



# Corrosion investigation of fire-gilded bronze involving high surface resolution spectroscopic imaging



G. Masi<sup>a,\*</sup>, C. Chiavari<sup>a,b</sup>, J. Avila<sup>c</sup>, J. Esvan<sup>d</sup>, S. Raffo<sup>e</sup>, M.C. Bignozzi<sup>a</sup>, M.C. Asensio<sup>c</sup>, L. Robbiola<sup>f</sup>, C. Martini<sup>g</sup>

<sup>a</sup> Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, via Terracini 28, 40131 Bologna, Italy

<sup>b</sup> C.I.R.I. (Centro Interdipartimentale Ricerca Industriale) Meccanica Avanzata e Materiali, Università di Bologna, Bologna, via Terracini 28, 40131 Bologna, Italy

<sup>c</sup> Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint-Aubin, France

<sup>d</sup> Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux, Université de Toulouse, 4 allée Emile Monso, 31030 Toulouse, France

<sup>e</sup> Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, viale Risorgimento 4, 40136 Bologna, Italy

<sup>f</sup> TRACES Lab (CNRS UMR5608), Université Toulouse Jean-Jaurès, 5, allées Antonio-Machado, 31058 Toulouse, France

<sup>g</sup> Dipartimento di Ingegneria Industriale, Università di Bologna, viale Risorgimento 4, 40136 Bologna, Italy

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## ABSTRACT

Gilded bronzes are often affected by severe corrosion, due to defects in the Au layer and Au/Cu alloy galvanic coupling, stimulated by large cathodic area of the gilded layer. Galvanic corrosion, triggered by gilding defects, leads to products growth at the Au/bronze interface, inducing blistering or break-up of the Au layer. In this context, fire-gilded bronze replicas prepared by ancient methods (use of spreadable Au–Hg paste) was specifically characterised by compiling complementary spectroscopic and imaging information before/after accelerated ageing with synthetic rain. Fire-gilded bronze samples were chemically imaged in cross-section at nano-metric scale (<200 nm) using high energy and lateral resolution synchrotron radiation photoemission (HR-SRPES) of core levels and valence band after conventional characterisation of the samples by Glow Discharge optical Emission Spectroscopy (GD-OES) and conventional X-ray photoelectron spectroscopy (XPS). We have found a net surface enrichment in Zn and Sn after fire-gilding and presence of metallic Hg, Pb and Cu within the Au layer. Moreover, the composition distribution of the elements together with their oxidation has been determined. It was also revealed that metallic phases including Hg and Pb remain in the gilding after corrosion. Moreover, selective dissolution of Zn and Cu occurs in the crater due to galvanic coupling, which locally induces relative Sn species enrichment (decuprification). The feasibility advantages and disadvantages of chemical imaging using HR-SRPES to study artworks have been investigated on representative replicas.

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## 1. Introduction

### 1.1. System under investigation

In outdoor conditions, gilded bronzes (widely used in historical monuments and in architectural elements) are often affected by severe corrosion of the bronze substrate, due to the presence of pores and defects in the gilding layer. In particular, degradation of gilded bronze is induced by galvanic coupling between

bronze and gold. Defects such as thickness variation and pores in the gilding layer are mostly due to the gilding procedure. The main gilding methods used in antiquity were based (i) on the application of gold foil or leaf, (ii) on selective leaching of elements not as noble as gold (the so-called “depletion gilding” method) or (iii) on the use of spreadable gold–mercury amalgam paste, followed by mercury evaporation, as described in several papers [1–3]. In the present paper, the investigation is focused on amalgam-gilded (or “fire-gilded”) bronze for which, after mercury evaporation, the matte gold-rich layer must be “burnished” (*i.e.* plastically deformed and compacted) by a smooth and hard tool (*e.g.* agate stone), so as to obtain a shiny surface [4]. This technological sequence produces a gilding layer with peculiar features. The most relevant characteristic is the presence of residual mercury (usually Hg concentration ranges from about 7 to 10 wt.% in the gilding layer, although values up to 17 wt.% were also reported [4]), but also

\* Corresponding author. Tel.: +39 051 2090361; fax: +39 051 2090322.

