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Electrodeposited white bronzes: a comparison between Zn-bearing and Zn-free coatings

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Introduction

White Bronzes are teranry alloys composed by Cu, Zn and Sn, named after their bright whitish colour. This class of alloys share excellent hardness, corrosion and tarnishing resistances, and it is commonly adopted in galvanic industrial processes as technological grade coating, as a substitute to Nichel films, to obtain layers with particular aestethical and/or anticorrosive properties. Despite the widespread employment of white bronzes, recent literature lacks a characterization of these electrodeposited alloys in respect to more common binary (Cu-Sn) white bronzes.

In this poster a comparative study between a Zn White Bronze and a Zn-Free White Bronze is proposed. The aim of this study was to develop a better understanding on the role of Zinc on the technological properties of the coating.

Samples:

a. *Cu-Zn-Sn* **(Zn-bearing)** White Bronze

b. *Cu-Sn-Pd* **(Zn-Free)** White Bronze

Question:

What is the influence of zinc on the technological properties of the coating?

Sample Preparation

Two series of deposits: a Cu-Zn-Sn (Zn-Bearing) white bronze and a Cu-Sn-Pd (Zn-Free) white bronze were prepared by ITALFIMET S.R.L. (Monte San Savino, Ar, Italy) using two of their commercial galvanic baths. Depositions were performed galvanostatically. For each series, three deposit thicknesses were produced: 0.5, 1.0 and 1.5 microns. Brass (67% Cu, 33% Zn) flat surfaces were used as cathodes for the deposition. By naked eye examination, samples display similar colour and silvery mirror-like finishing.

A preliminary FIB-SEM cross sectioning procedure was performed to confirm film thickness (Fig.1). Subsequent EDS analisys was carried out on the surfaces using a beam energy of 12 keV, to acquire the average composition of the alloys (Fig.2). The correct value of the beam energy was derived from Monte Carlo simulations, in order to avoid signals from the substrate, as described in [1].

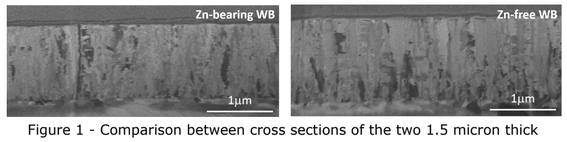

Figure 1 - Comparison between cross sections of the two 1.5 micron thick samples, images acquired using ion beam probe.

Sample	Element	Weight %			Atomic %			Error %		
		0.5 µm	1.0 µm	1.5 µm	0.5 µm	1.0 µm	1.5 µm	0.5 µm	1.0 µm	1.5 µm
Zn Bronze	Cu	48.77	50.57	50.16	56.56	58.05	57.73	4.18	4.02	4.06
	Zn	22.95	23.11	23.00	25.88	25.78	25.73	7.49	7.50	7.50
	Sn	28.28	26.32	26.84	17.56	16.17	16.54	3.09	3.02	2.96
Zn-free Bronze	Cu	62.50	61.37	62.14	75.66	74.70	75.36	4.97	5.03	4.98
	Pd	0.61	1.71	0.79	0.44	1.24	0.57	29.88	7.65	26.08
	Sn	36.88	36.92	37.07	23.90	24.06	24.07	3.04	2.78	2.81

Figure 2 - Compositional EDS results for the deposits. C and O quantification is not reported.

From the preliminary analysis:

- Galvanostatic deposition thicknesses were coherent with the data acquired by cross-sectioning for all the samples;
- A **similar columnar growth** was noticeable for both the series of deposits (in line with the electrochemical growth of thin film deposits);
- **Zn-free deposits grow slower** (X2 times) in respect to Zn-bearing ones.
- **Average metal composition** of the deposit was approx Cu 50%, Zn 23% and Sn 27% for the Zn-bearing alloy, and Cu 62%, Pd 1% and Sn 37% weight for the Zn-free alloy (**The content of Pd is very small**).

Characterization

In order to understand the role of Zn, we report XRD, XPS and Corrosion resistance analisys performed on the samples.

XRD

XRD data of all the samples were acquired and fitted, as in Fig.3.

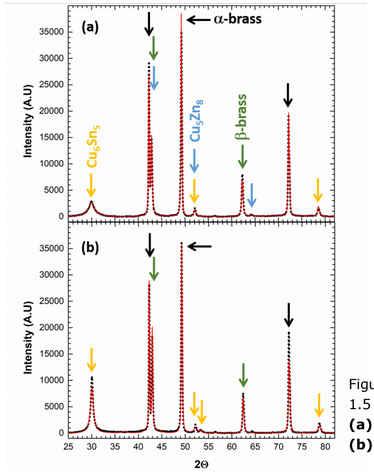

Figure 3 - XRD spectra of the 1.5 micron thick samples: **(a) Zn-Bearing** and **(b) Zn-Free** alloys

Tipically electrodeposited white bronzes consist of intermetallic compounds such as Cu_6Sn_5 and Cu_5Zn_8. The XRD of the Zn-bearing and Zn-free alloys both showed a peak at 30° due to the (101) reflection of the Cu_6Sn_5 structure; its presence was also confirmed by the fitting. The occurence of the Cu_5Zn_8 phase in the Zn-bearing material was harder to prove, as its peaks superimpose with those of Cu_6Sn_5 in the brass substrate. Howeverthe the fit of the diffraction pattern matches the intensities of the peaks much better when the Cu_5Zn_8 phase is added. From the Zn-free XRD, it is possible also to conclude that the addition of a small amount of Pd does not significantly affect the coating structure. All the diffractograms clearly showed the peaks of the substrate (alpha and beta phases). The full pattern analysis yelds a crystalline size of 70 nm for the Zn-bearing bronze, and of 50 nm for the Zn-free bronze.

