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New insights into the manufacturing technique and corrosion of high leaded antique bronze coins☆

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ABSTRACT

Selected ancient Greek bronze coins held in the Coin Collection of the Kunsthistorisches Museum Vienna (KHM) were studied concerning their preservation and conservation. The coins had been minted during the Roman Imperial time (50 to 280 AD) using alloys with high lead and/or tin contents. Today a number of these highly leaded bronze coins, altogether different singular pieces, show progressive whitish corrosion in spots or well-defined areas on their surfaces. Different analytical techniques were used for the documentation and study of the different states of corrosion, the corrosion phases developing in the whitish parts as well as the cause of the specific corrosion phenomena.

Further studies focused on the analysis of the corrosion phases – combining results from μ-XRD and neutron diffraction investigations – as well as on the manufacturing techniques of the antique Greek coins. The μ-XRD analysis applied a beam spot of 300 μm allowing for a localised determination of corrosion phases on the surfaces of the objects. The main corrosion products consist of metal (Cu, Pb, Cu/Sn) oxide phases. As minor components also metal sulphide and chloride phases could be assigned. To enable the distinction between different manufacturing techniques 35 coins and eight self-made 'replicas' were analysed in a non-destructive way by bulk neutron texture analysis which reveals changes in the microcrystalline structure of the alloys related to the mechanical minting processes.

1. Introduction

The Coin Collection of the Kunsthistorisches Museum Vienna (KHM) is one of the largest in the world. Within its collections it holds a variety of ancient Greek bronze coins which were minted during the Roman Imperial time. These so-called Greek imperials were produced in the eastern, Greek speaking provinces of the Roman Empire between c. 50 and c. 280 AD and are represented in the collection as singular pieces or – more seldom – in low numbers. Compared to the Roman Imperial coinage blanks made of highly leaded bronze alloy were used more frequently in the Eastern provinces. Those coins were issued by a great number of municipalities and were primarily used as local currencies; therefore, also their images are of more local character and provide us with unique historic and otherwise unattested information of their cities.

Only a tiny fraction of the collection is on display in the permanent exhibition at the KHM; its major part is stored in wooden storage cabinets (Fig. 1). Due to the release of organic acid pollutions from the wood [1,2] and together with other air pollutants (i.e., SO_2, NO_2, NO_x, O_3) the antique bronze coins with high lead and/or tin contents develop severe corrosion [3–8]. The coins start to show some points or areas of whitish, powdery corrosion products on the surface (Fig. 2). For single objects the corrosion even leads to a complete destruction of the coin's core, by only leaving an intact outer shell of metal and/or patina. When this shell breaks in certain areas it reveals a completely transformed inner part containing only the corroded powdery material [9,10] (Fig. 2). The development of this corrosion starts from the surface and occurs towards the bulk along lead inclusions formed during the casting process (see below) similar to other corrosion phenomena observed on highly-leaded antique bronzes before [10–12].

Within a four year research project, funded by the Jubiläumsfonds der Oesterreichischen Nationalbank, the corrosions developing on about 1200 coins were studied by different non-destructive analytical techniques, e.g., optical fluorescence microscopy, HIROX 3D-microsopy, scanning electron microscopy with energy dispersive X-ray detection (SEM–EDX), X-ray fluorescence spectrometry (XRF), X-ray and neutron radiography and tomography (Paul Scherrer Institute, Switzerland),

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Fig. 1. Historic wooden storage cabinets still in use in the Coin Collection of the KHM.

μ-X-ray diffraction (XRD; Vienna University of Technology) and neutron diffraction (ISIS, UK), to better understand the development of corrosion and to enhance the preservation of the antique coins [13]. The bulk compositions of a selected number of objects were investigated by non-destructive neutron diffraction and the presence of lead rich inclusions in a copper rich matrix within the bulk of the objects by applying neutron tomography studies (Fig. 3) [13,14].

The further studies described in this paper focused on the analysis of the corrosion phases – combining results from μ-XRD and neutron diffraction investigations – as well as on the manufacturing techniques of the antique Greek coins.

2. Materials and methods

As well-known from a variety of studies on the compositions of antique bronze objects, e.g., statues, statuettes, and vessels, as well as antique bronze coins the use of leaded bronze alloys was very common in processing bronze within Greek history, BC and AD, even before the Roman period [15–18]. The addition of comparatively high amounts of lead is based on economic factors, lead being considerably cheaper than copper and tin, as well as on technological reasons as the addition of lead lowers the melting point of the alloy; it also makes the molten bronze more mobile [16–20]. Although brass was used in the Roman

Fig. 2. Different grades of typical corrosion phenomena visible on Greek imperials.