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Spectroellipsometric and ion beam analytical studies on a glazed ceramic object with metallic lustre decoration

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ABSTRACT

In this work recently produced and commercially available glazed ceramic object with metallic lustre decoration was studied by using a spectroscopic ellipsometer with rotating compensator. The thickness and metal content of the surface lustre layers are determined by ion beam analytical techniques, i.e., Rutherford backscattering spectrometry and external beam particle-induced X-ray emission and the results were utilized in the construction of multilayer optical models for the evaluation and interpretation of the spectroellipsometric measurements.

1. Introduction

In the 9th century in Mesopotamia a special technique for the decoration of ceramic objects appeared — lustre, a precursory nanotechnology, which is able to transform simple earth into ceramic masterpieces, thus giving them beautiful metallic shine, including the appearance of gold [1]. Lustre decoration of medieval and renaissance pottery consists of silver and copper nanocrystals, dispersed within the glassy matrix of the ceramic glaze [2]. Roqué et al. aimed to establish a basis for understanding lustre nanostructure linked to its optical properties [3]. Pradell et al. performed Rutherford backscattering spectroscopy (RBS) and optical measurements on laboratory prepared lusters and they have found that the high volume fraction of metal nanoparticles is responsible for the metallic shine [4]. Recently, a metallized glaze has been produced from sepiolite-n (Cu, Fe) containing metallic nanoparticles and applying a fast-firing fabrication process by Moya et al. [5]. Based on ellipsometric and reflectance measurements, Moya et al. draw the conclusion that copper nanoparticles in the topmost glaze layer are prerequisite to obtain a metallized glaze.

Particle-induced X-ray emission (PIXE) allows for the fast and simultaneous identification of a large number of elements with reasonable accuracy [6] whereas RBS is a widely used method for the surface layer analysis of solids [7] with good depth resolution. Polvorinos del Rio et al. studied lustre glazed ceramics from the medieval Seville by PIXE and RBS [8]. Their simulation of RBS spectra shows the existence of thin layers containing metallic silver and/or copper. One of the early examples of lustred object produced in Italy is Baglioni's albarello, this emblematic object was studied by Padeletti et al. using PIXE and RBS among other methods to gain deeper insight into the characteristics of the lustred film [9].

The processing route to obtain a glazed ceramic object with lustre decoration consists of three steps: i) high temperature firing of the ceramic body (<1000 °C), ii) application and firing of the vitreous glaze at intermediate temperature (500–900 °C), and iii) application of a special mixture containing clay, metallic (Ag, Cu) salts and organic compounds (for example vinegar) and firing in reducing atmosphere at moderate temperature (600 °C). During this latter treatment metallic nanoparticles are formed which remain embedded in a thin near-surface layer of the ceramic object [1].

In this work a recently produced commercially available heart-shaped glazed ceramic pendant with metallic lustre decoration was studied by spectroscopic ellipsometry (SE). The thickness and metal content of the surface lustre layers were determined by ion beam analysis, i.e., RBS and PIXE. The results of ion beam analysis helped us to construct multilayer optical models for the evaluation and interpretation of the SE measurements. The photograph in Fig. 1 shows the heart-shaped ceramic pendant together with two coins for comparison in size.

2. Experimental details

2.1. Ion beam analysis

The surface of the recently produced, commercially purchased heart-shaped ceramic pendant with metallic lustre decoration has a

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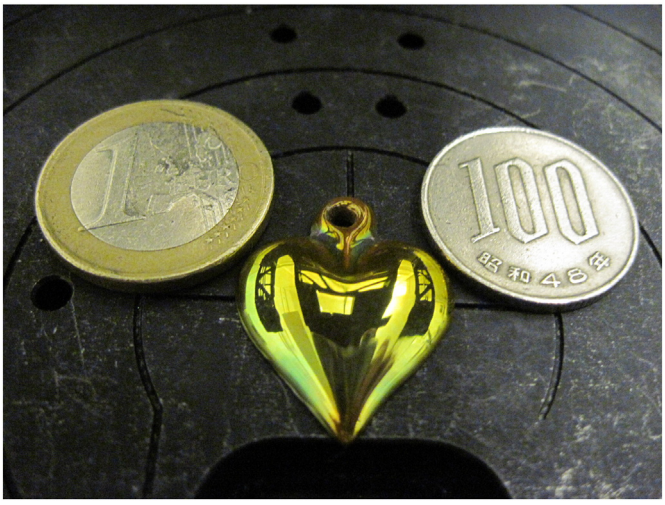

Fig. 1. Photograph of the commercially purchased heart-shaped ceramic pendant with metallic lustre decoration.

certain degree of curvature. Considering this, to minimize the uncertainty of the applied measurement geometry (i.e., actual sample tilt angle, layer thicknesses, etc.) in the spectrum evaluation process, the areas for ion beam analysis and optical investigations were selected on surface regions of minimum curvature.

The external beam PIXE and RBS analysis were performed using the 5 MV Van de Graaff accelerator at the Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest.

