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Analysis of surface stains on modern gold coins

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ABSTRACT

It is a mandatory practice in the European Mint Houses to provide a certificate of guarantee of their products specially when issuing commemorative gold or silver coins. This practise should assure satisfaction and trust both for the mint house and for the demanding numismatic collector. For these reasons the Mint Houses follow a strict quality control in all the production steps in order to ensure a no-defect, fully supervised output. In spite of all the undertaken precautions, different surface stains with diverse origin on gold coins recently minted in Europe were observed. Those were compositionally studied by means of IBA techniques at the end-stage nuclear microprobe installed at IST/ITN. From this study it was possible to identify several possible sources for these stains. The presence of defects at the surface of these commemorative coins address the need of improving the quality control system and the results here presented point out where these improvements should occur, in order to reduce/eliminate them and give the customer a product that with time probably will be revalued.

1. Introduction

Gold coins are struck by mints all over the world as bullion coins or to celebrate special events. In general, mints hold a quality certificate, namely the ISO 9001:2008, ensuring that the procedures and products fabricated follow the more stringent international standards. In order to provide a no-defect, fully supervised output, mints follow a chain of procedures which can be categorized in four steps: (1) the gold blanks provided by external suppliers, also holding an international quality certification, are examined in the quality control laboratory in terms of visual appearance, purity, hardness, dimensions and weight; (2) after this control, the accepted blanks go to the production line. Now, depending on the coin finish, the procedure varies in terms of cleaning and polishing of the blanks, dies, and rate of production. For an uncirculated (FDC) finish, the coins are minted on selected blanks with no cleaning or polishing processes, using new dies that are slightly polished with brass brushes and polishing paste. For the Numismatical Proof (Proof) finish, the coins are minted on specially prepared blanks which are cleaned and polished using steel spheres in a chemical bath inside a rotating drum, then washed with ultrasounds and dried with hot air. The dies are polished with diamond paste until a mirror like finish is obtained. The die frosted areas are obtained with sand blasting or a laser beam. (3) The actual minting stage, using modern coin presses, highly automated including blank feeding, can produce around 800 coins per minute. Exception is the proof blanks which are manually fed into the presses, since the high quality required for proof coins does not allow any mass production. While a press is in operation, the press attendant will pick up a finished coin for inspection, examining it under a magnifier and looking for any defects during operation; (4) at the end, coins are packed in plastic holders and accompanied by a guarantee certificate issued by the mint.

However, these procedures are being questioned by the appearance and growth of surface stains on 99.9% pure gold coins minted recently. These are more interesting as gold is stable in the presence of water and moist or dry air, even when heated. These stains not only reduce the coin artistic/numismatic value with obvious consequences for the coin owners, but also show that the fabrication procedure still needs improvement. First termed as "gold corrosion", stains observed in gold coins, both modern and ancient, analysed by Gusmano et al. [1] and Liang et al. [2], show that they are essentially silver (Ag) clusters of uncertain origin on the coin surface that along the time forms a patina layer of Ag_2S. Mayerhofer et al. [3] also reported similar stains on historic gold coins, where Ag, Cu and S elements were identified.

In this work we use the IBA techniques to characterize from the point of view of composition some stains that are visible at naked eye. In order to identify the origin of these stains it is vital to know their composition, which will allow the implementation of the necessary procedures to minimize and even to eliminate their presence. The IBA techniques have been successfully applied to the

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compositional study of ancient coins based on different metal alloys [4] or to investigate the elemental content of modern Lebanese coins [5]. In this work the IBA techniques were applied to assess the quality procedures followed by the European Mint Houses and eventually contribute to their improvement, minimizing the defects found in the gold commemorative coins.

2. Experimental

The coins analysed during this work are part of a private numismatic collection, which has among others, silver and gold coins from different years. Among them, two gold coins recently minted by different Mint Houses from the European Union in 2006 and 2011 were selected. They both have 14 mm in diameter and are made of Au 999. One (coin A) was minted with a FDC finish and the other one (coin B) with a Proof finish.

The coins were bombarded with a 2 or 1 MeV proton beam produced by the 2.5 MV Van de Graaff Accelerator of the ITN/IST (Lisbon, Portugal). An Oxford Microbeams type nuclear microprobe was used (OM150 triplet system), which allowed the proton beam to be focused on the coin with a spatial resolution of $3 \times 4\ \mu m^2$. Also, it is possible to perform beam scans over the surface of the coins up to $2640 \times 2640\ \mu m^2$ when using 2 MeV proton beams [6]. The experiments were carried out under vacuum conditions; the used 80 mm^2 Link X-ray detector has a 145 eV energy resolution and it is positioned at 135° to the beam direction. To filter the low energy X-ray signal and prevent backscattered protons from entering the X-ray detector when working with 2 MeV proton beam, a 50 μm foil of Mylar is used, although it was removed when the signal from Na had to be recorded in some of the stains. In these cases a proton beam of 1 MeV had to be used. The backscattered protons are collected by a PIPS detector in Cornell geometry at 140° to the beam direction.

