

Technology of production of polychrome lustre

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Abstract

Lustre is a decoration consisting of a few hundreds of nanometres thick surface layer of silver and copper metal nanoparticles incorporated into the glaze. Polychrome lustreware with several combinations of colours and shines was produced in Abbasid Iraq in the 9th century AD. Three colour combinations, black plus red, white-silvery plus red-copper and yellow-golden plus red-copper, have been studied, and the materials and methods of production determined. Two separated firings the first for the copper and the second for the silver lustre were performed. The black, white, yellow and green colours of the silver lustres are associated with the different sizes of the nanoparticles and to their distribution in the layer. Although the addition of lead and tin in the initial mixture is demonstrated, their incorporation in the glaze has been found to be the key factor in the production of the red-copper and yellow-golden lustre.

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1. Introduction

Lustre is a metallic-like decoration applied on ceramic glazes. It consists of a thin surface layer (from few hundreds of nanometres up to several microns) of metal nanoparticles of silver and/or copper incorporated in the glaze and with sizes ranging between 2 and 50 nm.^{1–3} The production process comprises first ion exchange between the Ag⁺ and/or Cu⁺ ions from an initial mixture applied on the glaze surface, which is fully removed after firing, and the Na⁺ and K⁺ ions from the glaze, followed by reduction of Ag⁺ to Ag⁰ and Cu⁺ to Cu⁰ and finally, nucleation and growth of metallic copper/silver nanoparticles.^{4,5} Reduction of the ions to the metallic state may be obtained either

by an external reducing gas but also by the addition of reducing agents to the glaze such as Sn²⁺ and/or Fe²⁺ among other.⁶ The lustre layers show peculiar optical properties (colour iridescences and metallic-like shine) consequence of the quantum confined optical response of the metallic nanoparticles (Surface Plasmon Resonance, SPR). As a consequence, a narrow range of the electromagnetic wavelengths is absorbed by the nanoparticles; an absorption peak at 400 nm is observed for metallic silver nanoparticles and at 560 nm for metallic copper nanoparticles.⁷ The colour obtained is essentially that due to absorption by the small nanoparticles (green–yellow for silver and red for copper) but also to the relative amount and oxidation state of silver and copper in the layer.^{5,8} However, increasing the size of the nanoparticles (above 30 nm for silver and 50 nm for copper) high multipolar interactions are responsible for the splitting and red shift of the absorption peak, at the same time that scattering becomes more important^{7,8}; as a consequence the colour of the silver lustres changes from green–yellow to orange and brown showing also often blue iridescences.^{5,8,10} On the other hand,

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increasing the concentration of the metallic nanoparticles in the layer the optical response cannot be attributed anymore to scattering by individual particles but should rather be considered as the result of collective scattering by an ensemble of particles¹¹ providing intense colours and strong reflectance similarly to what happens in photonic materials.¹² For silver and copper nanoparticles characteristic golden-like^{8,10} and coppery¹³ reflectance is observed respectively. It is known that the addition of large divalent cations such as lead in the glaze results in a reduction of the diffusivity of the alkali cations.^{14,15} Consequently, high concentration of metallic nanoparticles in the lustre layer is obtained in lead richer lead-alkaline glazes. As a global outline of previous studies on the lustre production process⁵ the metallic shining effect is mainly controlled by the diffusivity of metallic ions in the glass substrate,^{8,10,13} while colour is mostly dependent on the relative concentrations of silver and copper in the initial lustre mixture and on the processing parameters, i.e. thermal protocol and reducing agents present in the glaze.

