

Surface defects on collection coins of precious metals

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The presence of various defects of different colours and sizes on precious collection coins is the cause not only of the rejection of defective coins but also of an increase in the production costs. In this work, the surface defects on the Austrian collection coins have been investigated by using the techniques of XPS, AES and SEM/EDS.

Multi-technique surface analysis revealed the presence of silver and sulfur in the stains on the golden coins. Auger spectra and chemical images proved that both Ag and S are located in the coloured surface areas. From the XPS results, it was concluded that the coloured stains consist of Ag₂S. XPS depth profiling revealed the difference in the thickness of the dark-grey and red stains. In both cases, the topmost layer of silver sulfide has a thickness of a few nm, whereas the inner layer of silver is about 300 nm thick in the dark stains and only about 2–3 nm in the red ones. The origin of these stains has been attributed to foreign particles of silver embedded onto the coins.

The chemical composition of the visible stains on silver coins is quite different. AES results revealed that some defects contain chlorine, potassium and oxygen; the others include iron and oxygen. In all these cases, the surface contaminants were attributed to occasional problems that occurred during the manufacture of the coin. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: XPS; depth profiling; AES; SEM; metals; surface contamination

INTRODUCTION

In recent years the presence on historic gold coins of coloured spots, from red to black, often referred to as 'gold corrosion', has been detected in Austria, France, USA and other countries. For example, such defects have been observed on gold coins and medals of the collection at the Kunsthistorisches Museum in Vienna.¹ The same problem has also been found in gold coins produced in the last years.² The occurrence of spots of different shapes and colours, has been observed also for silver coins produced by different mints. Therefore, the phenomenon of defective coins has a wide relevance, but the existing literature is very poor for papers dealing with analytical studies on these defects and their origins.

Concerning the so-called 'gold corrosion', according to the Pourbaix diagram³ of the system Au/H₂O, gold and its alloys can be oxidized only in particular conditions, that hardly could be imagined even in a very polluted environment. Therefore, it can be supposed that the phenomenon is not really caused by the oxidation of gold.

What is the origin of this deterioration? And why does the colour of different stains on the same coin change from light red to dark grey or even black?

In order to understand the real nature of various stains, observed on both gold and silver collection coins, the surface analysis of coins and blanks was carried out using the multi-technique analyses: XPS, AES/SAM and SEM.

EXPERIMENTAL

The following gold coins were analysed: an Austrian Ducat, minted in 1915 and made of the historical alloy Au 986, and a number of Wiener Philharmoniker coins (2000, 1000, 500 and 200 Austrian schillings) made of gold 999.9 and minted in the last few years. Several other collector coins, e.g. Haydn (25 ECU) and Maximilian, and various blanks of silver (Ag 999, Ag 925 and Ag 900) have also been examined. The total number of coins investigated, manufactured in the period 1992–2002, was over 20. The production technology, similar for all the alloys, can be summarized in the following steps: melting in graphite crucibles, continuous casting in strips, rolling of the strips to the desired thickness, annealing in inert atmosphere, punching, cleaning and coining.

An Escalab MkII (VG Scientific), equipped with a 5-channeltron detection system and a standard Al K_α excitation source, was employed for the XPS/AES/SAM experiments. The samples were positioned with respect to the analyser at the electron take-off angle normal to the surface, and the analyser was set to a constant pass energy of 50 eV. XPS depth

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profiles were acquired by using a 3.0 keV energy Ar^+ beam, rastered over an area of the window in the Cu mask. The ion sputtering rate was calibrated by measuring reference samples (films of Au and Ag) and applying the medium value of 0.3 nm/min. More experimental details on the XPS depth profiling have been reported elsewhere.⁴ Multipoint Auger and SAM experiments have been performed by a sub-micron spot electron gun LEG 200, using beam energies up to 10 keV and minimum beam diameter $\approx 0.2 \mu\text{m}$.

The morphology of the defects was investigated by using SEM (Cambridge Instruments 360) operated at 20 keV and equipped with an energy dispersive spectrometer (Link Analytical).

