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Analysis of metals with luster: Roman brass and silver

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ABSTRACT

Non-destructive PIXE analysis using in-air proton beam was used for the studies of earliest brass coins issued during the 1st century BC by Greek cities in Asia Minor, Romans and Celts, and for the studies of plated low grade silver coins of the 3rd century AD. The analysis determined the levels of zinc and important trace elements, notably selenium, which confirms spread of selenium-marked copper from the east. For plating, combined tinning and silvering was identified by the mapping technique for the mid 3rd century AD, which evolved into mere plating by 270 AD.

1. Introduction

This paper focuses on two innovations of the Roman mints: the introduction of coins made of brass and the simulation of silver-like coins using surface enrichment and plating. In antiquity, brass was manufactured by the cementation technique, which is based on simultaneous reduction of zinc ore and diffusion of zinc into finely divided copper [1,2]. The maximal zinc content achieved by this procedure is 28% [3], though most of investigated objects show low zinc content in the range 22–28% [3] or even 18–22% [4].

Brass is recorded sporadically during the first millennium BC [1] but becomes widely used only around 100 BC. Brass was an attractive material because it can be polished to resemble gold. Around 60 BC, Romans started to use brass for manufacturing parts of the military equipment [5], after the first mass-production brass coins were issued by Mithridates VI (132-63 BC) in the Kingdom of Pontus and in the Greek cities of Phrygia and Bithynia [3,6]. Romans adopted brass coinage late: small series of brass coins were issued under Julius Caesar between 46-44 BC and under Roman proconsuls in Asia Minor and Macedonia [3,7]. It was the monetary reform of Augustus in 23 BC that created brass dupondius and sestertius. Around 50 BC brass is introduced in the Celtic and Gaulish monetary alloys; according to several author suggestions since 1963, brass coins were issued in 52 BC in the besieged Alesia in a replacement of gold issues [8]. This hypothesis is based on the typological resemblance of gold and brass coins and on the location of brass coin finds that are concentrated in the area of the siege. We shall concentrate on the coins bearing the legend "VERCA". According to an explanation lanced in mid 19th century, these coins were attributed to Vercassivellaunus, a cousin of Vercingetorix [8]. As described by Julius Caesar in his work [9], Vercassivellaunus was one of the leaders during the relief attack on the Romans besieging Alesia; the attack failed and Vercassivellaunus was caught during flight.

Quite a large fraction of denarii in circulation in the Roman Empire were fakes made by platting – a silver foil was applied on an iron or copper blank [10] – others were coated. The denarius was the most important coin in circulation during the Roman Republic and early Imperial period, equivalent to ten copper asses or four brass sestertii. Early measurements performed by neutron activation analysis [11,12] and even simple physical methods based on the specific heat measurements [13] showed that the mean silver content of the denarius (and the double denarius or antoninianus, introduced since 215 AD) decreased from about 70% to several percent by the year 270 AD. In spite of the silver alloy debasement, the coin surface looked like silver as a result of blanks coating. By exposing the copper-silver blanks to a corrosive environment or by heating those blanks in an oxidizing atmosphere, the less noble blanks are removed from the surface; the surface that could result porous was then smoothed when the blanks were struck into coins [14].

In this work we analyzed by PIXE several Greek and Celtic brass coins together with a group of Roman brass coins issued during the first decades after the monetary reform of Augustus. The results

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are expected to clarify the spread of raw materials and identify possible differences in the metallurgy of brass, notably the zinc content. We also considered a group of antoniniani containing low amounts of silver, spanning the period 240–280 AD. The effect of wear is high for coins in circulation. Elemental mapping by PIXE which involves the areas submitted to different wear rates, the most exposed surfaces and the depressions, can then reveal the composition of both bulk and near surface regions. It is thus possible to distinguish the plating material.

2. Experimental

Measurements with PIXE were performed at the Microanalytical Centre of the Jožef Stefan Institute in Ljubljana. A 1.5 MV Tandetron accelerator was used to deliver 3.034 MeV proton beam to the samples. The beam intensity was a few nA to keep the counting rate <500 cps. The target impact energy was 2.77 MeV after the protons had passed a 2 μm thick tantalum foil used for the exit window and a 1.1 cm air gap. The induced X-ray passed a 6.0 cm air gap between the target and Si (Li) detector. The beam intensity profile at the target was Gaussian, with 0.8 mm full-width at half maximum.

The number of earliest brass coins on our disposal was small, yet we selected coins of low numismatic value (Fig. 1), which allowed polishing small areas of about 1–2 mm across for the analysis. Polishing was completed using a rotating wheel or a rotating or even normal rubber. In one case (no. 5 in Fig. 1), polishing was not desired, so a fraction of the coin where patina was removed by long-year handling was used for the analysis and the beam dimensions were reduced to about 0.3 mm by aluminum diaphragm [15]. Three spectra were taken in a particular measuring point. The basic measurement was taken using a 0.3 mm aluminum absorber and a proton current of a few nA; the measuring time was about 400 s. This type of measurement provides good sensitivity of the elements between copper and antimony, including heavy elements around lead that were determined according to their L-lines. It also yields good discrimination between the K X-ray lines of arsenic and the L X-ray lines of lead, as the filter increases the relative intensity of arsenic Kβ lines and lead Lβ lines of spectra. However, its disadvantage is low sensitivity for iron (above 1%), as iron K-lines coincide with the escape peaks of copper. Low Z elements between silicon and copper were then measured using the air gap of 6 cm as the only absorber; the proton current was set to a few tenth of nA and the measuring time was 300–400 s. The third spectrum was measured using a selective absorber of 15 μm cobalt foil; the measuring time was again 400 s though the counting rate was lower, about 200 cps. The measured spectra were treated by the AXIL program [16] and the obtained line intensities were calculated into concentrations (in mass %) using the code [15]. The procedure used is essentially based on independent physical parameters and requires no standard; yet the naval brass standard NIST 1107 containing 1.04% Sn was sporadically used to check the accuracy of the method and to adjust the thickness of the absorbers. It was found out that the transmission of cobalt absorber cannot be calculated precisely enough for using in the whole X-ray range, so we only used its data for the elements lighter than copper. As the cobalt line in these spectra is result of fluorescence in the filter, we checked the spectra measured in air only for an eventual presence of cobalt. The X-ray line intensities from the three spectra were then mingled into one set of data numerically, using calculated transmission of absorbers. The sum of all metals concentrations was normalized to unity. Test measurements on the 1107 standard performed on a flat surface at known geometry reproduced the nominal data to within 5%, yet rotation of the

Fig. 1. Non-Roman brass coins involved in the analysis. 1 – Mithridates VI, Amisos, 120-63 BC (SNG Cop. 165); 2 – Apamea, Phrygia, 133-48 BC (SNG Cop. 161), 3 – Pergamon, Mysia, 200-133 BC (SNG Cop. 400), 4 – Pergamon, Mysia, 200-133 BC (COP 389), 5 – VERCA, Arverni, before 44 BC (BMC 176), 6 – GERMANVS INDVTILLI L, Treveri, about 10 BC (RPC 506).