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Elemental concentration profile in ancient gold artifacts by ion beam scattering

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Abstract

A technical study of the surface of some ancient gold based artifacts from South America (Colombia) is performed using ion beam techniques. Rutherford Backscattering Spectroscopy with protons and alpha particles was employed to establish the Au–Ag–Cu concentration depth profile of the items. PIXE and α-IXE spectroscopies are also used as complementary techniques to determine the sub-surface composition and to corroborate the elemental depth profile. To perform these analyses, the incident energy of the projectiles is varied from 0.6 to 2.9 MeV. X-rays and charged backscattered particles are collected simultaneously. Outstanding information about the original metallurgical processes involved in the manufacture of the artifacts (copper depletion at the surface and gold alloy plating) is obtained from the analyzed results.

1. Introduction

Rutherford Backscattering Spectroscopy (RBS) is a non-destructive multi-elemental analytical technique suitable to establish the elemental depth profile up to 5 μm of depth from the surface. Amongst many applications, this technique may be employed to carry out analysis in the archaeological field [1], in particular in archaeo-metallurgy [2]. Moreover, if PIXE (Proton Induced X-ray Emission) and α-IXE (Alpha Particle Induced X-ray Emission) are simultaneously employed as complementary analytical tools, the composition of Au, Ag and Cu in the bulk and at the surface of the gold based artifacts may be obtained. This information is fundamental to characterize the metallurgical processes involved in the manufacture of the artifacts. The application of this kind of analysis to items of the pre-Hispanic period has a particular importance to understand the skill of the ancient Amerindian metallurgists. They were able to modify the surface composition by performing special treatments like gilding and silvering in order to change the surface colour by various original chemicals processes [3]. We present results of surface analysis on two artifacts: an anthropomorphic pendant (Fig. 1) and a butterfly pendant (Fig. 2) dating from pre-Hispanic South America (Colombia).

2. RBS analysis approach

RBS is a technique mainly suitable to determine the depth profile of heavy elements in light matrices. Normally, RBS is not expected to be suitable to establish the Au–Ag–Cu composition in an homogeneous matrix due to the poor elemental resolution of the technique: the kinematic factors of these elements are indeed very close for alpha particles and still much closer for protons as shown in Fig. 3a for a material with a composition close to tumbaga alloy (Au 60%, Ag 10%, Cu 30%). But in the case of a gold rich alloy layer (1 μm thickness) deposited on the same homogeneous alloy, the high energy region of the spectrum is modified due to the higher scattering cross section for gold (Z^2 dependence) as shown in Fig. 3b. If the layer is very thin (0.3 μm thickness) alpha particles are more suitable than protons to separate high energy edges. The spectrum is still modified if a Au profile occurs at the top surface (Fig. 3c). In the simulations of Fig. 3, we have used basic bulk concentrations and surface enrichment of gold close to the situation of ancient pre-Hispanic jewellery. Gold surface enrichment is indeed expected in ancient gold jewellery from America and RBS is suitable to study this enrichment, but some complementary data on the presence of light elements is necessary (frequent in ancient artifacts). For that purpose, NRA (Nuclear Reaction Analysis) may bring some light in order to complete the characterization of the whole surface composition.

3. Complementarity of ion beam techniques

From RBS spectra a Au profile in matrices with a surface gold enrichment may be established. Using PIXE, the mean elemental composition may be determinated. To check any non-homogeneity of the matrix, relative X-rays intensity measured for various energies of the incident beam may be used. So, a proton beam with a high energy

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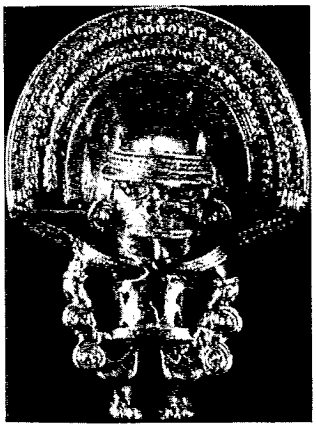

Fig. 1. Front face of the anthropomorphic pendant (Tairona style, 600–1560 AD, North of Colombia).

(about 3 MeV) may be used to determine the approximate bulk composition. If the incident beam energy is decreased the measured mean elemental composition corresponds to regions closer to the surface. If alpha particles are used (α-IXE), the elemental composition concerns only the extreme surface (< 1 μm). Thus, when RBS and PIXE spectra are simultaneously collected, the bulk and surface composition at the impact may be determinated.

Furthermore, it is known that the variation of Cu-K_α/Au-L_β ratios with incident ion beam energy are completely different if the target is not homogeneous but composed by a layered structure [4,5]. From one RBS simulation, the Cu-K_α/Au-L_β ratio may be calculated using the LARN PIXE program described in Ref. [6]. The calculated Cu-K_α/Au-L_β ratios are compared with the experimental Cu-K_α/Au-L_β ratios. RBS and PIXE results are then mutually corrected in order to achieve convergence. In this way, the Au–Cu depth profile is established [4].

