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Full Length Article

Combined use of FE-SEM+EDS, ToF-SIMS, XPS, XRD and OM for the study of ancient gilded artefacts

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ABSTRACT

Gilded brooches dating back to 16th–17th centuries CE were investigated by means of integrated and complementary analytical techniques such as high spatial resolution field emission scanning electron microscopy coupled with energy dispersive X-ray spectrometry (FE-SEM+EDS), time of flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and optical microscopy (OM). The results reveal in detail the surface and subsurface morphology and the chemical features of the micrometric decorative Au layer that has been deposited by means of the so-called fire-gilding technique based on the use of an amalgam. Moreover, the results allow to recognise chlorine, sulphur and phosphorous species as the main degradation agents and to identify the corrosion products naturally formed during the long-term interaction with the burial soil constituents. The findings show also that the galvanic coupling between the two dissimilar metals, i.e. Cu and Au, lead to enhancement of corrosion phenomena causing the spalling of the gold thin film and the disfigurement of the object. From a conservation point of view, the results suggest a targeted use of low-toxic inhibitors to hinder the detrimental role of chlorine as possible responsible of future further severe degradation phenomena. In conclusions, the micro and nano-chemical, structural and morphological investigations in a depth range from a few nanometers to micrometers have revealed the complex nature of corroded surface of ancient gold coated artefacts, highlighting some specific aspects related to their peculiar degradation mechanisms thus extending the scientific relevance of the tailored use of complementary and integrated surface and subsurface analytical techniques for the investigation of ancient coated artefacts.

1. Introduction

Since the beginning of metallurgy, the surface modification of metal objects and their decoration with noble metals has been a relevant activity aimed to improve the metal objects appearance with also fraudulent intent to produce forgeries [1–5]. Various mechanical, thermal and thermo-chemical manufacturing methods even in combination have been used to coat with an Au or Ag leaf, foil or thin film the surface of less precious substrates in order to produce artistic items or commonly used objects giving the impression of a solid silver or gold artefacts or for creating an attractive aspect by using the enchanting effect of the noble metals in combination with other materials [6–9].

The main purpose of the craftsmen was to develop surface modification methods to achieve a long-lasting and strongly adherent Au or Ag layer as thin as possible, in order to save precious metals, as well as to produce coated artefacts able to resist for a long period against wear [5–7,9]. In ancient times, amalgam fire gilding was likely the most sophisticated and a less expensive technology to coat with a micro-metric thin film of Au and Ag artistic or commonly used metal objects. The method was used widely and successfully due to its unique decorative effects, the consistent saving of precious metals, and the consequent increase of profit [3,4,10].

Over time, due to the environmental exposure, the ancient coated objects have been then subjected to different degradation phenomena including the burial that have remarkably modified

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their surface chemical nature giving rise to the formation of corrosion products caused by the often relevant interaction with the surrounding aggressive environmental agents.

Despite many authors have described the corrosion processes occurring in archaeological metal objects, few works regard the naturally grown corrosion products formed onto the gilded objects [10–12]. On the contrary, a wide literature regarding the application of different analytical techniques on ancient gilded art objects is available [13].

The composition of the gold thin film and the manufacturing methods was deeply investigated by using also sophisticated techniques such as particle induced X-ray emission (PIXE), particle induced γ-ray emission (PIGE) and Rutherford backscattering spectrometry (RBS) [14]. Table 1 provides a summary of the principal studies carried out on ancient gilded artefacts and aimed to describe manufacturing techniques and in some cases also degradation/corrosion phenomena.

The corrosion products and phenomena have been recently investigated in details highlighting the role of advanced analytical techniques for the characterisation of the surface chemical composition of corroded gilded objects [1,10–12].

In particular, in a previous work, by means of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy combined with energy dispersive spectroscopy (SEM+EDS) techniques we have studied some naturally corroded gold-coated commonly used copper-based objects such as studs, brooches and clasps dating back to 16th-17th centuries CE [1]. These artefacts were found during the cleaning of the Tiber river in Rome (Italy) and have severely interacted for several hundred years with soil constituents. The achieved information have highlighted the active role of some burial soil species in the metals corrosion phenomena.

With these considerations in mind, we have studied in more details other naturally corroded gilded artefacts in order to identify the role played by some anions such as Cl^- and PO_4^{3-} in the formation of the corrosion products under the gold film that is the major risk factor for the integrity of gilded artefacts. Indeed, the detachment and loss of the thin film of precious metals is caused by the mechanical thrust of the corrosion products growing under the gold thin film. The investigation has been also aimed to locate the presence of the aggressive species in the patina to better understand the interactions of the artefact with the surrounding environment otherwise difficult to identify. All these valuable information can support the tailored selection of long-lasting cleaning and conservation procedures of these relevant witnesses of the ancient art and technology.