The OMDAQ V5.2 software package [7] is used for data acquisition and treatment. This software also allows us to control the beam by the scanning control. Spectra evaluation and quantification was done with the GUPIX [8] code for PIXE spectra while RBS spectra were fitted with the NDF code [9].

3. Results and discussion

In both coins (A and B) it was possible to observe dark spots at naked eye on both sides of the coins. A close examination by stereomicroscopy reveals differences between them: shape, dimensions and the nuance of colours surrounding the spots. The results from the characterization analysis show that associated to the visual differences there is also a compositional difference.

Most of the stains are related with the presence of Ag-rich regions, showing a brownish-grey region in the central area and surrounded by a larger area with a nuance of colours from grey–green to red. From the PIXE spectra the presence of S in the stains can be inferred from the differences in the signal of the spectra recorded inside and outside the stain (Fig. 1), suggesting the presence of a very thin layer of patina composed of Ag_2S, where the S should come from the atmosphere, in the form of H_2S or other sulphur containing contaminants. Also the presence of Cu was detected on this stain. From the X-ray spectrum a PIXE analysis was performed obtaining the elemental abundances (wt.%) for the total analysed volume, i.e., until approximately 5.5 μm deep considering a 1 MeV proton beam, showing 6.03% for Ag, 1.49% for S, 0.10% for Cu and 0.02% for Fe.

Other defects were found also in coin B, where high content of aluminium and in some cases Si and Ca were also found. One of these defects is presented in Fig. 2 with the respective 2D map recorded from the X-ray spectra.

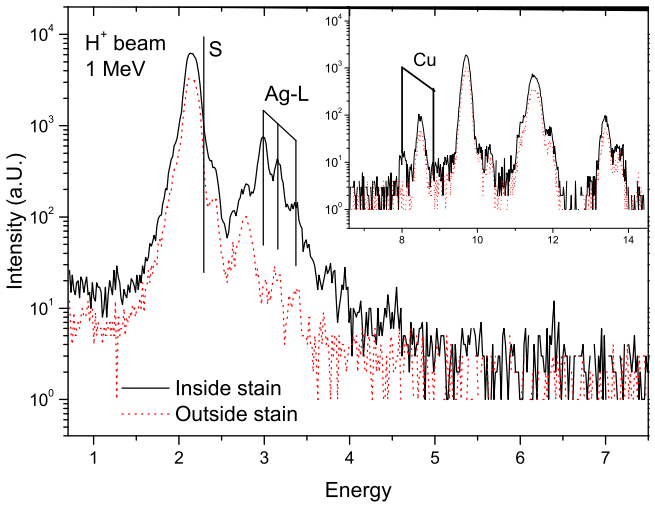

Fig. 1. X-ray spectra recorded using a 1 MeV proton beam. Solid-line: point analysis in the Ag-rich defect; dash line: point analysis outside the defect.

An interesting defect was found on coin B (minted in 2011) that seems to be related with the cleaning process of the blanks, presented in Fig. 3, which shows a stereomicroscopic detail and the 2D maps of the main elements present in the defect (Cl, K and Na) recorded at 1 MeV proton beam and without any filter in front of the X-ray detector.

Considering the high gold purity of these coins (Au 99.9%), several possibilities should be considered to establish the origin of the defects previously presented:

As proposed in [1,3] the Ag-rich defects may come from the gold blanks production process, as in many cases gold and silver blanks share the same production line during the lamination or cutting processes.

On the other hand, other alternative explanation may come from the presence of Ag aerosols in the coin presses room formed in previous works related with silver coins, which are smashed against the blank by the impact of the die. It is important to mention that these type of defects have been also reported in ancient coins made of Au986 preserved in Museums conditions [10,11].

The presence of aerosols could also explain the origin of the Al-rich defect (Fig. 2). In order to try to test this last option, a set of six nuclepore membranes with 8 μm pore size where placed near the coin press during the minting of gold. PIXE analysis performed on these filters did not show the presence of Ag or Al – rich particles. To our knowledge, the number of coins with these defects is very low, as such the results obtained with these membranes is not conclusive, requiring a continuous monitoring of the atmosphere in the presses room.

Other explanation for the Al-rich stain may come from debris that remain upon any area of the dies in the polishing process, but this is not at all usual since the corresponding Mint House for this coin do the polishing treatment with diamond paste, followed by a deep cleaning process by ultrasound.

Considering the elements identified in the defect presented in Fig. 3 and its shape (a liquid drop-like) its origin can be related with a drop of water from, perhaps, the ultrasound bath that after evaporation left a residue of Cl, K and Na. Confirming this hypothesis, is the fact that this stain disappeared after a cleaning process with alcohol.

