Experimental report

01/07/2016

Proposal:	**1-03-29**	**Council:**	10/2014
Title:	Corrosion kinetics of AgCu alloys exposed to sulphur containing atmospheres		
Research area:	Chemistry		

This proposal is a new proposal

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Local contacts:	Robert BARKER

Samples: Quartz/MPTS/Au/AgCu alloy in S2- solution

Instrument	Requested days	Allocated days	From	To
FIGARO	4	3	06/11/2015	09/11/2015

Abstract:

The aim of this proposal is to identify and fully describe the corrosion kinetics of AgCu alloys relevant to artefacts of archaeological and cultural heritage significance. This is impossible with other surface analytical techniques due to the estimated corrosion layer thickness (in the order of 100 nm). The present proposal considers dynamic in situ specular NR measurements of the corrosion behaviour of AgCu alloy films in S2- environments. The AgCu films will be electrochemically deposited in situ from deep eutectic solvent medium (1choline chloride, 1Ch+Cl-: 2ethylene glycol, EtGly) with CuCl and AgCl. The corrosion studies will be carried out by exposing the AgCu alloys to sulphide solutions of varying concentrations. The outcomes of this first approach will allow establishing a method for studying more complex systems as based gold ternary AuAgCu alloy corrosion studies.

ILL proposal: 1-03-29, 6th to 9th November 2015

Experimental team: Virginia Ferreira; Isabel Tissot, Emma Palin; Andrew Ballantyne

Title: **Corrosion kinetics of AgCu alloys exposed to sulphur containing atmospheres**

Proposed:

The Au-Ag-S compounds present on the thin film layer (estimated in the order of 100 nm) of corrosion products formed over time on cultural heritage ternary gold alloys (Au-Ag-Cu) are difficult to identify by the most standard surface techniques SIMS, XPS, XRD and Raman. The presence of Ag_2S and Ag_3AuS_2 and (AuAg(S,Se)) could however be identified by grazing XRD, which suggested that different phases of corrosion could occur. As the chemical reactions undergone by Ag-Au sulphides are still insufficiently studied to establish a direct relation between sulphide formation and corrosion development, we proposed as a starting point of this investigation that aims to define future conservation strategies for gold objects, the study by specular neutron reflectivity (NR) of the corrosion kinetics of Ag-Cu binary alloys. The corrosion kinetics of Ag-Cu alloys in sulphur environments is indeed poorly understood, only some corrosion products could so far be identified by XRD, XPS, IRRAS/QCM and SIMS. The data obtained for one of the main atmospheric corrosion pollutants and the most important metals in the gold alloys will allow a new strategic approach to the corrosion mechanisms of ternary gold alloys.

Performed measurements:

We have performed *in situ* kinetic NR measurements during the corrosion process of AgCu alloys exposed to sulphur containing solutions (Na_2S) with different concentrations (1-10 mM). The AgCu alloys were previously deposited, *ex situ*, on Au coated quartz blocks, from deep eutectic solvents prepared from 1 choline chloride : 2 ethylene glycol, containing 9 mM of AgCl and 1 mM of $CuCl_2$.
Due to constant film change during corrosion, such NR measurements were necessarily made at one incident angle but, by focusing on low q features and maximizing flux (by restricting lambda range and resolution), adequate statistics to ascertain fringe positions and film thicknesses can be obtained in tens of seconds from data in the range $0.009 < q / Å^{-1} < 0.08$. The data was acquired in slices of 10 s. Additionally, before and after corrosion, the alloy films were characterised in longer timescale measurements at 2 angles (full q-range) providing precise details of final ("as grown") and “corroded” film structure, composition and solvation. Moreover, similar measurements were performed for silver and copper single metal films, for which a 2.5 mM Na_2S solution was used for corrosion studies.
In addition to the NR measurements, the Au and corroded AgCu surfaces have been morphologically characterised by atomic force microscopy in order to obtain roughness values for data fitting as well as AgCu film thicknesses after reaction.

Outcomes and findings:

The corrosion process starts immediately from the moment the metal surface contacts with the Na_2S solution. To overcome this situation, it was used an inverted cell that allowed the cell filling after the alignment. However, the film surface was sensitive to the filling process and the Ag and the AgCu films developed a heterogeneous corrosion layer showing the filling pattern which correspond to the formation of a corrosion film with distinct thickness (Figure 1a). Also, due to the corrosion process, some of the AgCu and the Cu films peel off the surface during the experiment being impossible to characterise those films after corrosion (Figure 1b). For this reason, the first qualitative analyses was carried out by comparison of the NR profiles of the AgCu films before and after corrosion at t=600 s, value selected to allow the comparison between the different films before peeling the surface.

