



Characterisation of a centuries-old patinated copper roof tile from Queen Anne's Summer Palace in Prague

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ABSTRACT

This paper presents an in-depth characterisation study of the patina formed on a copper tile taken from the roof of Queen Anne's Summer Palace in Prague after > 300 years of exposure to the action of the atmosphere. A wide variety of techniques have been used, including metallographic and chemical analysis (electrogravimetry, AAS, XRF) of the copper matrix, and spectroscopic and microscopic investigations (GIXRD, FTIR, TEM/EDS and SEM/EDS) to determine the composition and structure of the patina. The major conclusions of the study are: (a) the base copper contains abundant inclusions mainly of rosiaite (PbSb_2O_6); (b) the patina is formed by an inner sublayer of cuprite (Cu_2O) and an outer sublayer of brochantite [$\text{Cu}_4\text{SO}_4(\text{OH})_6$] and antlerite [$\text{Cu}_3\text{SO}_4(\text{OH})_4$] and traces of azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$]; and (c) the brochantite/antlerite crystals are randomly doped with Fe and Cu.

1. Introduction

Copper and its alloys are important functional materials that are widely used in indoor and outdoor environments. Due to their inherent resistance to atmospheric corrosion and the formation of an aesthetically pleasing corrosion product layer (patina), these materials have for centuries been used in architectural and cultural applications such as statues, sculptures, ornaments and monumental buildings, e.g. copper roofs on castles and churches, frontages, facades, and gutters.

There is abundant literature on the atmospheric corrosion of copper and its alloys, and much information is available on copper patina formation mechanisms in the short, mid and even long term. Thorough reviews of the atmospheric corrosion of copper have been carried out by several researchers, including recent general reviews of this topic by de la Fuente et al. and Hedberg et al. [1,2].

Numerous studies of copper patina formation in atmospheric conditions report the formation and growth of copper (I) oxide, cuprite (Cu_2O), as the initial corrosion product. Its growth rate, thickness and physical barrier properties are subject to the prevailing environmental conditions. In environments rich in SO_2 the patina gradually acquires a greenish appearance related to the formation of sulphur-rich corrosion products which form locally and grow on top of the Cu_2O layer. The growth rate and chemical composition of these corrosion products are dependent on the prevailing pollution levels, and the predominant corrosion products in this surface-adhering patina are relatively stable

and of poor solubility. The resulting patina acts as a protective barrier to the underlying copper object for long time periods [3].

Studies of the long-term atmospheric corrosion of copper (100 years or more) are very scarce. The literature contains a number of studies carried out on architectural or cultural artefacts (sculptures, bells and works of art), either on the items themselves or on samples taken from them. Perhaps the most widely reported is the study carried out on 100-year-old samples obtained during the restoration of the Statue of Liberty in New York [4] and the study of FitzGerald et al. [5] on old patinas (from 7 to 332-year-old samples). Thus it is of great interest to undertake an in-depth characterisation of the patina formed on a copper tile that was exposed to the atmosphere for > 300 years on the roof of Queen Anne's Summer Palace in Prague, as presented in this paper. Other studies referring to the same copper tile have been published elsewhere [6–8].

The aim of this study has been to determine the characteristics of the base copper used to produce a roof tile in the 16th century (1563) and the nature of the corrosion products formed on the copper in changing atmospheric conditions during the tile's lifetime in service on the palace roof.

2. Queen Anne's Summer Palace. Historic Background

Queen Anne's Summer Palace, also known as Belvedere, was built to the orders of Ferdinand I for his wife, Queen Anne, between 1538 and

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Fig. 1. View of the Royal Summer Palace in Prague.

1560 at the eastern end of the Royal Palace Gardens in Prague (Fig. 1). The Summer Palace was intended to house events organised for the entertainment of the court and as a feature to enhance the pleasure of a visit to the gardens. It is perhaps the most remarkable renaissance building in Prague. It was designed by Paolo Della Stella in 1535–1537 but was not completed until 1558–1563 under the direction of the architect Bonifaz Wohlmut. The building is surmounted by an extraordinary curvilinear copper roof which was completed in 1563. According to existing records, the initial copper plates were produced by the Hungarian company Banská Bystrica [9].

The Summer Palace has undergone a number of renovations [7,9,10], the most important being: (a) after the attack of Swedish troops in 1648, extensive rebuilding was carried out in 1688, on this occasion using copper roofing sheets produced by the company Kutná Hora [8]; (b) in the late 18th century the Summer Palace was placed at the disposal of the Austrian army and after it left in 1836 the building was thoroughly refurbished; and (c) extensive rebuilding work was performed after a fire in 1989 where part of the building was damaged.

