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When gold stops glittering: corrosion mechanisms of René Lalique's Art Nouveau jewellery

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Art Nouveau jewellery created by René Lalique is presently corroded. To identify the corrosion processes, Au–Ag–Cu alloys with compositions comparable to those used in René Lalique's jewellery were fabricated to be exposed to sulphide-containing environments. Using SEM-EDS, XRD, UV-Vis spectroscopy and ellipsometry, it was for the first time demonstrated that at the surface of tarnished Au alloys forms a corrosion film with a layer-by-layer structure. Considering the complex refractive indices of bulk Cu and Ag oxides and sulphides, a two-step corrosion mechanism was proposed. The formation of Cu-based compounds during the early corrosion stages is followed by the formation of Ag-based compounds. The thickness of the formed film, shown for one of the gold alloys to be 80 nm, is due to the corrosion kinetics controlled by the presence of Au and by the formation of a Au–S self-assembled monolayer. The corrosion mechanism of gold alloys raises a new conservation challenge concerning the removal of nanometric layers.

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1. Introduction

When modified by atmospheric corrosion, gold alloys have a dull appearance and undergo a colour variation from red to brownish-black. The corrosion process might, with time, cause damage to objects.^{1–3} Surface modification has a direct impact on the aesthetic perception that the public has of the objects exhibited in museums. An example of this situation is the collection of Art Nouveau jewellery created by René Lalique (1860–1945) exhibited at the Calouste Gulbenkian Museum in Lisbon.⁴ Currently, over fifty of the eighty jewels show more or less large coloured areas with different appearances. For example, the corsage ornament Serpents (Fig. 1) in gold and enamel, shows red coloured areas (Fig. 2).

The coloured corroded gold alloy surfaces have been mainly ascribed to the presence of Ag₂S,³ an expected corrosion product, as sulphur-based compounds, such as H₂S and SO₂, are current pollutants in museum environments.^{5,6} Other corrosion products such as CuS, Cu₂S, Ag₂O, AuAgS and Ag₃AuS₂ have also been identified in the corroded layers of objects made from gold alloys exposed to high sulphide

containing atmospheres.^{7–9} The dependence of the colour variation on the corrosion layer thickening was also emphasised. For high-purity gold (Au > 99 wt%) 5–350 nm thicknesses were



Fig. 1 Corsage ornament Serpents created by René Lalique in 1903–1904 (Acc.n.1216), Calouste Gulbenkian Museum, Lisbon (photography M. F. Guerra). This is one of the most representative René Lalique's creations, who applied materials like enamels, stones and mother of pearl on silver and gold substrates.^{11,12}

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