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Ion beam analysis of golden threads from Romanian medieval textiles

Z.I. Balta [a,*], L. Csedreki [b], E. Furu [b], I. Cretu [c], R. Huszánk [b], M. Lupu [c], Z. Török [b], Z. Kertész [b], Z. Szikszai [b]

[a] National History Museum of Romania, Calea Victoriei 12, Sector 3, Bucharest, Romania
[b] Institute for Nuclear Research, Hungarian Academy of Sciences, H-4001 Debrecen, P.O. Box 51, Hungary
[c] National Art Museum of Romania, Calea Victoriei 49-53, Sector 1, Bucharest, Romania

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ABSTRACT

In this study, metal threads from Romanian religious embroideries and precious velvet brocades dated from 15th to 18th century were analyzed by using IBA methods (PIXE and RBS) which, in comparison to the traditional analytical techniques (XRF, EDS), allowed the detection of their structures and accurate identification of the trace elements (detection limits of few tens of ppm). PIXE results confirmed that both types of the metal threads studied – wires and strips – have layered structures being made of fine silver, refined by cupellation, and gilded most probably with pure gold, and not of Au–Ag alloy, or gilded Ag–Cu alloy or Au–Ag–Cu alloy, as resulted from the previously performed SEM-EDS analysis. Trace elements of historical interest like lead, mercury and bismuth have been also possible to be detected by PIXE. The resulting elemental maps allowed us to identify the areas from which the metal thread structure and quantitative composition could be accurately determined. RBS measurements revealed that the gilding layer is separated from the silver bulk by an interface layer resulting through atomic diffusion of silver into the gold, which lead to the conclusion that the methods used for gilding were probably either the diffusion bonding or the fire gilding. The gilding layers thicknesses were estimated by PIXE with the GUPIX software and also determined from RBS measurements.

1. Introduction

Technical studies by classical techniques routinely used for analysis of cultural heritage materials (XRF, SEM-EDS) have been done previously in order to determine the chemical nature and morphology of the metal threads used in ancient textiles [1–4]. Some studies revealed that XRF and EDS could not distinguish between alloys and layered structured materials for the small and extremely thin gilded metal threads. Besides, EDS may sometimes give erroneous results. It was observed that the gold concentrations resulted for the gold coating and reported in previous publications are often too low depending on the high accelerating voltage used (usually 20–30 keV in practice), and thus incorrect [5,6].

Recently, in order to overcome some of these difficulties, more sensitive analytical techniques like AES, XPS, SIMS and laser-ICP/MS have been used, and to our knowledge, few characterization studies by using IBA methods have been done so far [5–8]. Elemental analysis either on surface or in a depth profile by IBA methods are non-destructive and could provide unique information at the trace level sensitivity which make them ideal for the study of the very small and thin, possibly multilayered metal threads. Aim of our study was to demonstrate the necessity of integrating the advanced IBA methods with the classical analysis techniques frequently used in museums, for an in-depth applied interdisciplinary research that brought new developments and rich accurate information on golden threads constituent materials, especially the trace elements, elemental depth distributions and layers thicknesses, the ancient production technologies, metal threads structure, their provenance and origin. IBA measurements were carried out within the EU FP7 CHARISMA FIXLAB Transnational Access programme, in two phases: the projects IBATEX 1 and IBATEX 2.

2. Selection of textiles

Metal threads selected for ion beam analysis were taken from medieval gold brocaded velvets and religious embroideries preserved in the textiles collections of the Putna Monastery Museum and the National Art Museum of Romania. For the PIXE and RBS analysis 23 textiles were chosen, most of them with known provenience (Moldavia, Italy, Near East and Greece) and consistent dating as appeared in the art historical literature [9,10]: brocades with

* Corresponding author.
E-mail address: balta_z_i@yahoo.com (Z.I. Balta).

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the inscription of donation embroidered, embroideries typologically and stylistically similar and brocades with no inscription of donation.

Embroideries were made in most cases for liturgical purposes, worn by priests as church vestments or used during the religious services (epitrachelion, nabedernita, altar door curtain, aer, epimankia, etc.), most of them being produced locally in the Putna Monastery's Embroidery School. They were worked in the traditional Byzantine technique of pattern couching, using the cartoon models painted on religious themes similar to those in the mural paintings dating from the 15th to 17th centuries. According to the sources, Byzantine embroidering technique consisted in laying golden threads on the surface of the background material and attaching them with stitches made of silk threads. The stitches were passed over the golden thread at regular intervals, creating different patterns [10].

Brocaded velvets were imported and produced abroad in the Italian workshops from Venice or Florence, or in the Ottoman Empire workshops, as mentioned in the art historical literature [10]. Brocades were sumptuous materials of silk velvet fabrics richly decorated with golden metal threads that were used in the articles of clothes of Italian and Oriental influence by the Moldavian and Wallachian princes, princesses and boyars (ceremony costumes, court vestments, caftans, granatza, etc.). They were sometimes donated to churches and monasteries after being worn. With a simple cut, those clothes could be dismantled, the resulting fabric fragments being used during the religious services as temple veils, covers for lecterns and the Communion Table or as tomb covers.