The study presented in this paper was carried out on a fragment of a copper tile removed from the palace roof during the fire incident in 1989. It was given by Dr. P. Holler of G.V. Akimov's State Research Institute for the Protection of Materials (SVUOM) to one of the authors during a visit to the Institute. It is difficult to specify the exact date when this tile was first placed on the palace roof. It may initially have been laid in the final stages of building work in 1563, or it could have been incorporated during any subsequent renovation work involving the roof. Kreislova and Geiplova consider that the tile, whose initial thickness was 0.8 mm, has been exposed to the atmosphere for 325 years [7]. In a recent paper by Chang et al. [8] it was considered that the copper tile had been exposed during 425 years.

3. Experimental

3.1. Chemical Analysis and Metallographic Studies of the Base Copper

On a $1 \times 1 \text{ cm}^2$ sample of the tile fragment, from which the patina was previously fully removed from the substrate, quantitative chemical analysis was performed by wavelength dispersive X-ray fluorescence emission spectroscopy (XRF) using a Bruker S8 Tiger unit. The analysis was performed without patterns and based on fundamental parameters using QuantExpress analytical software, employing a sample holder with a 23 mm mask. The copper sample was analysed together with a reference material of similar characteristics to the test sample.

Shavings of the substrate were subsequently taken and used to carry out chemical analysis in order to determine the content of the following

elements: Cu, Ag, Pb, Sb, Fe, Ni, Mn, Cr and Al. The electrogravimetric method was used to assess the Cu content, while the content of the other elements and any copper remaining after electrolysis was determined by atomic absorption spectrometry (AAS) using a VARIAN FS220 spectrometer. Finally, the S content was determined by combustion in an induction furnace and subsequent detection by infrared absorption.

The metallographic study of a $1 \times 1 \text{ cm}^2$ sample of the tile fragment was carried out on metallographic specimens obtained for transverse and longitudinal sections. Microscopic observation was performed using a Nikon model Epiphot 300 polarised light optical microscope equipped with an Infinity 2 camera.

3.2. Patina Composition

X-ray diffraction (XRD) measurements were carried out with a Bruker AXS D8 diffractometer in both grazing incidence condition (GIXRD) at an angle of incidence of 1° and conventional θ – 2θ scanning. In the setup used, an X-ray Co tube ($\lambda = 1.78897 \text{ \AA}$) is equipped with Goebel mirror optics to obtain a parallel and monochromatic X-ray beam. A current of 30 mA and a voltage of 40 kV were employed as tube settings. Operational conditions were selected to obtain X-ray diffraction diagrams with sufficient counting statistics. XRD data was collected between 15 and 70° with a step size of 0.02° and a counting time of 5 s/step. To obtain information on the evolution of the phase fractions in the patina as a function of depth, the patina was progressively removed manually with a 2000 mesh SiC paper, and subsequent X-ray measurements were performed under the same conditions. Quantitative determination of phases in the patina was done by the Rietveld fitting method, a powerful tool for calculation of structural parameters from diffraction patterns of polycrystalline materials. In order to eliminate the instrumental contribution to peak broadening, instrument functions were empirically parameterised from the profile shape analysis of a corundum sample measured under the same conditions. In this study, version 4.2 of the Rietveld analysis programme TOPAS (Bruker AXS) has been used for XRD data refinement. Refinement analyses were carried out using space group and crystallographic information for Cu, cuprite, brochantite, rosielite (PbSb_2O_6), antlerite and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) obtained from Pearson's Crystal Structure databases [11]. The refinement protocol also included the background, zero displacement, scale factors, peak breadth, unit cell parameter and texture parameters. The quality and reliability of the Rietveld analysis were quantified by the corresponding figures of merit: the weighted summation of the residual of the least squares fit, R_{wp} ; the statistically expected least squares fit, R_{exp} ; the profile residual, R_p ; and the goodness of the fit (GoF) (sometimes referred to a chi-squared) [12]. Since $\text{GoF} = R_{\text{wp}}/R_{\text{exp}}$, a $\text{GoF} = 1.0$ means a perfect fit.

One by-product of GIXRD is that the area illuminated by the beam can be significantly larger than the sample used for the analysis ("beam spill-off"). The use of parallel beam optics guarantees that the beam length and penetration depth can be fixed during the scan by the incident angle setting. Although quantitative phase analysis can be performed in this condition, as the irradiated volume remains constant, the diffracted beam signal may include information from the edge of the sheet used for XRD. In this work a slit of 1 mm and an incidence angle of 1° were used, and the length of the beam illuminating the sample was about 50 mm, with which a small amount of Cu was observed in the diffractograms recorded in the outermost layers under the grazing incidence condition.

To know more about the in-depth characteristics of the crystallites forming the patina layer, a powder sample of the outer portion of the patina was obtained by smooth abrasion and studied by transmission electron microscopy (TEM). The sample was ultrasonically dispersed in n-butanol and transferred to carbon-coated nickel grids. Crystal-by-crystal chemical composition was determined by energy-dispersive spectrometry (EDS) carried out on a JEOL JEM300FEG microscope

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