In case of external beam PIXE, the pin-hole collimated proton beam of 2.5 MeV energy was extracted to air through a 7.5 μm thick Kapton foil. The sample holder with the ceramics used in the RBS measurements was simply set to face to the extracted beam. The final target positioning was achieved using a mechanical "aiming pin pointer", see the photograph of the measurement setup in Fig. 2. X-ray spectra were collected by a computer controlled Amptek X-123SDD spectrometer of 25 $mm^2 \times 0.5$ mm active detector volume, 8 μm thick Be window and 130 eV energy resolution for the Mn K_α line. In front of the detector an Al absorber of 0.1 mm thick was used. The net X-ray peak intensities were evaluated with the GUPIX program package [10]. The overall sensitivity of the setup is in the 10–50 ppm range.

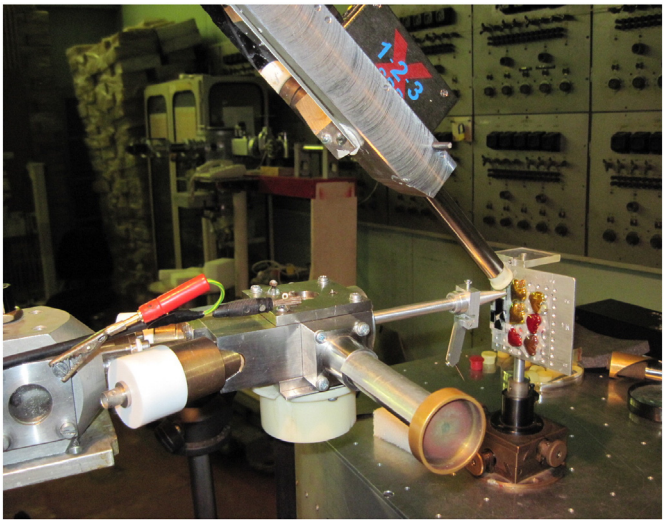

Fig. 2. The external beam PIXE setup.

For RBS, the sample Z1 was fixed to a sample holder of a scattering chamber equipped with two-axes goniometer. During the experiments the vacuum in the chamber was better than 1×10^{-4} Pa using liquid N_2 traps along the beam path and around the sample. The ion beam of 2000 keV $^4He^+$ was collimated with 2 sets of four-sector slits to the necessary dimensions of 0.5×0.5 mm^2. The ion current of typically 10 nA was kept constant via monitoring by a transmission Faraday cup [11]. The spectra were collected with a measurement dose of 4 μC.

The RBS measurements were performed with an ORTEC surface barrier detector under a solid angle of 4.15 msr. The energy calibration of the multichannel analyzer (2.99 keV/channel resolution and with energy offset of 104.7 keV) was performed by using known peaks and surface edges of Au, Si and C, respectively. To identify the surface elements and buried peaks, the RBS experiments were performed at tilt angles of 7° and 45°, respectively. To determine the lateral homogeneity of the sample RBS experiments were repeated on three different spots of the heart-shaped ceramic pendant. The three spectra taken on the sample were then fitted using the layer structure obtained from the RBX simulation program [12].

2.2. Spectroscopic ellipsometry

The optical properties and the thicknesses of thin film structures can be derived from (Ψ, Δ) values measured by SE, where Ψ and Δ describe the relative amplitude and relative phase change of polarized light during reflection, respectively. In the present experiment Ψ and Δ were measured by a Woollam M-2000DI rotating compensator ellipsometer in the 191–1690 nm wavelength range at angle of incidence of 70°. A 0.3 mm diameter microspot option was applied in the measurement. The calculated (generated) spectra were fitted to the measured ones using a regression algorithm. The measure of the fit quality is the mean square error (MSE) which was compared for different optical models. The unknown parameters are allowed to vary until the minimum of MSE is reached. Since the regression algorithm may end up in a false "local" minimum, therefore a careful global search procedure should be applied in case of complex multilayer structures. That means that one should start the evaluation with a wide range of initial parameter values in order to find the global minimum. For complex sample structures this procedure can be time consuming.

3. Results and discussion

Fig. 3 shows a typical PIXE spectrum measured on the heart-shaped ceramic pendant. The X-ray lines corresponding to various elements with $Z \geq 26$ (i.e., Fe and above) are identified. The relative amount of the various metal components can easily be calculated from the peak areas. Significant amounts of Fe, Cu, Zn, Zr, Ag, Sn and Pb were found in the surface layer.

The depth distribution of the above elements was determined by RBS. Fig. 4 shows the RBS spectra taken on the centre part of the heart-shaped ceramic pendant along with the simulated ones. Besides the metallic elements found by PIXE O, Si and Na were also detected in the evaluation. To obtain a good quality agreement between measured and simulated RBS spectra about fifteen different layers of various composition and layer thickness were introduced. Basically, the ceramic matrix, which can be considered as the substrate, was formed by the elements of Si, O, Na, Fe, Cu, Zn, Sn and Pb. Although the energy spread effects were calculated in the simulation [13], several layers had to be introduced to describe the shape of the Zr and Ag peak of various concentration. The concentration of Sn and Pb was also found to vary with depth.

Comparison of the spectra taken on various spots on the sample suggests the presence of some inhomogeneity in the lustre layer. The thicknesses of the Zr and Ag containing layers, as well as that of the third matrix layer slightly vary.

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