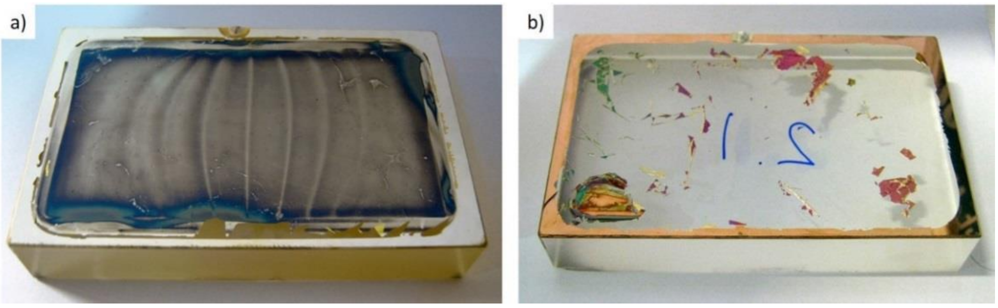

Figure 1 – a) Corroded AgCu film showing the filling cell pattern b) Corroded Cu film that peel off the surface.

As shown in figure 2, the NR profiles obtained for the different AgCu films before corrosion presents accentuated differences, with the exception to the films 1.2. and 1.3. These differences are related to the quartz and gold substrate and do not allow the direct qualitative comparison between films.

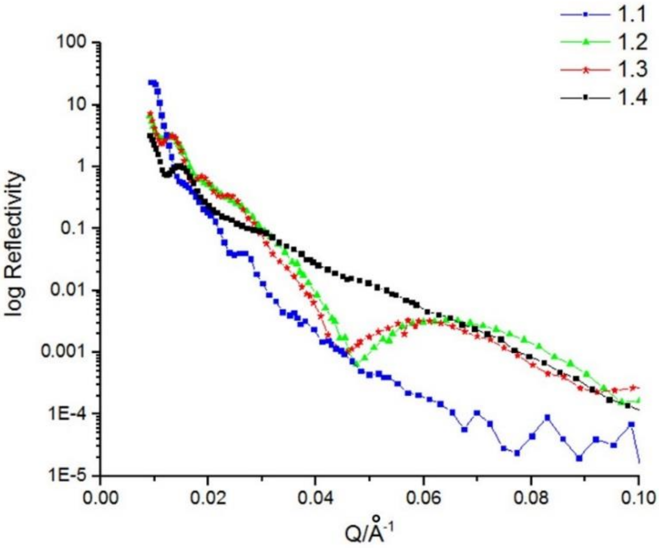

Figure *2* – R(Q) profiles of the four AgCu films before corrosion.

Figure 3 show the NR profiles obtained for the AgCu films before and after corrosion in Na_2S solutions with different concentrations at t = 600 s. The NR profile of the AgCu film corroded in the 1 mM solution is almost similar to the film before corrosion suggesting the corrosion rate is slow at this concentration. With the increase of the S^{2-} concentration the differences in the reflectivity profile are more pronounced suggesting the corrosion rate increases with the S^{2-} concentration, as expected. This behaviour is clearer for the films corroded in the solutions at 2.5 mM and 5 mM. Also the fringe~~s~~ definition decrease suggests an increase of the surface roughness which can be related to the formation of corrosion products. Moreover, at low Q values, the fringes shift to lower values, suggesting a decrease of film thickness.

Considering the NR profiles obtained for the AgCu films the 2.5 mM solution was chosen to carry out the corrosion study of pure metals (Cu and Ag) aiming to investigate the contribution of these elements on the corrosion development of the AgCu films corrosion.