E-mail addresses: [giulia.masi5@unibo.it](mailto:giulia.masi5@unibo.it) (G. Masi), [cristina.chiavari@unibo.it](mailto:cristina.chiavari@unibo.it) (C. Chiavari), [jose.avila@synchrotron-soleil.fr](mailto:jose.avila@synchrotron-soleil.fr) (J. Avila), [jerome.esvan@ensiacet.fr](mailto:jerome.esvan@ensiacet.fr) (J. Esvan), [simona.raffo2@unibo.it](mailto:simona.raffo2@unibo.it) (S. Raffo), [maria.bignozzi@unibo.it](mailto:maria.bignozzi@unibo.it) (M.C. Bignozzi), [maria-carmen.asensio@synchrotron-soleil.fr](mailto:maria-carmen.asensio@synchrotron-soleil.fr) (M.C. Asensio), [robbiola@univ-tlse2.fr](mailto:robbiola@univ-tlse2.fr) (L. Robbiola), [carla.martini@unibo.it](mailto:carla.martini@unibo.it) (C. Martini).

Cu–Au interdiffusion due to heating for mercury evaporation [1] and the detrimental influence of alloying elements such as Pb on the gilding process [4] should be mentioned.

In a previous paper [5], we characterised quite extensively a fire-gilded quinary bronze (Cu–Sn–Zn–Pb–Sb) in the as-gilded condition, obtained according to ancient recipes. Specifically, Focused Ion Beam (FIB) milling followed by cross-section observations, both by field emission SEM and by ion channelling contrast with Ga<sup>+</sup>, clearly showed the morphology of the Au-rich layer, partly compacted by burnishing but still retaining sub-micrometric porosity. It was also possible to reveal annealing twins in the recrystallised microstructure of the Au-rich layer, as well as the strain-hardened (hence very reactive) layer in the bronze immediately beneath the gilding. This layer consisted of small grains elongated in the direction of material flow due to mechanical polishing of the bronze before gilding. However, it was not possible to make detailed investigations, mainly due to the limits of the conventional X-ray spectrometry technique using Mg or Al anodes.

As regards the corrosion of fire-gilded bronzes, the Paradise Door (*i.e.* the Eastern door of the Baptistery of Florence, created by Lorenzo Ghiberti, 1425–1452) is a famous example [6]. This masterpiece was exposed to outdoor atmosphere in Florence, Italy, since its production until the Arno flood in 1966. As for many others gilded monuments, such as the horses of Saint Mark's basilica in Venice [7], the growth of corrosion products at the gold/bronze interface (with the formation of characteristic corrosion craters) led to blistering or break-up and loss of the gold layer [6,8]. The corrosion products detected beneath the gold layer in the case of Ghiberti's Paradise Door mainly consisted of copper oxide, basic sulphates and copper carbonates [9], with lesser amounts of chlorides and nitrates [10]. Furthermore, due to the action of acid rains, copper salts also dissolved and diffused above the fire-gilded surface, where brochantite, antlerite, paratacamite and copper hydroxyl nitrate [11] were identified by X-Ray Diffraction and IR spectroscopy. The presence of soluble nitrate-based compounds is often attributed to interaction with the polluted urban atmosphere, but they were also hypothesised to derive from residues of bronze pickling reagents used in the ancient past by goldsmiths before application of the gold-mercury paste, for improving the adhesion of the gilding layer on bronze [11].

The presence of several corrosion products, including hygroscopic compounds at the gold/bronze interface, makes fire-gilded bronzes quite unstable and complex systems [9,12,13], requiring specific restoration and conservation procedures [8]. In particular, cleaning procedures based both on chemical and on laser methods were applied [11,14,15]. After cleaning, conservation actions must be implemented on gilded bronze artworks to ensure their long-term corrosion protection. Both preventive techniques, such as microclimate control [9,16] and use of coatings and inhibitors [12,17,18], were investigated. In order to help microclimate control, specific sensors based on the measurement of galvanic currents in gold/bronze couples proved to be useful in finding the most suitable climatic parameters which ensure negligible corrosion rates [16].