Nuclear reactions $^{16}O(^3He,p)^{18}F$ and $^{12}C(^3He,p)^{14}N$ [7,8] allow us to determine the C and O profiles and then to complete the elemental depth distribution.

4. Experimental setup

RBS and PIXE (α-IXE) spectra are collected simultaneously. The irradiation is performed under vacuum conditions in a standard RBS chamber adapted to perform PIXE experiments with a Si(Li) detector in a fixed geometry [4]. The backscattering angle and the detection angle for the PIXE detector are respectively 175° and 170°. The particles and X-rays are detected in the backward direction in order to minimize uncertainties on the calculation of the outgoing path when an irregular surface is irradiated. The incident proton beam energy is varied from 600 keV to 2.9 MeV, in order to obtain signals from different depths of the irradiated material. For RBS-α and α-IXE experiments, a 2 MeV beam energy was used to study the extreme surface of the items. In experiments with protons, various calibrated plexiglas windows were used as non-selective absorbers to manage various counting rates of X-rays at different incident energies. A gold collimator of 1.5 mm in diameter was set in front of the RBS PIPS detector. Inspection of the artifacts using a Scanning Electron Microscope (SEM) indicates that the surface of the butterfly pendant was highly corroded. NRA, using a 2,9 MeV $^3He^+$ ion beam to induce $^{16}O(^3He,p)^{18}F$ and $^{12}C(^3He,p)^{14}N$ nuclear reactions, was performed in another experimental assembly to estimate C and O concentrations [8].

Fig. 2. The butterfly pendant, same origin as the anthropomorphic pendant.

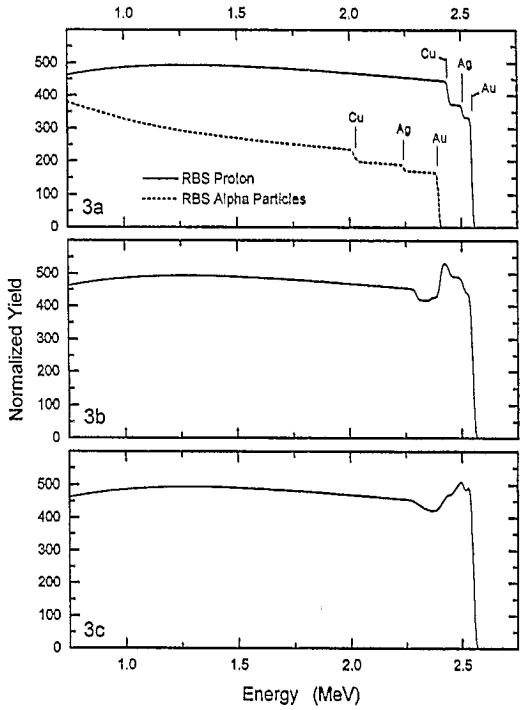

Fig. 3. (a) RUMP RBS spectra simulations [9] of a homogeneous matrix alloy for 2.6 MeV protons and alpha particles. Alloy composition: 60% Au, 10% Ag, 30% Cu. (b) RUMP RBS-proton spectrum simulation of a gold rich alloy layer (1 μm) on a matrix with the same composition as in (a). Layer composition: 73% Au, 12% Ag, 15% Cu. (c) RUMP RBS-proton spectrum simulation of a non-homogeneous matrix with a superficial gold enrichment. Au profile ranges from 80% (surface) to 60% (bulk) in 1 μm of depth from the surface.

5. Results and discussion

Fig. 4 shows a typical RBS-proton spectrum obtained during the irradiation of the anthropomorphic pendant. In this spectrum, we can observe that a gold rich layer was plated on a matrix composed by a lighter alloy. PIXE elemental composition was established using a Au–Ag–Cu–Cd–Zn homogeneous standard alloy as reference material. A RUMP simulation [9] was then established using the bulk and surface composition determined by PIXE and α-IXE respectively. This RBS simulation was corrected following the process described in Section 3. In Fig. 5, the elemental depth profile corresponding to the back of this item is shown. The surface layer is 1.5 μm thick with a nearly uniform composition. Similar results were obtained at the front face of the item. We observed that this face exhibits a thicker layer. This difference can be explained, if we consider that the jewellery item could have been worn: the back of the item (and accordingly the layer surface) could have been eroded by rubbing on the cloths. PIXE and RBS analyses show that the interface between the layer and the matrix is not sharp and that diffusion occurred. The gold content in the bulk determined by RBS and PIXE analyses is very low (10% in mass). PIXE indicates that the bulk contains also Zn in the percent range. The determination of Zn is impossible due to the strong interference of Zn-K lines with Cu-K and Au-L lines.