RESULTS AND DISCUSSION

The surfaces of the studied gold coins (ancient and modern) exhibited various spots of different sizes and colours. The colour of these stains varied from light red to black. A thorough SEM/EDS analysis³ exposed the morphology of these defects and the presence of silver in all the spots. Typical results of XPS measurements of the red spots are shown in Fig. 1. It is clear that these spots contain Ag, S and a lower amount of Cu. The SEM image and SAM chemical map (Peak-Background) of Ag of the same stain are presented in

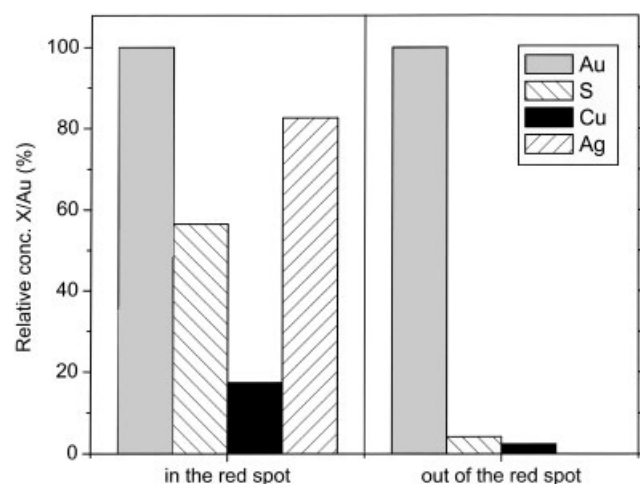


Figure 1. XPS results on the 200 Austrian schillings coin (Au 999.9).

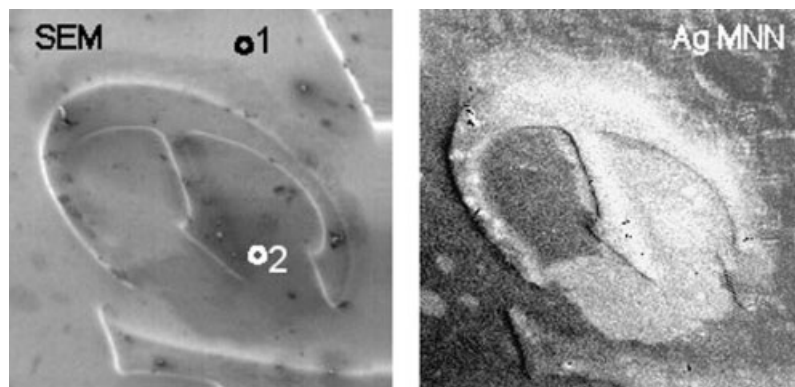


Figure 2. SEM image and SAM chemical map (Ag MNN) of the red stain on the 200 Austrian schillings coin (Au 999.9). The image size is $1.8 \times 1.8 \text{ mm}^2$.

Fig. 2. Multipoint AES analysis (Fig. 3) of the clean surface (1), red stain (2) and a smaller black spot (3, out of the area shown in Fig. 2) reveals the nature of these defects. The reddish stains contain Ag, S and Cu (peak not shown in Fig. 3).

Only from the *BE* value of the Ag $3d_{5/2}$ peak (368.0–368.2 eV) is it impossible to identify the chemical state of Ag, because it has very small values of chemical shift.^{5,6} In order to determine the state of silver, we have measured the modified Auger parameter $\alpha' = BE(\text{Ag } 3d_{5/2}) + KE(\text{Ag } M_4N_5N_5)$, where *KE* values were obtained after the smoothing and differentiation of Auger spectra. The value of α' obtained for all investigated samples was 725.2–725.3 eV, which corresponds to silver sulfide.⁵ The presence of Ag_2S was also confirmed by the XPS data on the S 2p peak, which was found to be at *BE* = 161.6–161.9 eV. In the literature^{5–7} these values correspond to sulfides, while sulfates are characterized by higher *BE* of about 168.6 eV

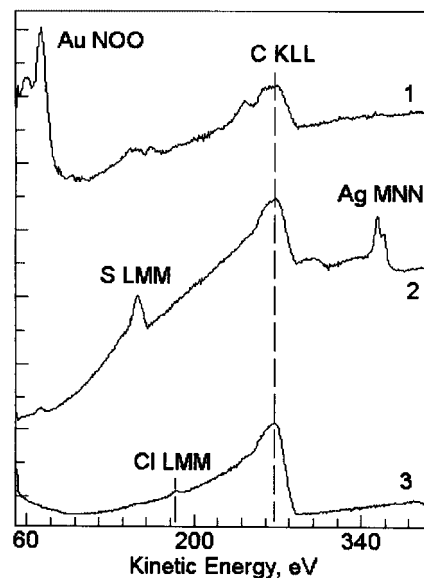


Figure 3. Multipoint Auger spectra of the 200 Austrian schillings coin (Au 999.9). Points 1 (clean surface) and 2 (in the red stain) are indicated in Fig. 2; point 3 (black spot) is out of the area shown in Fig. 2.

