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Gold leaf decoration on medieval islamic glazed ceramics – in search of technological features with XRD

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Abstract. Considered as luxury earthenware, *haft-rangi* ceramics are sometimes enlightened with gold leaves. This type of decoration appears on vessels in the Iranian world in the 12th-13th centuries and is exported to Central Asia on architectural tiles in the 14th-15th centuries.

The questioning raised by this type of decoration mainly concerns the production process, its genesis and evolution in its well defined geo-chronological context. The innovative approach of the physico-chemical analysis of such a decoration so peculiar to medieval Islamic ceramic is thus essential.

The study is concerned with the micro-structural features of the gold leaf itself. Because the studied samples are part of the cultural heritage, the non-destructiveness of the experiments is of very high interest. Therefore, some diffraction patterns, characteristic of the polycrystalline gold surface of the archaeological artefacts, have been obtained by synchrotron radiation at the ESRF. The results show that the diffractograms bear the signature of both mechanical and thermal treatments which the gold leaves underwent.

Introduction

Among luxury medieval Islamic glazed ceramics, the most famous are lustre ware, *haft-rangi* ceramics (*haft rang* meaning seven colours in Persian language) as well known as *mina'i* (*mina* being the Arabic word for enamel) and *lajvardinah* (*lajvard* designating lapis lazuli in Persian). These potteries are considered as luxury products not only because of the precious raw materials involved in their making (copper and/or silver salts for lustre, glazes and decorations coloured by metallic oxides and gold leaf embellishments for the latter types) but also because of the specific firing the decoration needs (in reducing atmosphere for lustre, in oxidising atmosphere for *haft-rangi* and *lajvardinah* ceramics), the latter firing adding value to the ceramics themselves. [1]

Gold leaf decorations raise issues concerning the production process as well as the evolution of this decoration technique in a perfectly known geo-chronological context: this type of decoration appears at the end of the 12th century mainly on vessel in Iran [1]. It is also very much used during the 14th and 15th centuries on architectural tiles in Central Asia. [2]

The innovating feature of the study must be underlined: as a matter of fact, ancient and modern lustre wares [3], gold-leaf-decorated mosaic tessera [4] or modern gilded glasses [5] have already been studied, but the gold leaf decoration of medieval Islamic glazed ceramics has never been through physico-chemical analyses. Moreover, in order to preserve the ancient samples, non destructive analysing methods are privileged.

The aims of the study at stake are: to identify the raw materials and to search for technological features enabling to determine the production process.

The present article proves that the manufacturing and annealing treatments in the archaeological gold leaves have important effects on the XRD data.

Studied material

In Shakhrisabz (Uzbekistan), home town of Tamerlane – alias Timur i-Leng (1336-1405) – huge monuments such as the Ak Saray (meaning White Palace, built in 1380-1405) and the Dorut Tilovat complex (made of a mosque and mausoleums erected in 1435-1437) still present gold-leaf-decorated tiles on their façades. [2]

The studied tiles come from archaeological excavations made on the mentioned sites by the Amir Temur Museum's archaeological team. They consist in sherds of different dimensions from 2x3 cm² up to 12x15 cm² and are all covered with several cm² gold leaf decorations in a very good state of conservation as they have been preserved from strong mechanical frictions and underwent a soft cleaning during the excavations and only ethanol and demineralised water washings afterwards.

Identification of the raw materials

Is the gold used alloyed or not? In order to answer this question, the chemical composition of the gilded surfaces has been measured with X-ray spectroscopy (EDS) in SEM.

These non destructive measurements made on 23 samples revealed a high weight concentration of gold, superior to 99% and a silver ratio inferior to 1% in every analysed decoration.

The weak proportion of silver in the gold leaves indicates that it is probably a trace element present in the auriferous ore [6]. Thus, the gold used is not alloyed.

