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Characterization of brass alloys aged at open circuit potential in neutral solutions

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Since centuries, brass (Cu-Zn alloys) are used as material for wind instruments due to the ease of manufacturing, their high corrosion resistance and their good acoustic properties [1]. Contemporary musical practice intends more and more to play original instruments in concerts, following the "historically informed performance practice" (HIP). When historical instruments get regularly played, the main concern of museums and conservators is corrosion of the brass instruments due to the high humidity inside the instruments formed during playing [2] that might damage the artefacts on long-term. The aim of the multi-disciplinary project was to get an insight in the corrosion of brass used for the wind instruments. The project will provide the conservators the necessary information on the corrosion rates that might be expected inside the instruments and to check if preventative methods (e.g. drying the instruments with warm air) are effective.

The actual corrosion state inside the ancient instruments can be determined with non-destructive and portable techniques. In previous works [1, 3] a small electrochemical sensor was developed and used to assess corrosion potentials (OCP) and corrosion rate (i_{corr}) on tuning slides of different brass instruments before and after being played. Full interpretation of the results requires knowledge of the surface state at the point of measurement inside the historical instruments [1] – thus a clear relation between electrochemical and surface analytical information is needed.

The scope of this work was to establish this relation combining electrochemical and surface analytical techniques. Model brass alloys with 18 to 37% of zinc were exposed for 1, 3 and 16 hours to solutions simulating the environment that could be present inside the brass wind instruments during and after playing: a diluted phosphate buffer solution (pH 7) and, more aggressive, an artificial saliva solution [4]. The ageing process was investigated with electro-chemical measurements such as open circuit potential (OCP), linear polarization resistance (Rp), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results showed that corrosion rates were, as expected, initially higher in the artificial saliva compared to the phosphate buffer solution. With prolonged exposure (ageing) to the artificial saliva the OCP values became more positive and the corrosion rate decreased strongly.

X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES) surface analytical techniques were used to characterize the surface state of the same brass samples before and after the contact to the solutions. X-ray photoelectron spectroscopy

(XPS) is particularly well suited for characterizing cultural heritage artefacts because it is non-destructive, has excellent surface sensitivity in the nanometre depth range, can identify the elements and their chemical state. For brass this is however more complex. As it is well known both copper and zinc do not show a chemical shift in the XPS Cu2p and Zn2p signals, distinction between the metallic and oxidized state is not possible [5]. Thus first an analytical method based on the X-ray excited Auger signals CuLMM and ZnLMM to identify the chemical state of copper and zinc was developed. Based on standards where the XPS Me2p and XAES MeLMM spectra were measured, an analytical procedure was developed that allows the quantitative analysis of thin-layered systems on brass alloys [5].

Based on the chemical state plots of copper and zinc the different surface state of brass can be clearly distinguished: mechanically polished alloys showed a thin ZnO and Cu_2O film on the surface, “as received” samples of the model brass alloys showed natural cupric oxide and hydroxides and ZnO layers while ancient artefacts exhibited the presence of a thick altered layers mainly constituted by oxides, hydroxides and carbonates. This different surface state allowed us to partially explain the results of the electrochemical measurements carried out inside the instruments [1]. In this work, prolonged exposure to the artificial saliva solution formed a thick surface film composed of CuSCN and $Zn_3(PO_4)_2$, in phosphate buffer solution pH 7 only thin films mainly Cu_2O, CuO and $Zn(OH)_2$ were detected. Thus the decrease of the corrosion rate with the immersion time of brass alloys in artificial saliva can be explained with the formation of a protective film on the surface.

Surface analytical (XPS and XAES) and electrochemical experiments on laboratory samples with known surface state are on going in order to create the necessary basis to correlate the results of electrochemical measurements inside the historical instruments to the otherwise not directly accessible surface state.

References

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