that plated samples did not corrode in salt water.

The aim of this work is to investigate the effect of a white bronze intermediate layer underneath the gold layer, as an alternative for nickel replacement, and also that of a thin layer (0.1  $\mu\text{m}$ ) of palladium applied on bronze and beneath the gold coating on the corrosion resistance of the whole coated system. In previous study [15], white bronze itself showed it acts as an intermediate layer of proper corrosion resistance, but the deposition of gold on the surface generated a galvanic cell due to defects in the gold coating that diminished the corrosion resistance and led to the formation of a dark corrosion product on the surface. This occurrence has also been observed with some commercial jewelry during use [15].

## 2. Experimental

The effect of two types of intermediate layers electrodeposited layers on polished brass on the corrosion resistance of the coated system were investigated in this study. These were white bronze and palladium thin film on bronze layer. All intermediate layers tested were coated with a thin layer of gold coating. The samples with white bronze intermediate layer were prepared by electrodeposition in an acid copper bath and white bronze bath. These samples were then coated in an acid gold bath. Some samples with white bronze layer were coated with a very thin layer (thickness of 0.1  $\mu\text{m}$ ) of palladium and then gold. Table 1 shows the types of baths, their composition and the thickness of the bronze and palladium intermediate layers and gold layer.

All electrochemical tests were carried out using a three-electrode set-up, with a platinum wire and Ag/AgCl as counter and reference electrodes, respectively, and the samples as working electrodes. The tests were performed at 25 °C in a phosphate buffer solution (PBS) [17] and in synthetic sweat whose chemical composition are presented in Tables 2 and 3, respectively.

Electrochemical measurements were carried out using a Gamry® Frequency Response Analyser EIS 300 coupled to a potentiostat model PCI4/300 and controlled by Echem Analyst® 135 software. The tests were performed at 7 days of immersion in the PBS solution and at 2 days of immersion in synthetic sweat solution. All diagrams were obtained in the potentiostatic mode at the open circuit potential  $E_{\text{ocp}}$ , in the frequency range of 100 kHz to 10 mHz, with 10 mV of voltage perturbation amplitude and an acquisition rate of 10 points per decade. The polarization curves were performed after the EIS tests, from the  $E = -200$  mV lower than  $E_{\text{ocp}}$  up to 1.5  $V_{\text{SCE}}$  at a rate of 1.0 mV/s.

**Table 1**

Specifications of the electrolyte of acid copper, white bronze, palladium and acid gold used for electrodeposition [16].

Process	Electrodeposited layer
<i>Acid copper</i> Composition: CuSO <sub>4</sub> ·5H <sub>2</sub> O: 220.0 g/L H <sub>2</sub> SO <sub>4</sub> : 60.0 g/L Cl <sup>-</sup> : 0.08 g/L	Cu – 100% (wt.%) Thickness: 5 $\mu\text{m}$ Plating conditions: Current density: 4.0 A/dm <sup>2</sup> Operating temperature: 25 °C Time: 7 min
<i>White bronze bath [9] – Miralloy*</i> Bath type: alkaline cyanide  Composition: KCN: 50.0 g/L KOH: 30.0 g/L Copper salt Miralloy: 12.0 g/L Tin salt Miralloy: 79.0 g/L Zinc salt Miralloy: 0.93 g/L Brightener 1–1 Miralloy: 7.5 g/L Brightener 2 Miralloy: 5.0 ml/L Initial Solution 2800 Miralloy: 200.0 ml/L	Cu/Sn/Zn – 55/35/15 (wt.%) Thickness: 1.5 $\mu\text{m}$ Plating conditions: Current density: 0.5 A/dm <sup>2</sup> Operating temperature: 60 °C pH: 13.0 Time: 10 min
<i>Palladium [9] – 99.9%</i> Composition: NH <sub>4</sub> OH: 20.0 g/L Metal content: Pd: 3.0 g/L	Pd – 100% (wt.%) Thickness: 0.1 $\mu\text{m}$ Plating conditions: Current density: 0.3 A/dm <sup>2</sup> Operating temperature: 30 °C pH: 8.2 Time: 1 min
<i>Gold bath [9] – 23.7 K</i> Acid composition: Citric acid: 80.0 g/L Gold complex: AuK(CN) <sub>2</sub>  Metal content: Au: 4.0 g/L Ni: 1.2 g/L	Au/Ni – 99.7/0.3 (wt.%) Thickness: 0.25 and 0.12 $\mu\text{m}$ Plating conditions: Current density: 0.5 A/dm <sup>2</sup> Operating temperature: 25 °C pH: 4.8 Time: 4 and 2 min

\* The bronze, palladium and gold coatings were produced using the process named Miralloy, Palladium 467 and Auruna 535 (Umicore).