In search of the production process

About ancient written sources

Because ceramic art has always traditionally been transmitted from master to pupil in an oral way so as not to reveal production secrets, there are very few ancient written sources describing recipes and know-how. However, a manuscript dating from 1301 must be mentioned here [7]. Its author, named Abu'l Qasim Al-Kashani, used to be a civil servant at the Il-Khanid court in Iran. He was asked to write a manuscript dealing with mineralogy but, as he grew up in a several-generation-potter family, one part of his treatise is dedicated to the ceramic art. A chapter describes how to gild a ceramic in the following steps:

- Preparation of the gold leaf: the author describes the mechanical treatment of the gold leaves: "*they hammer (…) gold into 24 sheets putting paper covered with plaster between them*".
- Decoration of the glazed ceramics: this paragraph explains the adhesion process of the gold leaves on the glaze: "*they cut [the gold leaves] carefully with scissors and stick them with a pen onto the vessels with dissolved glue and smooth them with cotton*".
- Firing of the gilded glazed ceramics: Abu'l Qasim describes the thermal treatment of the gold decoration: "*each of these [decorated ceramics] is (…) fired from morning till night at a low heat*".

The following study has been done in the light of this text and the focus is made on the thermal treatment of the decoration.

Study of the gold leaf with XRD

A diffraction pattern, characteristic of the 10 studied samples, obtained by synchrotron radiation (ESRF-BM2) on an ancient gold leaf decoration (figure 1; bold line) presents the gold peaks (space group: Fm-3m, cubic close-packed). A beam size of the synchrotron radiation of 500 x 600 µm² was chosen in order to properly enlighten the surface of the gold decoration and also to have an optimal spectral resolution so as to get relevant information about the microstructure.

First, 2D-images of the diffracted signal of a gold standard and an archaeological gold decoration (respectively represented in figure 1 *(a)* and *(b)*) have been recorded on a CCD camera. The (111) and (200) Bragg rings of gold are well defined and show no redhibitory preferential orientation in the surface plane. Then some θ-2θ scans were made using a photomultiplier detector, which means that the registered information is dealing with the direction normal to the gold leaf, for a fast and easy assessment of the relation between the diffracted signal and the manufacturing process of ancient gold leaves. The calculated diffractogram of standard gold powder (figure 2; fine line) shows the same peaks but with different intensities. A modern gold leaf (supplied by the FREBA company and whose chemical composition is close to the ancient one), manufactured from a gold bar by rolling and cold hammering has been studied with a traditional θ-2θ diffractometer (Siemens D500) and is represented in figure 2, dashed line. In this latter pattern, the crystallites show a strong preferential <200> orientation normal to the gold film plane. It can be attributed to the mechanical treatment of

the gold leaf. The same preferential orientation can be observed on the diffractogram of the archaeological sample as well. The comparison of the three patterns indicates that XRD may produce information concerning the mechanical and thermal story of the gold leaf decoration.
In order to understand the influence of a thermal treatment on the XRD pattern of a gold leaf decoration, some reference samples have been prepared and studied.

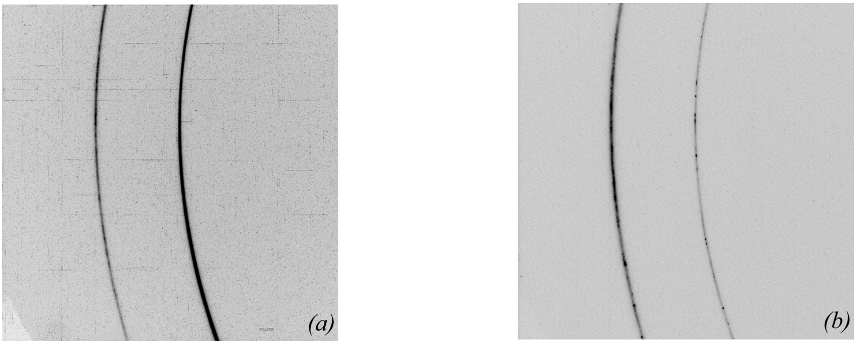

Figure 1. 2D-images of the diffracted signal of a gold reference (a) and an ancient gold decoration (b)

