Original Article

Technology of production of Syrian lustre (11th to 13th century)

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A B S T R A C T

Lustre is a decoration consisting of a surface layer of silver and copper metal nanoparticles, a few hundreds of nanometres thick and incorporated into the glaze. It shows a colourful metallic and iridescent appearance which makes use of the quantum confined optical response of the metallic nanoparticles. Three apparently unrelated lustre decorations, yellow-orange golden (*Tell Minis*), a dark brown-reddish with iridescences (*Raqqa*) and yellow-brown golden (*Damascus*) were produced in the same area in successive periods over tin and lead-free glazes which is known to require specific strategies to obtain a metallic shiny lustre. The composition and nanostructure of the lustre layers are analysed and the materials and specific firing conditions followed in their production determined. The optical properties of the lustre layers have been analysed in terms of the nanostructure obtained and correlated to the specific processing conditions.

1. Introduction

Lustre is a glaze decoration with a colourful metallic and iridescent appearance which makes use of the quantum confined optical response of metallic nanoparticles (Surface Plasmon Resonance, SPR). Lustre is a micrometric layer, from few hundreds of nanometres up to several microns thick, made of metallic silver and/or copper nanoparticles ($\approx 2\,nm$ to $100\,nm$) beneath the glaze surface [1–5].

Lustre production starts with ion exchange between metal ions (Ag^+ and Cu^+) from an initial mixture applied on the glaze surface, which is fully removed after firing, and alkali ions (Na^+ and K^+) from the glaze; then diffusion of the metal ions inside the glaze surface, reduction of the metal ions to the metallic state (Ag^+ to $Ag°$ and Cu^+ to $Cu°$) and finally, nucleation and growth of metallic nanoparticles [6,7]. The reduction of the metal ions to the metallic state is obtained either applying an external reducing gas or adding reducing agents to the glaze (Sn^{2+}, Fe^{2+}) [6]. Lustre must be fired at a temperature above the glass transition temperature to boost ionic diffusivity of the alkali ions, and below the softening temperature to avoid the lustre mixture sticking to the glaze. Specific materials and firing procedures give rise to differences in the lustre nanostructure and consequently to differences in the colour (green, yellow, amber, red, brown, white), and metallic (golden, coppery, silvery) or iridescent (bluish, purplish) shine. The yellow-greenish

and red colours obtained are due to the dominant dipolar contribution to the SPR absorbance cross section of silver nanoparticles ($\leq 30\,nm$) and copper nanoparticles ($\leq 50\,nm$), respectively, but also to the relative amount and oxidation state of silver and copper in the layer [7–9]. For larger nanoparticles, higher SPR multipolar contributions become more important and are responsible for the splitting and red shift of the silver absorption peak and also for the increase in the scattering contribution [10,11], changing the colour of silver lustres from yellow-greenish to orange then brown and creating blue-purplish iridescences [7,9,12].

Nevertheless, the most distinctive characteristic of lustre is the metallic like shine; golden [9,12] or copper [13] from silver and copper nanoparticles respectively. Similarly to what happens in photonic materials [14], the optical response of an ensemble of particles cannot be attributed to the scattering by individual particles but rather from the collective effect [15] which produces intense colours and strong reflectance. Generally speaking, a higher concentration of metallic nanoparticles and/or of their size increase the scattering effect [5–9]. This may be obtained by reducing the diffusivity of the ions in the glaze, and can be achieved by simply adding large divalent cations [16,17] into the glaze such as barium or lead [7] and introducing a stronger reducing atmosphere.

Although all this may suggest a product of modern nano-technology,

the fact is that the first lustre was produced at least 1250 years ago. The complexity of lustre technology suggests a direct transmission of knowledge between production centres as copying is improbable. Consequently, it is commonly accepted that the main mechanism of geographical expansion of lustre technology occurred by the migration of artisans to other production centres [18–20].

Previous studies demonstrated that each lustre production has distinctive characteristics: chemistry (silver/copper content and oxidation state), nanostructure (size and concentration of particles) and layer thickness [2–9,12–14,20,21]. Differences in all cases are related to a combination of variations in the production process and materials used. In particular, the addition of PbO to the alkaline glaze increases the probability of obtaining a lustrous layer; an increase from nearly 0 up to 30 wt% in the PbO content is observed from Abbasid to Fatimid lustres [9]. The low lead content of some of the earliest polychrome Abbasid productions prevented them from attaining a metallic lustrous layer [7]. A high firing temperature, stronger reducing atmosphere and the application of several lustre pigments with successive firings [8] helped to increase the size and concentration of nanoparticles in the lustre layers, were thus required. Subsequent productions used mixed lead-alkali glazes with the exception of some Syrian and Iranian productions [20,22]; in particular, the Syrian lustreware productions which are the subject of this work.

During the 11th century Syria was under the Fatimid rule until the Seljuks took control (c. 1084–1086. Later Saladin (c. 1175–1185) conquered Syria and established the Ayyubid dynasty until defeated by the Mamluks (1260–1400). Three lustreware productions directly related to the Seljuk, Ayyubid and Mamluk periods exist: *Tell Minis* (late 11th- first half of the 12th century AD), *Raqqa* (second half of the 12th-first half of the 13th century AD) and *Damascus* (second half of the 13th century AD) [18,19]. The names are given after the geographical areas where main workshops (*Raqqa* and *Damascus*) or some fine objects (*Tell Minis*) have been found. The three productions are characterised by the use of stonepaste bodies (a synthetic ceramic paste made of sand, clay and glass frit), tin-free glazes and apparently unconnected lustre decorations. *Tell Minis* ware has distinctive fine compact bodies, a transparent mixed lead-alkaline glaze and a range of greenish-yellow to orange golden lustre (Fig. 1a) [23,26]; *Raqqa* ware is coarser and more porous, has an alkaline glaze and a dark brown-reddish lustre with iridescences (Fig. 1b) [22,24–26]. Finally, *Damascus* ware often shows more rounded sand grains, has a cobalt tinged either alkaline or mixed lead-alkaline glaze and a yellow-brown golden lustre (Fig. 1c) [23,24,26].