**Table 2**

Composition of phosphate buffer solution (PBS) used as electrolyte.

NaCl	8.77 g/L
Na <sub>2</sub> HPO <sub>4</sub>	1.42 g/L
KH <sub>2</sub> PO <sub>4</sub>	2.72 g/L

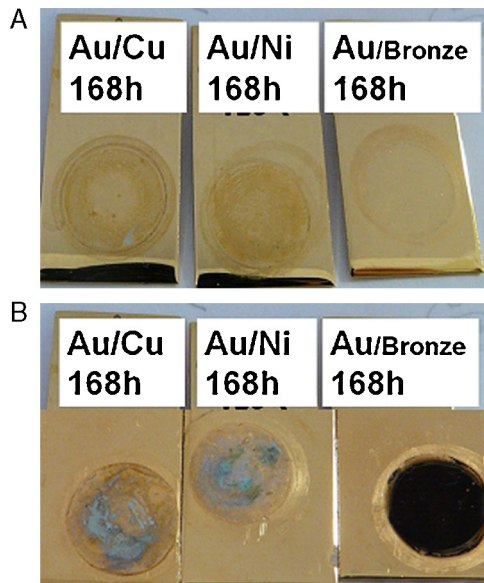
## 3. Results and discussion

Previous work has been carried out to evaluate the corrosion resistance of white bronze as intermediate layer and a potential replacement for commercial intermediate layers made of nickel and copper [15]. It was found that an intermediate layer of white bronze highly improved the corrosion resistance of gold plated samples in comparison with nickel and copper, in a PBS solution.

**Table 3**

Composition of synthetic sweat used as electrolyte.

NaCl	20.0 g/L
NH <sub>4</sub> Cl	17.5 g/L
H <sub>3</sub> C-COOH	2.0 g/L
H <sub>3</sub> C-CHOH-COOH	15.0 g/L
H <sub>3</sub> C-C-OO-COOH	2.5 g/L
H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>2</sub> -COOH	5.0 g/L
(NH <sub>2</sub> ) <sub>2</sub> CO	5.0 g/L