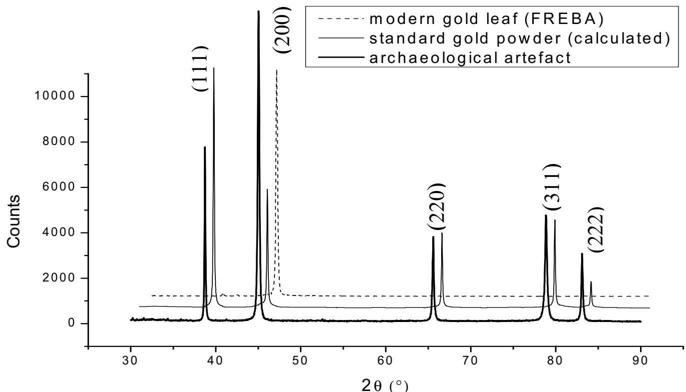

Figure 2. Comparison of 3 XRD patterns obtained on an ancient gold leaf decoration (bold line), a standard gold powder (calculated; fine line) and a modern gold leaf (dashed line).

Study of laboratory made samples
On a glass substrate, a piece of the mentioned modern gold leaf is simply deposited. Then the gilded glass goes through a firing in an electric kiln with the following parameters: the increasing and decreasing temperature rate is of 100°C/h and a 30-minute level is set at the highest temperature. Once cooled, the XRD pattern is measured with a θ-2θ diffractometer (Siemens D500). The resulting diffractograms obtained for different firing temperature are represented in figure 3. The XRD pattern of the 500°C sample is similar to the one measured on the modern gold leaf taken as a reference, i.e. without any thermal treatment (figure 2, dashed line): only the (200) peak can be observed. At 600°C, the (111) peak appears and at

700°C, it is the only visible peak (with its (222) harmonic), as the (200) has completely disappeared. Therefore, from these results, there is obviously a correlation between the relative intensities of the (111) and (200) peaks and the thermal treatment of the laboratory-made samples.
To go further in the investigation of this effect, the evolution of the XRD pattern of a gold leaf on firing has been studied.

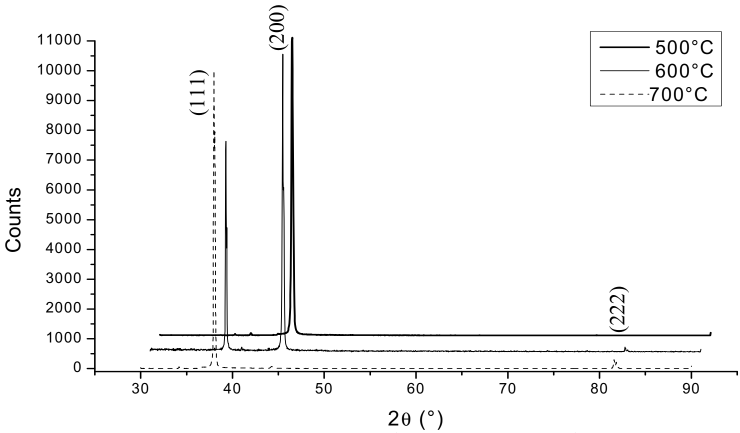

Figure 3. Comparison of 3 XRD patterns obtained on laboratory made samples that were fired at different temperatures.

