Tin Deterioration on Polychrome Stone Sculptures of the San Jerónimo Church (Granada, Spain)

/ CAROLINA CARDELL (1*), ISABEL GUERRA (2), AFRICA YEBRA-RODRÍGUEZ (3)

(1) Department of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain
(2) Scientific Instrumentation Centre, Campus Fuentenueva, University of Granada, 18071 Granada, Spain
(3) Department of Geology-Associated Unit IACT (CSIC-UGR), Faculty of Experimental Science, University of Jaén, Campus Las Lagunillas s/n, 23071 Jaén,Spain

INTRODUCTION

The church of San Jerónimo monastery is one of the most important examples of Spanish Renaissance thanks to the architect and sculptor Diego de Siloé, who worked there from 1528 to 1543. In its interior Siloé executed the crossing and the architectonical stone sculptural group placed in the upper apse. It seems that these sculptures were polychromed in the 18th century using the *temple* technique (Cardell-Fernández & Rodríguez-Gordillo, 2003). The substrate of the polychromes is a biocalcarenite (limestone) made of sand-size grains of fossils (Cardell 1998). This stone was covered with a gypsum-based preparation followed by one or two clay-rich primer layers (also containing calcite, quartz and white lead –mainly hydrocerussite), overlaid with diverse painting color layers (lead white, raw and burnt Sienna pigments, red ochre, yellow ochre and smalt) including gold and tin sheets.

The weathering of the paintings is alarming, mainly due to the presence of gypsum and clay minerals which are very absorbent of humidity, leading to the formation of lead chlorides and *Tutton* salts (double salts with formula $M_2M'(SO_4)_2(H_2O)_6$, e.g. $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$) due to reactions between pigments and infiltration water (Cardell-Fernández & Rodríguez-Gordillo, 2003). As a consequence, painting detachments and micro-fissures are very abundant, as are the formation of bowl like shapes in those parts of the polychrome containing tin layers (Fig. 1).

The literature reports two types of decay affecting tin-base objects: i) atmospheric corrosion in the form of oxidation of tin with SnO (romarchite) and SnO_2 (cassiterite) as the main corrosion products, and ii) the so-called *tin pest* which is the allotropic transformation of the tin crystal structure from white metallic β form (tetragonal) into the grey powdery non-metallic α form (cubic) that takes place ca. 13.2 ^{0}C (MacLeod, 2005). The allotropic transformation is influenced by the metal microstructure (increasing with decreasing grain size) and presence of impurities that either delay/hinder the transformation (e.g. Sb, Bi, Pb, Ag, Cd) or accelerate it (e.g.. Al, Zn, Ge, Cu). On the other hand, tin oxidation increases with addition of elements such as Fe, Pb, Mn, Sb and Bi, and decreases with Zn or P (Chiavari et al., 2006).

***fig 1**. Paint stratigraphy: from inner to outer: gypsum base, clay-rich prime, gypsum layer with dissolution pores and re-crystallized gypsum (arrow-like crystals), clay-rich layer and tin coat exhibiting bowl-like shapes and detachments. Transmitted light and crossed nicols. Bar = 0.5mm.*

In this work we present preliminary results of the composition and microstructure of tin layers used as decoration in polychromed stone-sculptures, and the corrosion products, to improve understanding of the decay processes affecting tin-rich paintings.