XPS

XPS analysis was performed for all the samples. Samples showed a different surface composition in respect to bulk. First, in both Zn-bearing and Zn-free coatings a significant amount of carbon and oxygen was observed. However the shape of the carbon peak shows that the contamination is dissimilar for the two coatings. Zn-bearing samples were the most contaminated, suggesting that additives (polyalcohols) used in the bath remained on the surface even after cleaning the surfaces with water and ultrasounds. For this reason, surface cleaning by in-build XPS sputtering gun was performed; spectra were collected prior and after the cleaning process. Spectra of the regions of interest (metals) can be seen in Fig.4.

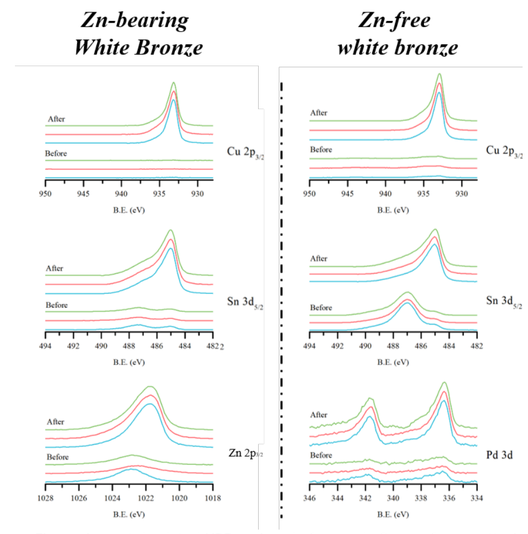

Figure 4 - metal-related XPS regions before and after surface sputtering (renewing) of different samples: 0.5 µm (green curve), 1.0 µm (red curve) and 1.5 µm (blue curve)

Surface of pristine samples showed no copper in the case of the Zn-bearing bronzes. Similarly, the pristine Zn-free bronzes showed a copper content significantly lower than what expected from the analysis of the bulk concentration, whit copper atoms in the form of oxide or hydroxide species. Additionally, surface tin was almost completely oxidised in the Zn-free samples, while a direct comparison with the Zn-bearing ones showed that a larger fraction of tin at the surface was metallic. In these samples, Zn was in the form of oxides. All the examined samples showed metal ratios much different from the bulk, with surface composition defective in copper. Results acquired after the sputtering showed better agreement with the results of the EDS composition for the Zn-free samples. The concentration of Zn and Sn was still noticeable in the Zn-bearing samples, despite a lower extent in respect to pristine samples. Pd content doesn't change significantly after surface sputtering, as its atomic fraction remains in line with the values acquired during EDS experiments. Moreover, all the elements in the bulk were in the metallic state.

Corrosion resistance

Electrochemical corrosion tests were performed first by acquiring the OCP value, and then by linear polarization (Fig.5). A NaCl 3.5 wt.% solution was used as elctrolyte, adjusting the pH to 8 by NaOH. Polarization tests demonstrate a nobler behaviour of the Zn-free samples in respect to the Zn-Bearing, whit smaller corrosion currents. Naked eye and SEM surface characterization was also performed before and after the corrosion process (Fig.6).

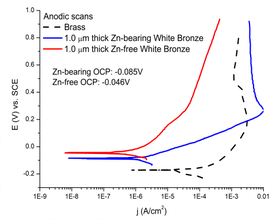

Figure 5 - Pol. Curves for 1.0 mm thick samples

Photography of the surfaces after the corrosion suggested an uniform corrosion mehanism for the Zn-bearing coatings, and almost no corrosion for the Zn-free samples. By SEM image analysis it was possibe to notice the formation on small holes on the Zn-free surface, evidencing some form of localized corrosion process.

Figure 6 - Samples after polarization: Photography (left) and SEM images (right) of the corrosion spots

Photographic evidence was in line whitwhat we can see from electrochemical corrosion tests. Zn-bearing curve displayed comparable currents in respect to the brass substrate (dotted line in Fig.5) due to coating dissolution; this increase in current was not visible for all the Zn-free sample series.

Conclusions:

a) Zn-free coatings showed a very hight content of tin (>37% wt.), which is primarly responsible for their silvery finishing. It is very difficult to find in recent literature a characterization of bronzes whit tin content >20 wt.%;

b) Zn-free coatings were two times slower to deposit in respect to Zn-bearing ones;

c) Zn-free coatings showed better corrosion resistance in respect to the Zn-bearing ones. Thisi is probably due to the formation of a tin oxide barrier in the former, when in the latter we can find metallic Sn (and zinc oxide);

d) No apparent influence of Pd!

Further work will involve **EIS** analysis, **micro- and nano-hardness** and study of **cross-section TEM lamellas**

[1] W. Giurlani, E. Berretti, M. Innocenti and A. Lavachi, **Coating thickness determination using x-ray fluorescence spectroscopy: Monte Carlo simulations as an alternative to use of standards**, Coatings (2019)

Data in the poster is part of an article under review.