(Ag_2SO_4) to 169.3 eV (CuSO_4). It is more difficult to determine the chemical state of copper due to the controversy

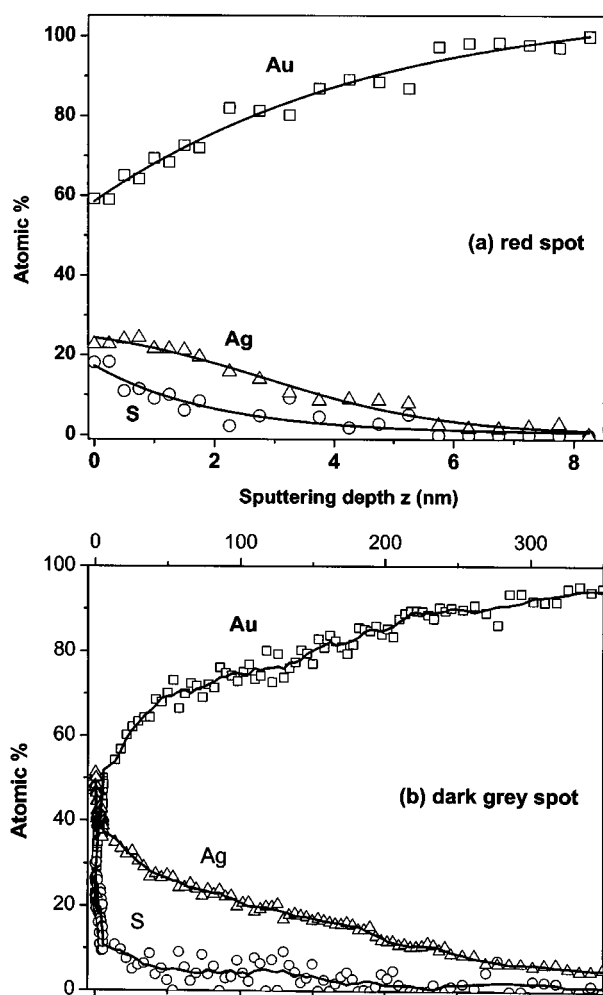


Figure 4. XPS depth profiles of the 1000 Austrian schillings coin (Au 999.9): (a) area of the red stain; and (b) area of the dark grey stain.

of the known data^{5,7} on the *BE* of Cu 2p_{3/2}. However, the absence of the satellites in the Cu 2p spectra indicates that we are dealing with Cu(0) or Cu(I). Our experimental *BE* value (932.9 eV) is similar to Cu₂S,^{5,7} but it could be also Cu₂O or metallic Cu(0).

The XPS and AES analyses of the dark stains gave results very similar to those of the reddish stains. Only the XPS depth profiling (Fig. 4) revealed the compositional differences of these stains. The total thickness of the red stains is about 5–6 nm and they consist of two sub-layers. In the first 2–3 nm, Ag_2S is dominant, while deeper in these defects only metallic Ag is detected. In the dark grey stains, the concentration of S rapidly decreases to zero in the first 5 nm, while the second sub-layer of metallic Ag continues in-depth for about 300 nm. Evidently the difference of colour is not due to the difference of chemical composition or of structure, but to the difference of thickness of the inner silver layer.

The nature and origin of the dark blackish spots on silver coins and blanks is quite different. Two different types of these defects were disclosed. Figure 5 displays the SEM image and EDS chemical maps of one of them on the surface of a Ag 925 blank sample. The morphology of these defects indicates that they consist of foreign particles, rich in Fe, embedded in the silver matrix. The presence of Fe was confirmed also by AES and XPS measurements of the dark spots. The dominant chemical state of iron is Fe^{3+} (two Fe 2p components at *BE* of about 711 and 713 eV), that remains stable even after 30 min of ion sputtering. Therefore, these spots consist of iron compounds produced by thermal treatment of steel, whereby their origin can be explained by focusing attention on the furnace used for the annealing of silver strips. Its lining is made of stainless steel which oxidizes forming a brittle scale. If some particles of this scale fall on the surface of the strips, they can be embedded onto the silver alloy by the successive rolling.