EXPERIMENTAL

Fresh and decayed tin samples were characterized at nano- and microscale using a combination of complementary analytical techniques. Crystalline phases were identified with X-ray diffraction (Bruker D8 Powder Advance diffractometer). Chip samples were analyzed after placing them onto a zero-background silicon plate with no preparation. Diffraction data were recorded using Cu Kα radiation, operated at 40 kV, 40 mA, 0.02 deg step size and 20 s integration time. Diffraction patterns were scanned over a $20° < 2\theta < 90°$ range. Minerals were identified using the *XPowder* software and the PDF2 database (Martín-Ramos, 2004). Samples were also prepared as polished thin sections and studied with optical polarizing microscopy (OM) using an Olympus BX60 and with a scanning electron microscope coupled with EDX microanalysis (Inca 350 version 17 Oxford Instrument, VP-SEM Leo 1430VP). SEM-EDX working conditions were 500 pA filament current, 20 keV beam energy, and 10 eV/ch resolution for pinpoint analyses, and 1 nA filament current and 20 eV/ch resolution for map acquisition. High-resolution maps (1024 x 768 pixels) were obtained with 500 frames and 10 ms dwell time. Mineral maps were compiled from elemental distribution maps by applying the *Phasemap* tool. This technique highlights the location, morphology and composition of mineral phases in paint stratigraphy.

Also tin samples were studied at nanoscale by transmission electron microscopy (TEM) using a Philips CM20 equipped with EDAX solid-state ultrathin-window energy dispersive X-ray (EDX) detector. The acceleration voltage was 200 kV, and the lens aperture 40 µm. Identification of mineral phases was done collecting selected area electron diffraction (SAED) patterns. Prior to TEM analysis, particles were dispersed in ethanol, sonic-vibrated for 30 s, and placed on Formvar© and C-coated Cu grids.

palabras clave: Corrosión estaño, Policromías, SEM-EDX, XRD.

key words: Tin corrosion, Polychrome, SEM-EDX, XRD.

* corresponding author:cardell@ugr.es

RESULTS AND DISCUSSION

Decayed tin layers show tarnishing at the surface at macroscopic scale and the formation of dark grey pustules, pinholes, cracks and bowl-like shapes/detachments. OM and SEM investigation show that several tin layers were applied in the polychrome on top of a layer rich in gypsum and calcite and a clay-based layer (Fig. 1). More in detail, the SEM study reveals that these tin layers display different degrees of weathering. Thus, there is a less-altered tin layer showing a more porous compact structure with polygonal fissures and scarce dark grey rounded stains, and a heavily altered dark grey tin layer, as shown in Fig. 2.

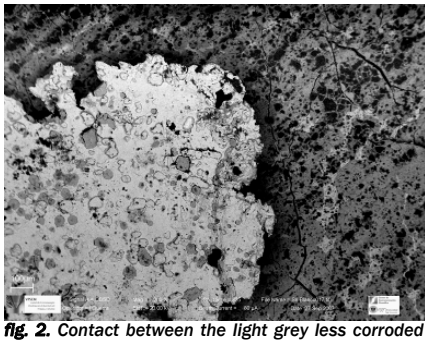

fig. 2. *Contact between the light grey less corroded and the intensely altered dark grey tin layers.*

In the brightest areas (fresher areas) of the light grey layer only Sn was found with SEM-EDX and XRD. Also, SEM analysis shows that solely in these fresh areas tin whiskers formation take place (Fig. 3). Tin whiskers are needle-like form conductive crystals that grow naturally from pure tin or high tin finished surfaces and are related field failures (Fang et al., 2006).

fig.3. *Tin whiskers extruding from polygonal cracks.*

According to XRD, grey areas are made of SnO (romanchite) (see small spots in Fig. 3), while in the darker grey rounded stains (Fig. 3), SEM-EDX identified diverse elements other than Sn, e.g. Pb, Fe, Al, Ag, Sc, S, Al... In the most corroded parts the XRD study identified romanchite and $ZnSnAs_2$.

In the heavily altered tin layers the weathering process is more intense, as can be seen in Fig. 4 which is a false color map obtained with the *INCA Phasemap*tool of the VP-SEM based on SEM–EDX elemental mappings: the green color corresponds to unaltered Sn, the blue color to tin oxide areas and the red color marks zones rich in tin and sulphur. In this layer tin-rich chlorides also were found with SEM-EDX and identified as abhurite, $Sn_3O(OH)_2Cl_2$.