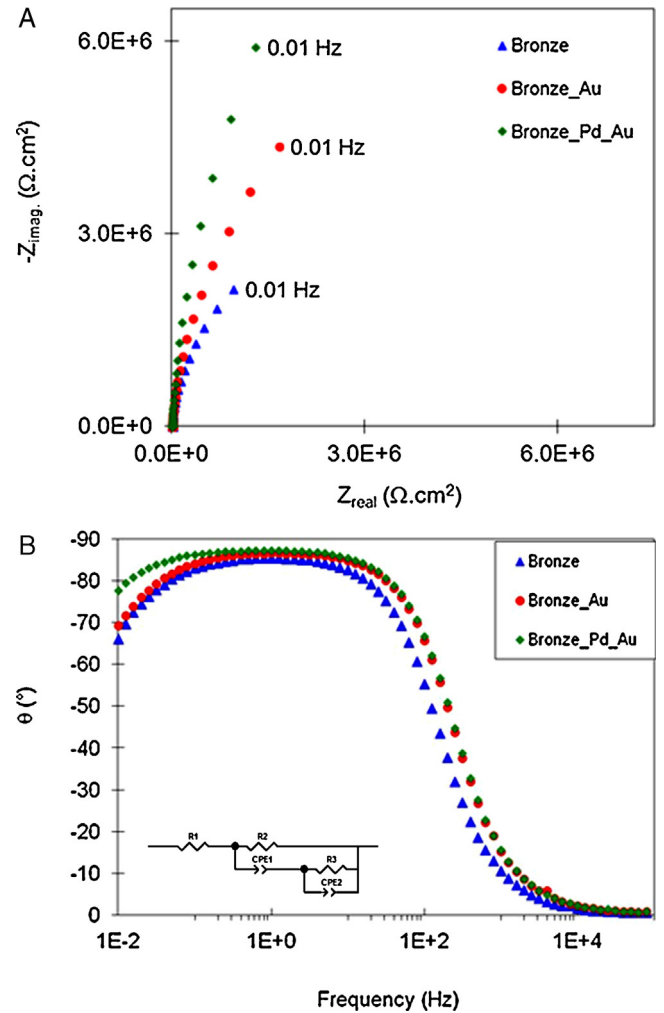


**Fig. 1.** Macrographs of the samples copper with gold, nickel with gold and white bronze with gold. (a) after 7 days of immersion in PBS solution, at room temperature and (b) after polarization tests performed after 7 days of immersion in PBS solution, at room temperature.

The use of nickel as an intermediate layer showed low corrosion resistance resulting in nickel dissolution from the substrate underneath the defects in the gold coatings [18].

Despite the higher resistance of white bronze comparatively to nickel, copper or brass, the thin layer of electroplated gold ( $0.25 \mu\text{m}$  of thickness) presents defects that expose the substrate leading to galvanic coupling with the coating material and consequently, to corrosion with generation of corrosion products. The final aspect of the samples must be considered due to the use of this process to make jewelry and decoration items. The thickness of the layers corresponding to the system Bronze/Pd/Au was  $0.12 \mu\text{m}$  of gold,  $0.1 \mu\text{m}$  of palladium and  $1.5 \mu\text{m}$  of bronze. This shows that the amount of palladium used is very low to allow its viability due to economical reasons.

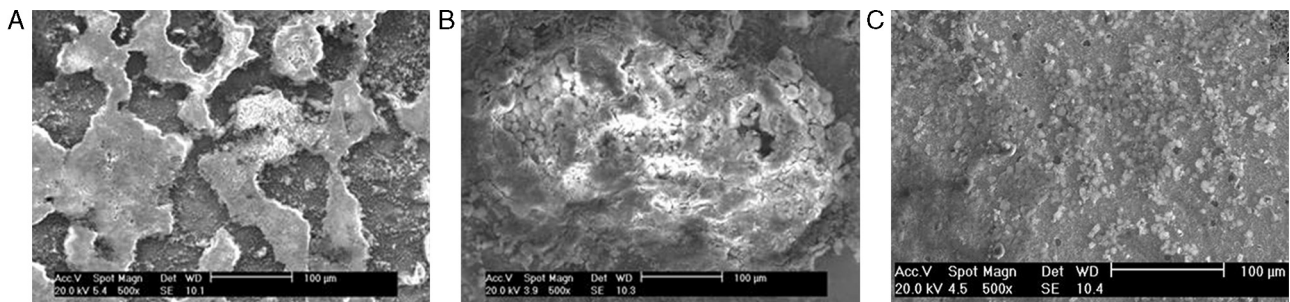
Figs. 1 and 2 respectively show the macrographs and the micrographs of the white bronze with gold coating after 168 h of immersion in the PBS solution followed by anodic polarization. The results showed the formation of dark corrosion products at the surface of the polarized areas. These corrosion products were not seen at the surface after 168 h of immersion prior to polarization showing these areas are formed by highly oxidizing conditions obtained during positive polarization. It also explains the formation of dark products during use of gold electroplated jewelry with bronze as intermediate layer. For comparison, samples with intermediate layers of nickel and copper were also tested in the same electrolyte



**Fig. 3.** Electrochemical impedance spectroscopy results: (a) Nyquist and (b) Bode phase angle diagrams and equivalent circuit fitted to the EIS results. Samples of bronze; bronze with gold; bronze with palladium and gold obtained after 168 h of immersion in the PBS solution, at room temperature.

under the same conditions (168 h of immersion followed by polarization) and their surfaces are also shown in Fig. 1.

The corrosion resistance of the samples of white bronze and palladium on white bronze, both with a thin layer of gold coating, were evaluated by electrochemical tests after 168 h of immersion in the PBS solution, at  $25^{\circ}\text{C}$ . The electrochemical impedance results for the tested materials are presented in Fig. 3. The Nyquist diagrams show higher impedances associated to the coating-electrolyte interface sample with the intermediate layer of palladium on



**Fig. 2.** SEM micrographs of the samples after polarization: (a) copper with gold, (b) nickel with gold and (c) white bronze with gold. Tests performed after 7 days of immersion in PBS solution, at room temperature.