The earliest lustreware was produced in Iraq (Bashra) in the 9th century during the Abbasid caliphate.¹⁶ It is characterized by the use of several colours on the same piece (polychrome lustre) while later productions are mainly monochrome.^{17–21} There are several combinations of colours and shines. The shines which are indicated in brackets are golden or silvery for silver-based lustres and coppery for copper-based lustres. The most common combinations are brown, with bluish iridescences resulting from scattering by large single silver nanoparticles, and ochre; brown, again with bluish iridescences, ochre and green (golden); red (coppery) and yellow (golden); red (sometimes coppery) and black and red (coppery) and white (silvery). Polychrome red (coppery) and yellow (golden) was not produced again until the last decades of the 15th century and during the 16th century in Deruta and Gubbio (Italy).^{22–26}

Those lustre decorations combining brown, ochre and green have already been studied.²⁷ They were produced under relatively light reducing conditions using an initial mixture applied on the glaze surface containing both copper and silver in various amounts. The green colour was obtained by adding silver while copper is either absent or present in very small amounts; the ochre, by adding both copper and silver in similar amounts; and the brown also by adding both but with silver in higher amounts than copper. The addition of copper helps the reduction of the silver ions to metal together with the precipitation and growth of silver nanoparticles while, conversely, copper is oxidized appearing as Cu^+ and also Cu^{2+} in larger or smaller amounts depending on the silver/copper ratio. Consequently, green lustres are formed exclusively by silver nanoparticles; ochre lustres contain copper mainly as Cu^+ and metallic silver nanoparticles; and brown lustres contain mainly metallic silver nanoparticles, Cu^{2+} and in lower amounts Cu^+ and cuprite nanoparticles. The different colours were applied on separate areas of the glaze surface, and in all cases, fired under light reducing conditions. Consequently, all the colour decorations could be applied at the same time. They are characterized by the presence of metallic silver nanoparticles and the absence of metallic copper nanoparticles, and so we usually call them silver lustres.

On the contrary red lustres (copper lustres) are characterized by the presence of metallic copper and cuprite nanoparticles and also Cu^+ in variable amounts, although some small amounts of silver nanoparticles may also be present.⁵ A stronger reducing environment is required to reduce copper to the metallic state. Consequently, the combination of silver lustres and copper lustres in the same decoration creates some difficulties, and specific methods of production are required. The three types of Abbasid lustreware combining both copper and silver lustre are studied with the object of determining the materials and method followed in their production. Although the three of them are very beautiful, it is quite obvious than these combining red (coppery) and yellow (golden) decorations are most probably the one sought. Therefore, we investigate the specific method of production followed to succeed obtaining this combination. Finally, the reasons for the different colours and shines observed are also studied and related to the specific nanostructures (type, size and distribution of the nanoparticles) of the lustre decorations.

The chemical and microstructural composition of the glazes and of the lustre layers is obtained by combination of Scanning Electron Microscopy with an Energy-Dispersive X-ray Spectroscopy attached (SEM-EDS), Focused Ion Beam (FIB), micro X-Ray Diffraction (μ -XRD), Rutherford Backscattering Spectroscopy (RBS) and Ultraviolet and Visible spectroscopy (UV–vis).

FIB was used to produce polished cross sections of the lustre layers, and subsequently, secondary electrons (SEM) images of the nanostructure were obtained²⁸; SEM-EDS was used to analyze both the glaze cross sections and the lustre surfaces. RBS was used to determine the cross section composition profiles of the lustre layers. μ -XRD and UV–vis were performed in order to determine the nature of the metallic nanoparticles in the lustre layers. The colour coordinates of the decorations were also obtained from the reflectance UV–vis spectra. Finally, the relationship between colour and shine of the lustre decorations and the chemistry and nanostructure observed is then discussed.

2. Materials and techniques

Fig. 1 shows the three samples characteristic of the polychrome 9th century Iraqi lustreware production combining copper and silver lustres that were selected for study. P624 and P717 belong to the Ashmolean Museum (Oxford) and IV163 to the Instituto Valencia Don Juan (Madrid). Sample P624 combines red and black decorations, P717 red, red-coppery and white-silvery, and IV163 red, red-coppery and yellow-golden with some green-golden spots.

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. 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 and in some cases at 2 kV to minimize the penetration of the electron beam. The compositions of ceramic pastes and glazes were obtained from polished cross sections by

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