In the case of the butterfly pendant, the RBS-α spectrum shows a very thin rich Au–Ag alloy layer (0.2 μm) on a light matrix (Fig. 6). PIXE and α-IXE elemental analyses (bulk and surface composition respectively) were used in the RUMP simulation, but the Thick Layer PIXE program can not be applied because the thickness of the gold alloy layer is too thin to give rise to variations of Cu-K_α/Au-L_β ratios with incident beam energies. Furthermore, the presence of light elements at the surface and at the interface between the layer and the matrix modifies the stopping power and the X-ray attenuation. Irregularities at the corroded surface (observed by SEM) are frequent in items with this copper matrix structure [10]. A possible Au–Ag–Cu–Zn profile obtained in this way, is shown in Fig. 7. The balance to obtain 100% is due to the presence of C and O.

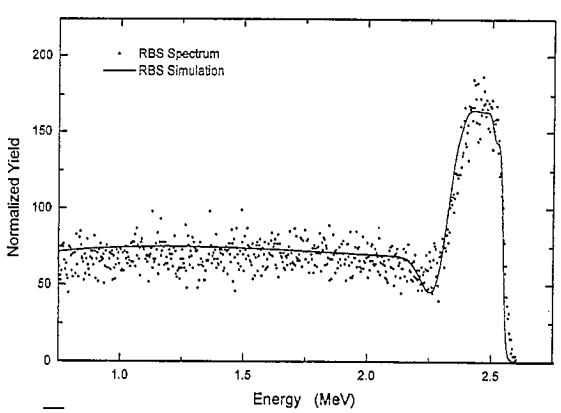

Fig. 4. Typical RBS-proton spectrum of the anthropomorphic pendant (2.6 MeV energy beam).

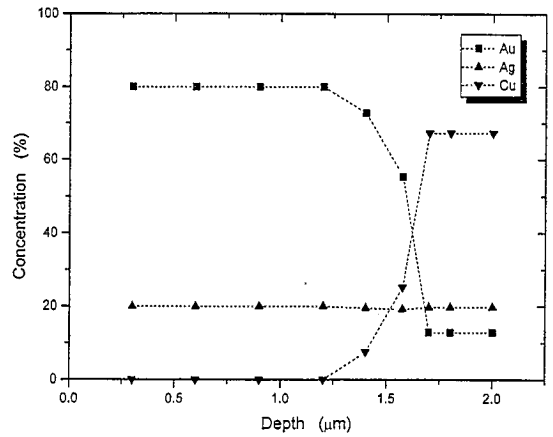

Fig. 5. Elemental depth profile of the anthropomorphic pendant (% of mass concentrations).

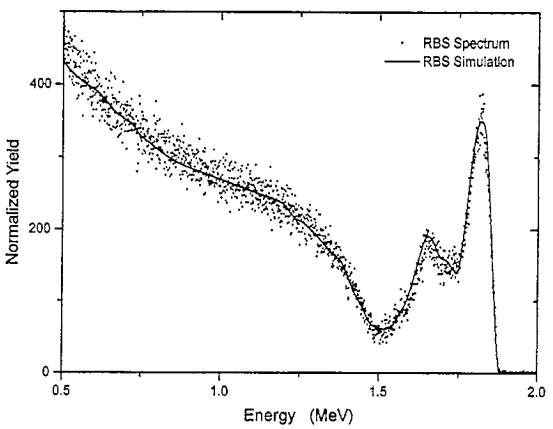

Fig. 6. Typical RBS-α spectrum of the butterfly pendant (2 MeV energy beam).

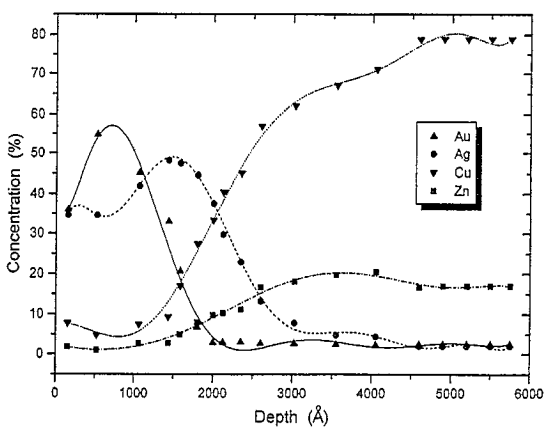

Fig. 7. Elemental depth profile of the butterfly pendant (% of mass concentrations).

6. Conclusions

RBS and PIXE results indicate that the artifacts were gilded by a plating process: an electrochemical plating assisted by a thermal treatment to deposit and to bond rich Au–Ag layers on the rich Cu matrix [11–13]. This process was well known in South America and it was developed independently of any European influence before the Spanish conquest (XVIth century). Depletion gilding observed on other artifacts [4] is not present here.

RBS complemented by PIXE (α-IXE) is a powerful method to determine the elemental depth profile in this kind of artifacts and to study the ancient American metallurgical procedures. In the case of a strong surface corrosion NRA is necessary to determine the light elements profile.

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