Evolution of the XRD pattern of a gold leaf during a thermal treatment
A modern gold leaf (supplied by FREBA) is fired from 25°C up to 700°C and cooled back to 25°C at a 100°C/h rate. The acquisitions are made every 100°C between 100 and 500° and every 25°C between 500 and 700°C with a θ–θ diffractometer (PANalytical X'pert PRO with an Anton Paar HTK1200 chamber). The XRD patterns measured during the firing have not been represented but it has to be noticed that during the increase of temperature, the (111) peak appears beyond 500°C and that it grows during the firing, according to the literature [8-9]. It does not vanish during the cooling and is still present at room temperature.
The study of the evolution of the relative intensity of the (111) peak, calculated from equation (1), is then carried out as a function of the thermal treatment (figure 4).

$$Ir_{(111)} = \frac{I_{(111)}}{I_{(111)} + I_{(200)}} \qquad (1)$$

As it can be observed on figure 3, the relative intensity of the (111) peak exhibits a memory effect on cooling. As a matter of fact, during the rising of temperature, the intensity ratio highly changes beyond 550°C up to 700°C. During the cooling, the relative intensity remains constant. This parameter could be a marker of the thermal cycle the gold leaf went through.
For instance, for the XRD pattern represented in figure 2 (bold line), according to equation (1), $Ir_{(111)} = 0.26$. So, in the case of the diffraction patterns measured on the archaeological artefacts, if the mechanical treatment is considered to be the same as the modern one (i.e.

rolling and cold hammering), then the ancient gold leaves did undergo a firing. One can therefore conclude that the manufacture process is close to Abu'l Qasim's.

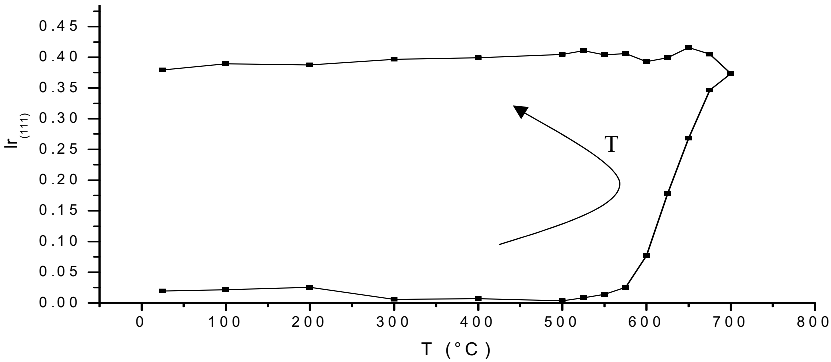

Figure 4. Evolution of the relative intensity of the (111) peak during the firing. It describes a memory phenomenon.

Limits of the study

In the practical and simplistic θ-2θ geometry, only the normal direction to the gold leaf surface is investigated. The texture is not completely determined.

A thermal treatment is characterized by the temperature increase rate, the duration of the step at a maximum temperature, and the temperature decrease rate. It can be debated that a specific thermal treatment of such a decoration exists for each workshop (and even probably for every firing in a traditional wood kiln), as it is part of a craft know-how empirically optimized.

Moreover, it was shown that gold is not alloyed but trace elements have not been analysed. The annealing response and recrystallization temperatures depend critically on dopants on a ppm level [10]. The trace elements might be very different from one sample to another: gold might come from local ores with a well-defined chemical composition but gold coming from different sources might have been mixed up, as Tamerlane was used to melting and reusing his war treasure [2].

The complexity of the materials and the above non-negligible limits must be kept in mind when modelling the ancient production process.

Conclusion and perspectives

The gold used by medieval potters to embellish these particular 14th-15th-century Islamic glazed ceramics is not alloyed and probably went through a manufacturing process very close to the one described by Abu'l Qasim in 1301.

The XRD seems of very high interest for this kind of study as the patterns apparently reflect whether the gold leaf underwent a firing, which is an essential technological output. Moreover, the diffractograms, more precisely the relative intensities exhibit a memory effect of the thermal effect the gold leaf underwent.

Nevertheless, to go further in this study, the texture should be properly determined by making pole figures on the ancient gold leaf decorations. Based on the present evidence of the sensitivity of the diffraction diagram on the treatment of the gold films, the Orientation Distribution Function of the reference and archaeological films will be examined more thoroughly using their respective pole figures. Moreover, we are also examining the microstructure of the gold decorations, in terms of crystallite size and residual strain.

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