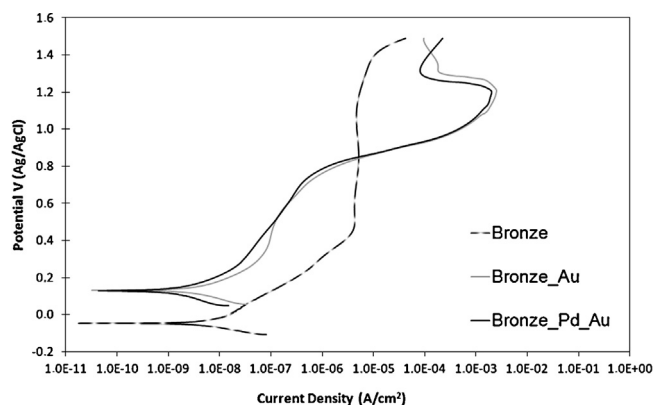


Fig. 4. Potentiodynamic polarization curves of bronze with gold; bronze with palladium and gold. After 2 days of immersion in synthetic sweat solution, at 25 °C.

bronze suggesting also a greater corrosion resistance associated to this kind of sample comparatively to that with bronze intermediate layer. The Bode phase diagrams (Fig. 3b) show the highest phase angles at low frequencies comparatively to the other types of tested samples.

The equivalent circuit fitted to the EIS results of the samples with gold coating finish is shown in Fig. 3b. The  $R_1$  represents the solution resistance; the  $R_2$ -CPE<sub>1</sub> pair corresponds to the high frequency results and is associated to the finish coating-electrolyte interface whereas the  $R_3$ -CPE<sub>2</sub> pair corresponding to the low frequency data is related to interfacial processes at the exposed substrate underneath the defects in the finish coating and the charging of the double layer [9]. The results of the fitting of the experimental data for the specimens tested with gold coating to the proposed

equivalent electric circuit (EEC) are shown in Table 4. Constant Phase Elements (CPEs) were used instead of the capacitances in order to take into consideration surface heterogeneities. A CPE is an equivalent electrical circuit component imitating behavior of an imperfect capacitor. The electrical impedance of a CPE can be calculated according to Eq. (1), where  $Q$  is a constant and  $n$  is a value representing the deviation from purely capacitive behavior. In all cases, the agreement between experimental and fitted data was very good

$$Z_{CPE} = \frac{1}{Q(\omega i)^n} \quad (1)$$

The resistances related to the specimens with palladium undercoat, either related to the coating-electrolyte interface ( $R_2$ ) or to the substrate exposed to the electrolyte underneath the coating defects ( $R_3$ ) were twice as that of bronze as the gold undercoat.

Despite the high corrosion resistance (impedances in the order of  $10^6 \text{ ohm cm}^2$ ) indicated in the electrochemical results for the samples with bronze as substrate, corrosion products were found at the surface. In fact, this type of corrosion product was seen at jewelry of this kind during use and it was reported as a drawback for their practical use [15]. Although this type of products was not identified at the surface of the samples immersed for 168 h in PBS, the surface of bronze gold coated samples was darkened, suggesting low resistance to tarnishing, after potentiodynamic polarization tests were darkened. This shows that highly oxidizing conditions are an essential factor leading to tarnishing of the surface.

Table 4 presents the values of the  $R$  and  $CPE$  parameters obtained from the fitting procedure. CPEs were used instead of the capacitances in order to take into consideration surface heterogeneities. In all cases, the agreement between experimental and fitted data was very good. The quantitative data demonstrate that the corrosion

