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Original article

Technology of Islamic lustre

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Abstract

Replications of the lustre layers have been produced using laboratory-controlled conditions, based on a 13th century AD lustre recipe. The characteristics of the lustre layers obtained by using different paint and glaze compositions, thermal paths and atmospheres are summarised. The key parameters needed to reproduce the colours, composition and metallic optical response shown by medieval lustres are given. Analysis of the microstructural, chemical and optical characteristics of the reproductions gives a deep insight into the conditions needed for the production of lustre layers with different colours and shines. The necessary changes and improvements in the lustre process from the beginning of the lustre production (Iraq 9th and 10th centuries AD), through the Fatimid (Egypt 11th and 12th centuries AD) and later Syrian and Persian (late 12th and 13th centuries AD) productions are reviewed.

Keywords: Lustre; Glass; Glaze; Islamic; Nanoparticles; RBS; EXAFS; SR-XRD; Microprobe

1. Introduction

Lustre is a metal glass nanocomposite thin layer made of metal copper or silver nanoparticles embedded in a silica-based glassy matrix. The metal particles range from 2 to 50 nm in size and the whole layer is from approximately 100 nm to 1 μm thick [1,2]. The most striking property of the lustre surface is its capability to reflect light like a metal surface and in particular to look like a gold layer [3]. Although we now know that the gold-like effect of lustre is a consequence of the nano-size of the metal silver nanoparticles present [3–5], the medieval artisans may have believed that the process was an alchemy whereby silver and copper was apparently transformed into gold. The lustre technique was first applied to glass objects in early Islamic Egypt and later to glazed ceramics in early Islamic times, Iraq 9th century AD [6–9]. The lustre technique involves a sophisticated and innovative process which entails the reaction of a lustre paint with the glass surface at a relatively low temperature of between 500 °C and 600 °C. This reaction results in the introduction of silver and copper ions into the glass by means of ionic exchange with the alkali ions from the glass. Once incorporated into the glass, different species: Cu^{+} and Cu^{2+} for copper lustres; and Ag^{+} and $(Ag_n^0)^+$ for silver lustres are formed. Subsequent application of a reducing kiln atmosphere will convert the metal ions to metal form, from which they can aggregate into metal nanoparticles [10]. The remaining paint is afterwards removed to reveal the lustre layer formed. The manufacture of lustreware therefore requires a sophisticated process, multiple firings and the use of expensive raw materials meaning that it is an expensive art form and the product of skilled artisans.

Lustre reproductions made under controlled conditions [11–13] have allowed the correlation of the archaeological data with the technological requirements; in particular, the effect of

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different paint recipes, glaze compositions, thermal paths and atmospheres on the final characteristics of the lustre nanolayer formed. Moreover, the key parameters needed to reproduce the colours, composition, and metallic-like optical response shown by medieval lustres, have been assessed. A summary of the conditions needed for obtaining the different colours and shines shown in lustres from early Islamic times is presented here. The necessary changes and improvements in the lustre process from the beginning of the lustre production (Iraq 9th and 10th centuries AD) [13], through the Fatimid (Egypt 11th and 12th centuries AD) and to the later Syrian and Iranian (late 12th and 13th centuries AD) productions [14] are thus exposed. This study provides a new contribution to the understanding of the evolution of the lustre technology during this period.

2. Samples studied and experimental techniques

Copper, silver, and mixed copper and silver lustres were obtained under controlled laboratory conditions, using a medieval recipe found during the excavations of the late 13th century AD workshop at Paterna (Valencia) [15,16]. Analysis of the archaeological lustre paint showed that it comprised 40% workshop clay with some extra quartz and iron oxides (7.5%), 30% cinnabar, 13% CuO and 2% Ag_2S. All the ancient recipes described in ancient texts include clay, iron oxides, copper and/or silver compounds and a sulfur bearing compound such as cinnabar. Based on the Paterna workshop paint we essayed lustre recipes including copper and/or silver compounds, 30% cinnabar and 50% of clay with the addition of some quartz and iron oxides. Several thermal paths and atmospheres (oxidizing, neutral, and reducing), lustre formulae and glaze compositions were tested in order to reproduce the colours and shines of medieval lustres. All the parameters considered and the detailed experimental procedures used are given in Refs. [10–13].