Even if the main phenomenological aspects of gilded bronze corrosion are known, an improved characterisation of this multi-layer system and the involved phenomena of decay is required, in order to pursue a deeper understanding of the corrosion mechanism, which is always a basic requirement for developing effective conservation strategies. Therefore, in the present work the same fire-gilded bronze as in the previous paper [5], was prepared according to ancient methods, so as to mimic the typical microstructure and morphology of amalgam-gilded bronzes. Ageing in conditions closely simulating outdoor exposure in runoff conditions (dropping tests [19]) was applied and these fire-gilded

bronze samples were preliminary characterised by microscopy and micro-spectroscopy techniques (FIB-FEG/SEM, EDS, micro-Raman) [5].

## 1.2. General XPS background

X-ray photoelectron spectroscopy (XPS) has been applied since more than thirty years to ancient bronzes and patinas, in order to analyse the chemical state of elements on the outermost surfaces and (by Ar<sup>+</sup> sputtering) to explore depth profile [20–22]. However, its use in cultural heritage materials science has been initially restricted, due to experimental constraints linked to sample size, analysed area (typically larger than 300 μm in diameter) but also to charge effects linked to weakly conducting surfaces [21,22]. This technique was often coupled to scanning Auger microscopy (Auger electron spectroscopy–AES) as an associate method highlighting the differences in the microchemical composition thanks to a smaller spatial resolution compared to XPS techniques [20–24].

Since the last fifteen years, the improvement in detection sensibility of XPS analyser and to the needs to accurately relate chemical binding to elemental or structural information led to more investigations on synthetic materials to be carried out. These investigations were mainly focused on chemical transformation of polished or artificially corroded Cu–Sn (Zn, Pb) bronzes in different conditions—as for example, in atmosphere under SO<sub>2</sub> or H<sub>2</sub>S gas pollution [25–28], in NaCl aqueous solution [29,30], in soil [31,32], from particular chemical solutions [33,34], but also related to the identification of specific copper or organic products [24,35,36] or on the efficiency of conservation protective treatments [37,38]. On ancient artefacts, XPS investigation was often associated to other analytical techniques (EDS–SEM, XRD, PIXE, SIMS, LA-MS) [31,39–44]. XPS analysis usually were performed on surface fragments, sometimes coupled to depth profile measurement from Ar<sup>+</sup> sputtering [21,22,39,40] or laser ablation [44]. It should be noticed that several studies investigated the effect of X-ray beam or (Ar<sup>+</sup>) ion sputtering on the surface evolution [21,24,26,28,39,41]. They revealed that lead carbonate species as well as copper sulphate or copper oxide can be reduced, which can cause the interpretation of XPS and AES to be problematic for copper species. XPS was also selected conducted on thick corrosion layers from cross-sections [31]. As regards mercury-amalgam plating on ancient bronzes, only very few studies applying XPS have been performed. In [45], surface analysis of several fragments of gilded copper base alloys clearly demonstrated the importance to combine surface analytical techniques helping to refine data on both the manufacturing process and the degradation state.

Recently, a multi-analytical approach including conventional XPS and synchrotron radiation–(SR) based techniques was applied to two leaded bronzes, revealing all the interest for getting mapping of the surface chemistry of the bronze at a sub-micrometric spatial resolution [41,42]. This global approach has been recently extended to synchrotron X-ray photoelectron spectroscopy and X-ray absorption spectroscopy on mercury gilded silver plates, differently coloured according to different applied treatments based on mediaeval writings [46]. This study pointed out the interest to use SR as a highly powerful X-ray source for performing XPS surface measurements.

## 1.3. Aim of the work

In the present paper, the main aim is to evaluate the application of highly energy and lateral resolution synchrotron radiation photoemission (HR-SRPES) for obtaining spatially resolved information on corroded bronze samples at a sub-micrometric level (<500 nm). In particular, special attention was paid to the mapping of chemical species and their state of oxidation. To this aim, state of the art

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