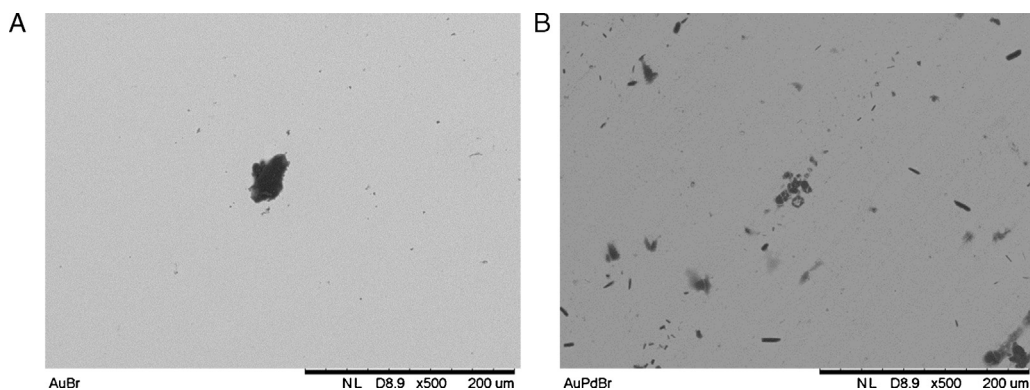


Fig. 5. Surface of (a) bronze and (b) bronze coated with palladium as undercoat for gold finish coating, after polarization curves in synthetic sweat solution.

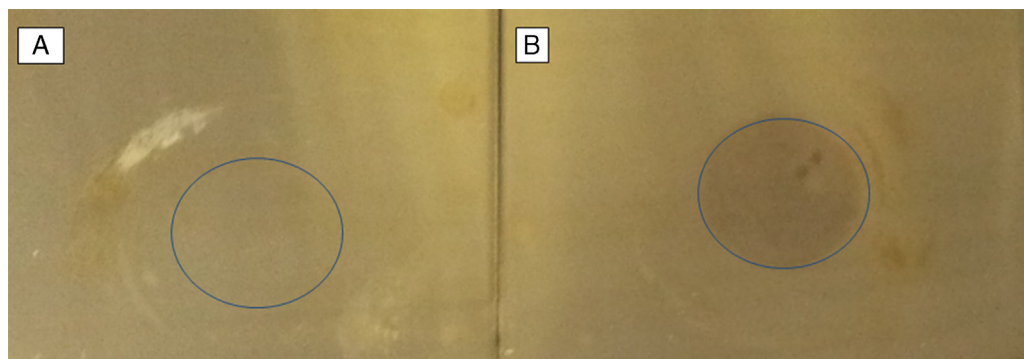


Fig. 6. Macrographs of the surfaces of (a) white bronze with palladium as an undercoat for gold finish and (b) white bronze with gold finish. The blue circles show the boundary of the tested areas. After potentiodynamic polarization tests in synthetic sweat solution, at 25 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 4**

Data obtained from the equivalent circuit fitted to EIS of bronze; bronze with gold; bronze with palladium and gold.

Sample	$R_1$ ( $\Omega$ cm <sup>2</sup> )	$R_2$ (M $\Omega$ cm <sup>2</sup> )	CPE1 ( $\mu$ cm <sup>-2</sup> s <sup>-1</sup> $\Omega$ )	$n_1$	$R_3$ (M $\Omega$ cm <sup>2</sup> )	CPE2 ( $\mu$ cm <sup>-2</sup> s <sup>-1</sup> $\Omega$ )	$n_2$
Bronze	81.93	2.71	0.20	0.99	0.12	0.68	0.89
Bronze + gold	91.76	5.52	0.10	0.99	0.17	0.47	0.90
Bronze + palladium + gold	98.77	10.56	7.81	0.99	0.41	0.95	0.86

resistance of the bronze was improved with the gold and became even higher with the addition of the palladium layer.

Fig. 4 presents potentiodynamic polarization curves performed after EIS tests of samples with bronze or palladium on bronze, both with a thin gold coating layer. The corrosion current densities at the corrosion potential were very low (order of  $\mu$ A/cm<sup>2</sup> or lower) which are typical of passive materials.

An active–passive transition was associated to the bronze–Au samples that occurred at potentials around 0.2 V<sub>Ag/AgCl(3M)</sub> likely associated to the formation of corrosion products of bronze at the defects of the gold coating finish leading to partial coverage of the defects. This is supported by the small decrease in current density seen for the bronze samples without gold coating at potentials around 0.1 V<sub>Ag/AgCl(3M)</sub>. The active–passive transition was followed by a passivity breakdown at potentials of approximately 0.5 V<sub>Ag/AgCl(3M)</sub> with the dissolution of the substrate. This must be associated to the formation of the dark corrosion products found at the surface after polarization tests of this type of tested samples. The results indicated a passive behavior for this material equivalent to the range from nearly 0.2 V<sub>Ag/AgCl(3M)</sub> to approximately 0.5 V<sub>Ag/AgCl(3M)</sub>.