A representative selection of Islamic lustres was obtained from the Ashmolean Museum; spanning the earliest polychrome Iraqi production and later Iraqi, Egyptian, Iranian and Syrian productions. In this study, the chemical and physical properties of ceramic pastes, glazes and lustre layers were considered. As will be shown, the role of the glaze is significant to the formation of lustre, but a consideration of the underlying ceramic is also important as this provides further insights into the original quality and value of the lustrewares.

The lustre layers were studied by using a selection of analytical tools including: Microprobe analysis of the surfaces, Synchrotron Radiation Micro X-ray diffraction (SR-Micro-XRD) and Ultraviolet and Visible (UV–vis) diffuse reflectance (DR) to obtain structural information of the metal nanoparticles (type and size). X-ray Absorption Near Edge Spectroscopy (XANES) end Extended X-ray Absorption Fine Structure (EXAFS) were used to obtain the oxidation state and local coordination of Cu and Ag. In selected cases TEM cross-sections and Rutherford Backscattering Spectroscopy (RBS) were performed in order to provide the thickness of the layer and volume fraction of nanoparticles in the layer. Details of the procedures are given in Refs. [10–17].

3. Lustre replications

Lustre paint recipes are very diverse but in all cases include clay, copper or/and silver compounds and a sulfur containing compound [8,15,16,18]. The use of copper sulfides, silver and sulfur are described in the early 14th century AD Persian treatise from Abü'l-Qäsim's [18], whilst cinnabar (HgS) has been identified in lustre paint from the late 13th century AD Hispano-Moresque workshop of Paterna [15]. The decomposition of cinnabar produces a sulfur-reducing atmosphere, which at temperatures between 500 °C and 600 °C forms copper and silver sulfates and sulfides and reduces Cu^{2+} to Cu^{+} [12,16]. These compounds are similar to those in the recipe described in the Persian treatise [18]. The formation of mixed alkali and Cu/Ag containing sulfates that melt at temperatures between 500 °C and 600 °C produces suitable conditions for ionic exchange [12]. The cinnabar containing recipe from the Paterna workshop was used in the creation of the replications described here. Although, broadly speaking, similar results are expected from the Persian recipe, the local oxidation/reducing conditions depend on the amount of sulfur-reducing compounds contained in the paint, and therefore, the external oxidizing and reducing atmospheres to be used in the kiln will vary for each recipe.

Green-yellow and green-yellow golden lustres are obtained using the silver containing lustre paint, whilst red ruby and red coppery lustres result from the use of copper containing lustre paint [11]. Yellow, brown, dark brown, amber, and orange, either golden or non-metallic lustres are obtained for lustre paint containing both copper and silver [12,13]. Although lustre layers are obtained for the whole range of temperatures studied from 450 °C to 600 °C, optimal lustres are obtained at temperatures of 550 °C and are shown in Fig. 1. For the lustre paint used, an initial oxidizing/neutral atmosphere followed by

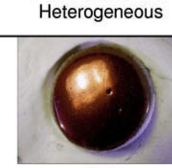
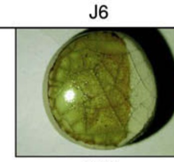
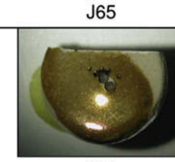
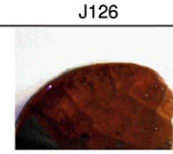
Glaze Size of nanoparticles Size distribution	Lead-free 10-20 nm Homogeneous	With 32%PbO From 3 to 50 nm Heterogeneous
Cu° and cuprite	 J6	 J65
Ag°	 J126	 J76
Cuprite, Cu^{2+} & Ag°	 J17	 J93

Fig. 1. Reproduction samples of copper (j6, j65), silver (j126, j76) and mixed copper and silver (j17, j93) lustres. The size and distribution of the nanoparticles was determined by SR-Micro-XRD, UV–vis spectroscopy and TEM.