2. Materials and methods

2.1. Samples

The gilded brooches were found in Rome (Italy) during the cleaning of the banks of the most important river of Rome (Italy), i.e. the Tiber. The artefacts are dated back to 16th-17th centuries CE and their surface was investigated following a cleaning carried out by using first distilled H_2O and then, CH_3CH_2OH to remove adventitious carbon contamination. The brooches were sampled by taking small representative fragments for the investigation of the layered corrosion products, i.e. the patina, and the underlying metallic substrate. In order to preserve the structure of the patina, the sampled fragments were embedded in a suitable resin for 24 h and carefully micro-sectioned by using a diamond saw, then, the polishing was carried out with different SiC papers gradually increasing until 1200 grit and the last polishing procedure was performed by using diamond pastes up to 0.25 μm.

2.2. Scanning electron microscopy with energy dispersive spectroscopy

Both SEM and FE-SEM investigations were carried out by using a SEM Stereoscan 360 (Cambridge, UK) equipped with a LaB_6 filament and a high-spatial resolution LEO Gemini 1530 (Zeiss, Germany) microscope equipped with a four-sector back scattered electrons (BSE) detector and an EDS INCA 250 and an INCA 450 system (Oxford Instruments Analytical, UK), respectively. SEM and FE-SEM images were recorded by collecting both secondary electrons (SE) and BSE modes at different acceleration voltages up to 20 kV.

Before the analysis, the surfaces of the brooch fragments (in as received conditions after the cleaning or cross-sectioned) were coated with a thin C or Cr film in order to avoid misleading charging effects. The C thin film was deposited by using an Emitech sputter coater K550 unit, a K 250 carbon coating attachment and a carbon containing cord at a pressure of 1×10^{-2} mbar in order to produce a carbon thin film with a nearly constant thickness of about 3.0 nm. The Cr coating was deposited by using a Bal-Tech SCD 500 equipped with turbo pumping for ultra clean preparations at a pressure of 5×10^{-3} mbar in order to produce a chromium thin film with a constant thickness of about 0.5 nm.

EDS quantitative analysis has been carried out at 20 kV beam voltage and the spectra have been processed by using the INCA software. The validity of the quantitative results expressed as weight percent (hereafter wt%) has been demonstrated by analysing large areas (2×3 mm) of polished (nearly atomically flat)

Table 1
Summary of the principal studies carried out on ancient gilded artefacts and aimed to describe manufacturing techniques and in some cases also degradation/corrosion phenomena.

Analytical techniques	Art objects	Aim of the study	Year	Reference
XR, XRD, OM, EPM, XRF	Egyptian bronze figurine of the god Osiris	Degradation and corrosion mechanisms	2002	[15]
PIXE, RBS	Chandelier of the Hildesheim cathedral (Germany)	Degradation and corrosion mechanisms	2008	[16]
PIXE, RBS, SEM-EDX	Floral decoration of armour, Islamic ring, Islamic brooch and coin from the times of Abderraman III	Manufacturing techniques	2008	[17]
OM, SEM-EDS, EDXRF, micro EDXRF	Copper nail and bronze artefact fragments	Manufacturing techniques	2010	[18]
PIXE, RBS	Reliquary from the XVI century, ostensorium from the mid-XVIII century, and ciborium	Manufacturing techniques	2011	[19]
XRF	Silver fibula with a gold central part, Decoration from the Silver Altar in the basilica of the church of the Assumption of Our Lady in Brno	Manufacturing techniques	2012	[20]
SEM-EDS, OM, XPS	Roman and Medieval artifacts coated with thin gold and silver films	Manufacturing techniques and degradation process	2013	[10]
PIXE, PIXE-XRF, SRXRF, ICPMS	Gilt artifacts dating back from ancient Egypt to 19th century	Manufacturing techniques	2013	[21]
OM, SEM-EDS, AFM, XPS	Gilt-bronze artifacts of the Proto-Three Kingdoms Period of Korea	Corrosion mechanisms	2013	[22]
XRF	Gilt artworks	Manufacturing techniques	2016	[23]
SEM-EDS, OM, XPS	Gilded brooches dating back to 16th-17th centuries CE	Corrosion products and mechanism	2016	[1]

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