Consequently, the study of Syrian lustreware is of particular interest not only because of the variety of apparently unrelated lustre decorations produced in the same area in successive periods, but also because of the use of tin-free and, at Raqqa, lead-free glazes which require specific strategies to obtain a metallic shiny lustre. Analysis of the composition and nanostructure of the lustre layers provides information about the technology of production. The differences observed between productions will be discussed in terms of the processes followed and of the optical properties obtained.

The chemistry, oxidation state and nanostructure of the lustre layers are obtained by combination of microanalytical techniques. Imaging of the lustre layers is obtained by Scanning Electron Microscopy (SEM) of Focused Ion Beam (FIB) cut and polished lustre cross sections; the crystalline compounds are identified by micro X-Ray Diffraction (µ-XRD); analysis of the lustre layers is either by an Energy-Dispersive X-ray Spectroscope attached to the SEM (EDS) or by Rutherford Backscattering Spectroscopy (RBS); the oxidation state of copper in the lustre layers is by X-ray Absorption Near Edge Structure spectroscopy (XANES) and the identification of the SPR from metallic nanoparticles by Ultraviolet and Visible spectroscopy (UV–Vis).

2. Materials and methods

Two *Tell Minis* (EA2217r and p8834/p8836) [27], five *Raqqa* (p9404, p620, p9403, p18777 and p18779) [28], and one *Damascus* (p8839) [27] shards were obtained from the Ashmolean Museum (Oxford), and three *Damascus* (c1293, c1295 and c1288) shards from the Victoria and Albert Museum. Pictures of all the samples analysed are given in the Tables S-I, S-II and S-III and S-IV in the supplementary material for the three lustre productions. Pictures of representative examples of the three types of decorations are shown in Fig. 1.

A crossbeam workstation (Zeiss Neon 40) equipped with SEM (Shottky FE) and Ga$^+$ FIB columns, was used to prepare cross sections of the lustre layers [29]. First, the sample surface was coated with a thin protective Pt layer (1 µm) by ion-beam-assisted deposition; then the cross section was cut and polished and a thin layer of Pt deposited to enhance conductivity. SEM images of the polished cross sections of the lustre layers were obtained at 5 kV (some at 2 kV). In some cases chemical line maps of cross sections of the lustre layers were also obtained. The compositions of ceramic pastes and glazes were obtained from polished cross sections by SEM-EDS (INCAPentaFETx3 detector, 30 mm^2, ATW2 window) operated at 20 kV, with 120 s measuring times, on representative areas of paste (3 mm × 2 mm) and glaze (~ 200 µm × 200 µm), calibrated using mineral and glass standards respectively. The data are an average of at least 2 measurements. Optical microscope and SEM-BSE images of ceramic and glaze cross sections of some of the sherds are shown elsewhere [22].

RBS measurements were performed using a 5 MV tandem accelerator [30]. A 3070 keV energy He-beam with square-section (1 mm in diagonal) was used, thus taking advantage of the elastic resonance ^{16}O (α,α) ^{16}O occurring at this energy and increasing the sensitivity to oxygen concentration by a factor of 23 [31]. The samples were kept in vacuum. A careful quantification was performed by employing the simulation code SIMNRA [32]. RBS data was fitted starting from the average chemical compositions obtained from the microprobe analysis of the layers and following a procedure described elsewhere [8,9,12,13]. To determine the chemical profiles of the lustre cross sections, a sequence of layers with varying silver and/or copper content was modelled. The thickness of each layer is given in units of areal densities, which can be converted into absolute thicknesses provided that the mean density of the layer is known. The mean density of the lustre layer was estimated by linear interpolation from the metal nanoparticle and glaze fractions taking 10.49 g/cm^3 for metallic silver, 8.89 g/cm^3 for metallic copper and, for the glaze, the density calculated from the RBS fittings after Fluegel [33].

Cu K-α edge EXAFS fluorescence spectra for lustre layers p620f, c1293 and c1295r were acquired using a SDD single channel fluorescence detector at beamline CLAESS (BL22) at the Alba synchrotron. X-ray absorption Near Edge (XANES) data was collected for the lustre layers on EA2217, p620, p8833, p8834/36 and p8839 samples. In all the cases a 100 × 200 µm^2 area was measured. Reference Cu foil and pellets of cuprite (Cu$_2$O) and tenorite (CuO) powders were measured in transmission mode. Data analysis was conducted using the Demeter (Athena for XANES and Artemis for EXAFS) suite of programmes [34].

µ-XRD of cross sections of the ceramic bodies, glazes and lustre decorations were performed in transmission geometry at beamline MSPD (BL04) at the Alba Synchrotron Light Facility using 0.4243 Å wavelength and a CCD camera detector (Rayonix SX165, Rayonix, L.L.C., Evanston, IL).

UV-Vis diffuse reflectance (R) measurements were performed directly on the surface of the samples using a double beam UV-Vis spectrophotometer (Shimadzu 2700) equipped with ISR 3100 Ulbricht integrating sphere. The spot size was a slit of 5 mm × 1 mm, and measurements were made between 200 nm and 800 nm at 1 nm resolution. A D65 standard illumination source was used and barium sulphate provided a white standard.

Cu and Ag chemical cross section profiles were determined either