The polarization curve corresponding to the bronze–Pd–Au samples shows that the current densities was in the order of 10 mA/cm<sup>2</sup>, that is, typical of passive materials. This corresponds to the ionic current through the defects in the passive film on the surface. A breakdown potential was not indicated in the polarization curve until potentials of 1.5 V<sub>Ag/AgCl(3M)</sub>, that is, well above the potential of the oxygen evolution reaction. This suggests that the passive film on palladium presents low conductivity, hindering this last reaction.

It is proposed that for the bronze samples without gold coating, the anodic reaction is the preferential dissolution of Sn in the alloy. This is supported by the formation of the dark corrosion products seen at the surface after polarization and tarnishing of the surface. On the gold coated bronze, the anodic reaction is also the preferential dissolution of Sn but in this it is located underneath the defects of the gold coating. As the gold electrodeposited layer on bronze was thicker than that on the samples with an intermediate layer of palladium, 0.25  $\mu$ m against 0.12  $\mu$ m of thickness over 0.1  $\mu$ m of palladium, the attack was more of the localized type comparatively to the sample with palladium intermediate layer, as shown in Fig. 5. A pit resulting from the localized attack is seen at the surface of the bronze gold coated sample.

For the samples with palladium as an intermediate layer underneath the thin gold finish, (0.12  $\mu$ m), the local pH decrease due to hydrogen oxidation, might decrease the stability of the thin gold layer leading to localized attack at the defective areas of the coating (see Fig. 5). However, the low current density associated to the comparatively larger number of attacked sites, resulted in the shallow attack at the palladium surfaces exposed to the electrolyte and the higher tarnishing resistance associated to this type of sample.

Observation of the surface of the tested samples after polarization test showed that the intermediate layer of palladium underneath the gold coating in fact increased the resistance to tarnishing of the gold coated samples, as shown in the macrographs of Fig. 6. The blue circles indicate the tested areas.

Surface observation by scanning electron microscopy of the bronze surface without gold coating after polarization, Fig. 7,

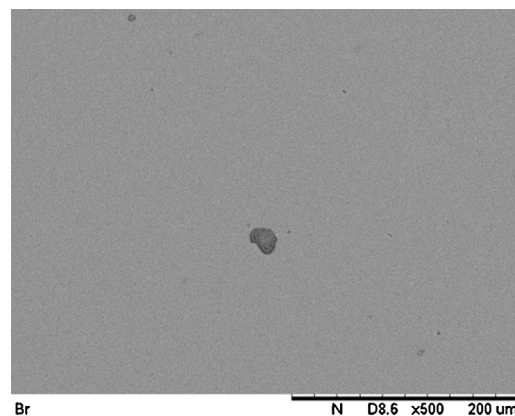


Fig. 7. Micrograph of the white bronze surface after polarization tests in synthetic sweat solution, at 25 °C.

showed only a slight attack of the surface, significantly more superficial than for the gold coated bronze, as shown in Fig. 5a. This results shows that the formation of microgalvanic cells at the gold coating–exposed bronze at underneath the coating defects was the reason for the more prominent attack on the bronze coated samples.

#### 4. Conclusions

The results presented in this paper shows that palladium has a beneficial effect as an intermediate layer on white bronze improving the corrosion resistance of the substrate in both solutions tested, phosphate buffer solution or synthetic sweat solution. It also avoided the formation of dark corrosion products leading to degradation of esthetic aspect which were found on the surface of white bronze as intermediate layer with a thin gold coating on top. Palladium was applied as a very thin layer or “flash” between the white bronze and the gold coating and the gold thickness was diminished to avoid increased production costs. The thin layer of palladium acted as a barrier layer between the white bronze substrate and the electrolyte that leads to dark corrosion products under high oxidizing conditions. Therefore, the use of a very thin layer of palladium on bronze prior to gold coating is recommended.

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