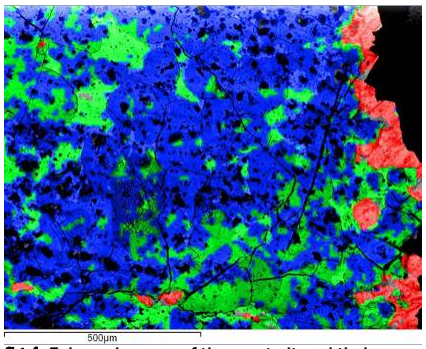

fig.4. *False color map of the most altered tin layer.*

A false color map of a paint stratigraphy is shown in Fig. 5. Here it can be seen that tin layers at the surface are made of Sn (green color) while the inner tin layer (blue) is composed of tin oxide. The red spots are made of tin-rich chlorides, while the pistachio color corresponds to the calcite/gypsum preparation layer and the violet color to quartz grains.

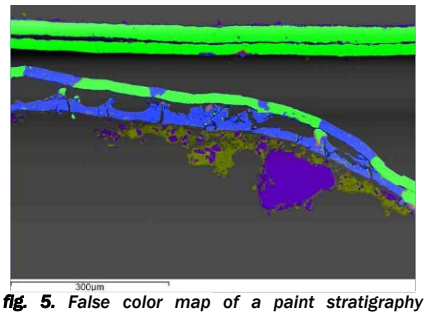

fig. 5. *False color map of a paint stratigraphy showing the fresh (light grey/green) and oxidized (dark grey/blue) tin layers.*

TEM analyses corroborated the presence of tin β (Fig. 6) and tin oxide in the fresh and oxidized areas respectively.

In summary, the combined analytical techniques used in this work (OM, SEM-EDX, TEM) have allowed a good characterization of the tin layers used in the polychromes of San Jerónimo church (Granada, Spain), as well as their oxidation and corrosion processes and products. Identifying the nature of tin weathering is of key relevance for restoration and conservation of these polychromes since while tin oxidized areas can be treated, those objects suffering from *tin pest* cannot be reconstituted. However, the *tin pest* process was not possible to be established with these analytical techniques. Therefore other more sophisticated techniques will be applied, such as the structural and chemical analyzer SCA, which is a tandem Raman spectroscopy and VPSEM-EDX.

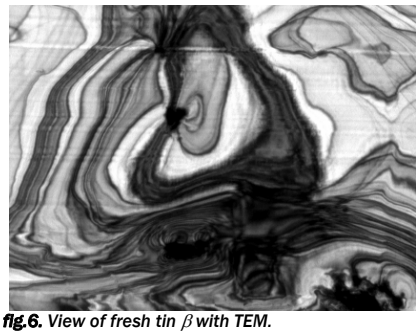

fig.6. *View of fresh tin β with TEM.*

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REFERENCES

Cardell, C. (1998): Cristalización de sales en calcarenitas: aplicación al monasterio de San Jerónimo, Granada. Tesis Doctoral, Universidad de Granada. 219p.

Cardell-Fernández, C. & Rodríguez-Gordillo, J. (2003): Policromías de la Iglesia del Monasterio de San Jerónimo de Granada: composición, alteración y técnicas de ejecución. Bol. Soc. Esp. ***26****, 113–121.*

MacLeod, I. (2005): The decay and conservation of museum objects of tin. Studies in Conservation, ***50****, 151-152.*

Chiavari, C. Martini, C. Poli, G. & Prandstraller, D. (2006): Deterioration of tin-rich organ pipes. J. Mater. Sci. ***41****, 1819-1826.*

Martín-Ramos, J.D. (2004): Using XPowder: A software package for Powder X-ray diffraction analysis. www.xpowder.com, (GR 1001/04. ISBN 84-609- 1497-6).

Fang, T. Osterman, M. Mathew, S. & Pecht, M. (2006): Tin whisker risk assessment, Circuit World ***32****, 25-29.*