Another kind of defect (see Fig. 6) consists of small round white stains, about 1 mm in diameter, with a dark spot in the centre. Small particles of 2–20 μm are distributed inside these

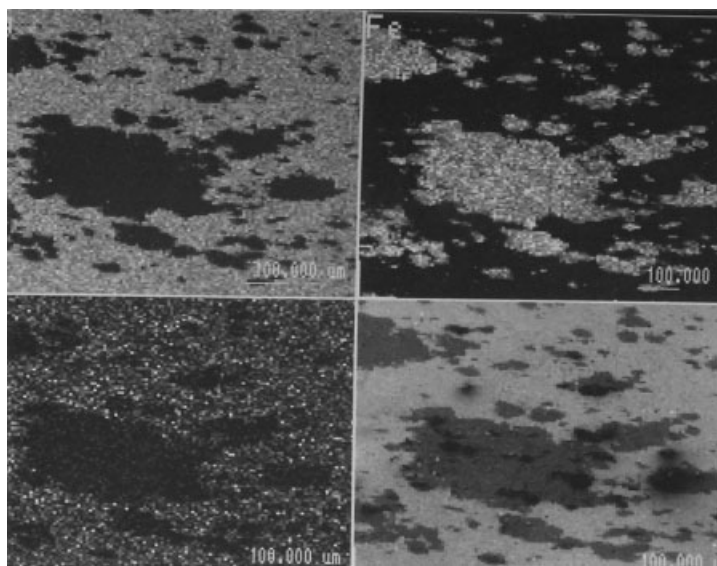


Figure 5. SEM image (bottom right) and EDS chemical maps of a Ag 925 blank sample with dark spots: Ag (top left), Fe (top right), Cu (bottom left).

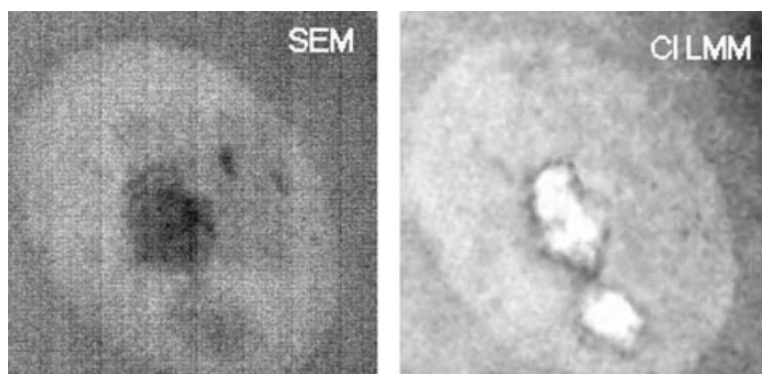


Figure 6. SEM image and SAM chemical map (Cl LMM) of the white stain on a coin of Ag 999. The image size is $0.8 \times 0.8 \text{ mm}^2$.

stains. EDS analysis disclosed that: (i) the ratio of chlorine and silver is constant ($\text{Cl}/\text{Ag} \sim 0.1$) over all of the area of the dark spot; and (ii) in the small particles the amount of Cl is higher.

The SAM chemical maps (Fig. 6) and XPS data, obtained after cleaning by ion sputtering, confirmed the presence of chlorides. This fact is quite important because silver, and even more so its alloys, in contact with an aerated solution containing Cl^- ions, is oxidized resulting in the formation of a surface film of AgCl. Other tests, made to reproduce these stains, confirmed that one of the commercial products used in the coins' production is contaminated with chlorides and these defects are actually composed of AgCl.

CONCLUSIONS

The multi-technique surface analysis of ancient and modern Austrian coins revealed the chemical composition of the coloured stains on their surface. The stains on the golden coins are composed of Ag_2S . The colour of the Ag_2S stains depends only on the thickness of the metallic Ag sub-layer: when it is very thin, the stains are red, while the thick ones result in a dark grey colour. Therefore, it is evident that the so-called 'gold corrosion' is a phenomenon caused by the surface contamination with silver. In the case of ancient coins (Au 986), it would be possible to suppose that silver from the alloy segregated towards the surface, but this hypothesis hardly could be supported for the modern coins (Au 999.9). It is much more credible that some silver particles, remaining on the tools used in the silver coin production, are mechanically transferred to the gold surface. It could happen

during milling, rolling or punching of the gold strips. Later, the sulfur-containing contaminants in air (like H_2S) cause the formation of Ag_2S on the coin surface.

One type of visible defect on the silver coins consists of iron oxides of thermal origin. The other one is composed of AgCl, that forms when silver comes in contact with chlorides containing substances present in the production cycle.

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