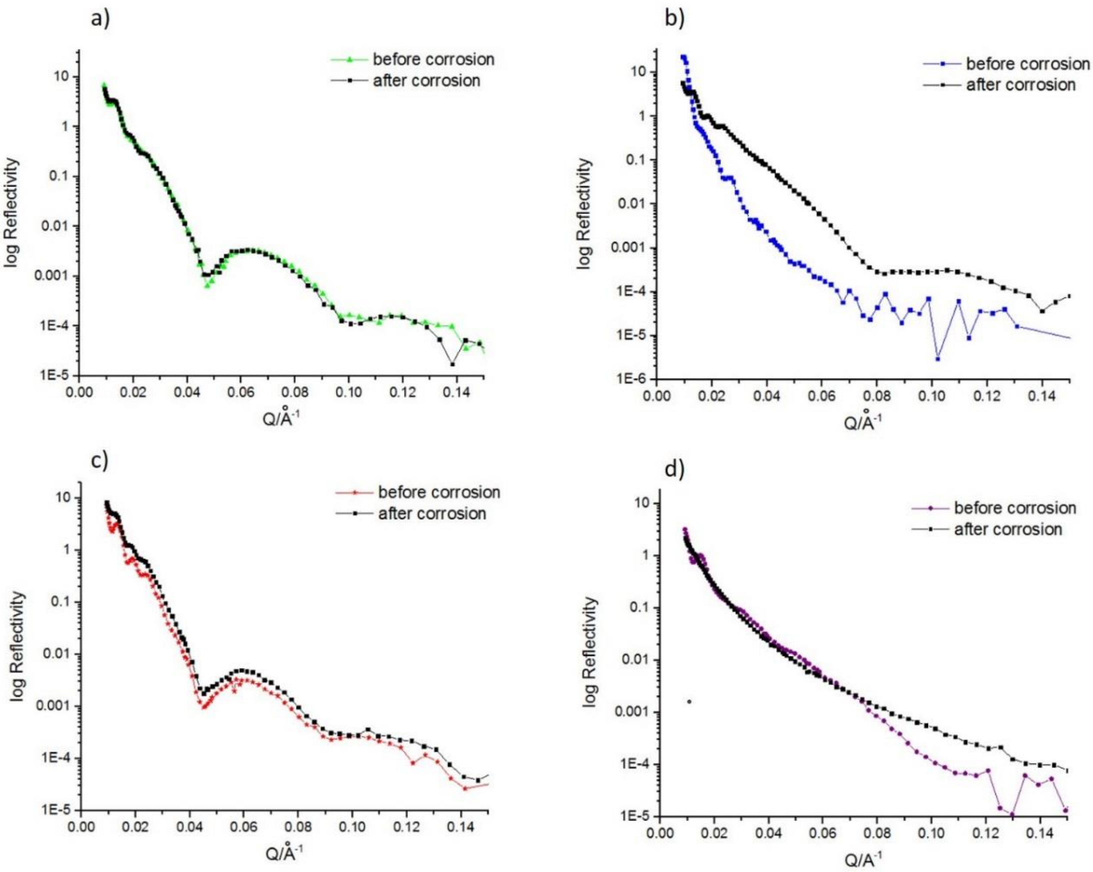

Figure 3 - R(Q) profiles of the four AgCu films before and after corrosion (t = 600 s) in a a) 1 mM b) 2.5 mM c) 5 mM and d) 10 mM Na_2S aqueous solution.

The NR profiles for the Cu and Ag films before and after corrosion are presented in figure 4. The corroded Cu film profile shows a reflectivity increase and a fringe widening which is more accentuated for Q < 0.03 Å^{-1}. The corroded Ag film has a distinct behaviour with a decrease of the reflectivity and the definition of new fringes at Q > 0.03 Å^{-1} possibly related to the corrosion products formation.

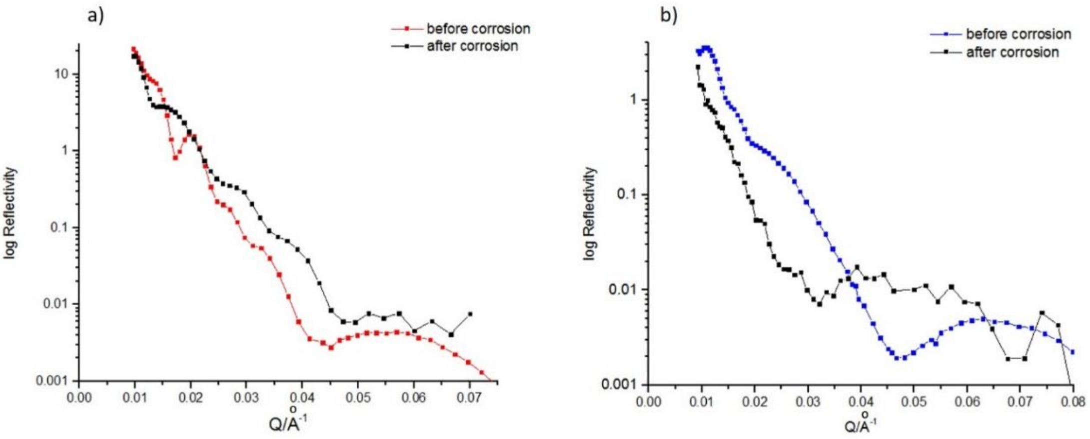

Figure 4 - R(Q) profiles of a) Cu and b) Ag films before and after corrosion (t = 600 s) in a 2.5 mM Na_2S aqueous solution.

These are preliminary results and data is now being fitted in order to identify the corrosion products and mechanisms and the corroded films characteristics.