Other hypothesis that was considered to explain these defects include the possibility of some fragments from a cracked die were incrusted in the surface of the coin during the coinage process. But, we did not detect the presence of Cr, a typical element present in the die (in a coating layer) used to increase its hardness. Also, it

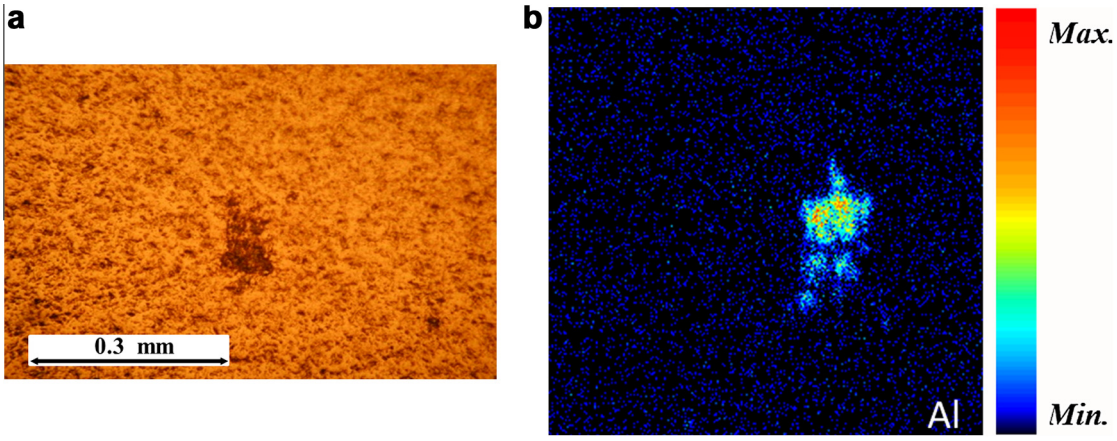

Fig. 2. (a) Detail of the defect Al-rich on coin B mint in 2011; (b) 2D-PIXE map of Al (530 × 530 μm^2).

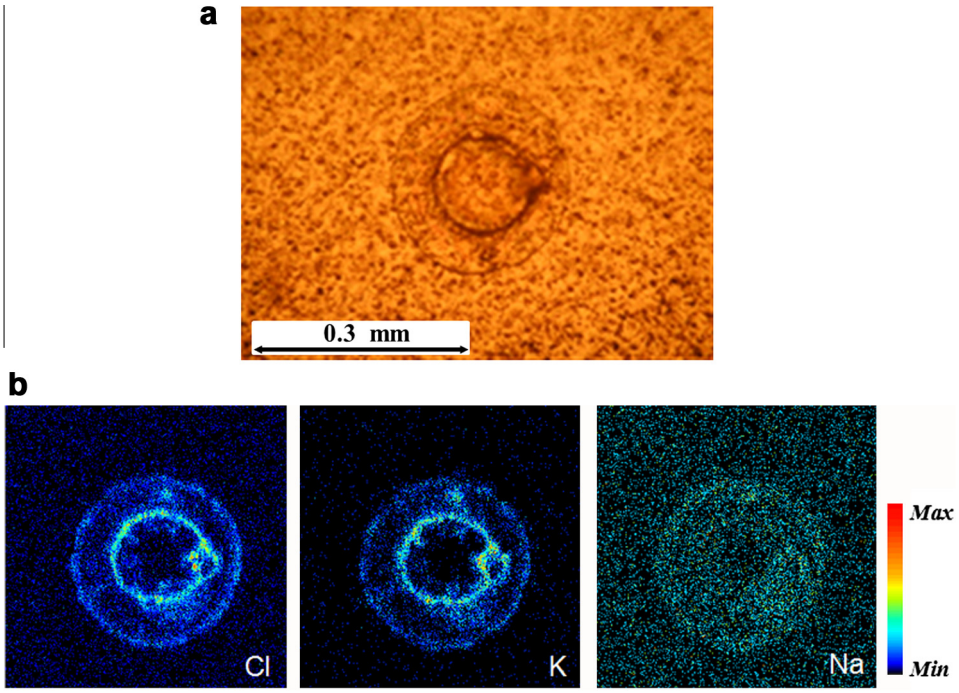

Fig. 3. (a) Detail of the low Z-rich elements defect present in coin B minted in 2011; (b) 2D-PIXE map of Cl, K and Na (530 × 530 μm^2).

was not possible to detect Fe, Ni, or Mn which are constituents of the steel used to manufacture the dies.

With the exception of the defect presented in Fig. 3, all other analysed stains are carved on the coin surface, and as such, a post coinage contamination is excluded.

4. Conclusions

The combination of different IBA techniques when combined with the 2D compositional maps using a nuclear microprobe has been proved as an excellent method to characterize the stains present in the gold coins surface and control the quality standards followed by different European Mint Houses.

Several possibilities were discussed over the text, to explain the high compositional variety of the analysed stains, showing the need to do more studies. In fact, in order to reduce/eliminate the number of these defects on coins, additional steps in the quality controls followed by the Mint Houses should be introduced, namely the monitoring of the presses room to assess whether a better air quality control should be considered. Also, the external gold blanks suppliers should improve their production lines, in terms of separating the gold and silver blanks production that still occurs.

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