3. Experimental

IBA techniques were applied at the Oxford-type nuclear microprobe facility in the MTA Atomki, Debrecen, Hungary [11–13]. The analyses were performed in vacuum and the size of the beam was typically about 2 μm. The length of the threads was approximately 3–10 mm.

PIXE measurements were performed on 50 samples taken from 18 medieval textiles (IBATEX 1) and on 23 cross-sections of threads prelevated from 8 textiles (IBATEX 2) by using a proton beam of 3 MeV energy and 100–500 pA intensity. PIXE analysis modes performed were: full area elemental mapping of the sample surface, selected raster, and point analysis. The resulting PIXE spectra were evaluated with the GUPIX code [14]. In IBATEX 1, three different types of metal threads were analyzed: wires wrapped around a dyed silk yarn, strips wrapped around a dyed or undyed silk yarn and wires with no core yarns. In order to obtain more precise and accurate results regarding the metal threads composition and chemical structure, our study continued with analysis on cross-sections within the IBATEX 2 project. Cross-sections were obtained by embedding the wires and strips in epoxy resin, the resulted specimens being cut in transversal sections which were then wet grounded and polished down to grit 8000.

RBS analysis were carried out on 10 samples taken from 6 textiles (IBATEX 1) and 26 samples prelevated from 12 textiles (IBATEX 2) using a He^{+} beam of 2 MeV energy and a few hundred pA intensity.

During the first phase (IBATEX 1), for the evaluation of the PIXE data, it was assumed that the bulk silver includes less than 1% gold, and the gilding layer contains only pure gold, all the trace elements being present in the silver substrate only. The gilding layers thicknesses were also estimated with the GUPIX software. For the second measurements phase (IBATEX 2), carefully cut and polished cross-sections were prepared to assess the silver bulk composition by PIXE without any possible contamination from the gilding layer or the silk yarn. The thicknesses of the gilding layers were measured by dedicated RBS analysis on metal threads using an ORTEC-type surface barrier silicon detector ("ULTRA" Ion-Implanted, 50 mm^2 sensitive area and 25 keV system energy resolution). The detector was placed at a scattering angle of 165° at Cornell geometry [15,16]. The scan size was set to 500×500 μm^2. RBS spectra were evaluated with the SimNRA computer code version 6.06 [17]. With the second approach (IBATEX 2), we also could check the validity of the assumptions made during the first phase (IBATEX 1).

Preliminary examinations in reflected and polarized light, at different magnifications, was performed in order to determine the metal threads technological and morphological characteristics, also the wires diameters (in cross-sections), with a Nikon Eclipse LV100D microscope equipped with a D90 digital camera, a Camera Control Pro 2.0 imaging software and a NIS Elements-BR3.0 image analysis software.

4. Results and discussion

Preliminary optical microscopy measurements showed that the strips had a total width of 0.2–0.6 mm and a thickness of 0.01–0.05 mm, while the wires diameters were of approximately 0.1–0.3 mm.

Optical microscopy and PIXE maps revealed that wires, and some of the strips (especially strips from the brocades), present striations on the surface caused by drawing in the manufacturing process. In Fig. 1, the parallel longitudinal lines on the surface of sample K3 could be visible.

Microscopy observations and PIXE lead to further information, two different types of strips – cut and flattened – being identified. According to written sources [5,18,19], the cut strips are early times threads dated from the 13th century onwards, uneven in size and quality and of variable thickness, obtained by cutting a gilt metal sheet. The flattened strips, dated from the 14th century

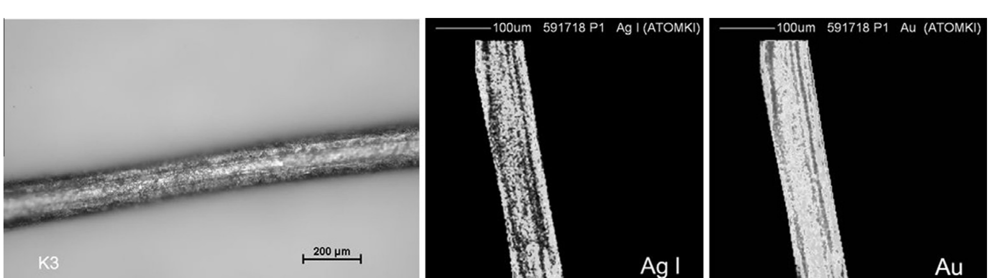

Fig. 1. The K3 – gilded silver wire microscopy image in reflected light and its corresponding AgL and Au PIXE maps. In the Au map, could be seen that the gold distribution is uneven showing some parallel lines.