Lessons in Nanotechnology from
Traditional and Advanced Ceramics
J.-F. Baumard (Editor)
© Techna Group Srl, 2005

SILVER AND COPPER NANOPARTICLES IN ITALIAN LUSTRE RENAISSANCE POTTERY

B.G. BRUNETTI, A. SGAMELLOTTI
Centre SMAArt and O.U. INSTM, Dipartimento di Chimica, Università di Perugia, Perugia, Italy

Lustre is one of the most important decorative techniques of the Medieval and Renaissance pottery characterised by copper and silver nanoclusters dispersed in the glaze layer, as demonstrated by the results of many optical and spectroscopic techniques. Furthermore, the local environment of copper and silver atoms has been studied by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy on original samples of gold and red lustre. It has been found that in gold lustre, whose colour is attributed mainly to the silver nanocluster dispersion, silver is practically all present in the reduced metallic form, while copper is almost completely oxidised. In red lustre, whose colour is attributed mainly to the copper nanocluster dispersion, only a fraction of copper is present in the reduced metallic form. EXAFS measurements on red lustre, carried out in the total electron yield mode to probe only the first 150 nm of the glaze layer, indicated that, in spite of the large heterogeneity, lustre nanoclusters are mainly confined very close to the surface. For this reason, even very small fractions of copper and silver in the reduced metal nanocluster form can produce significant lustre effects.

1. INTRODUCTION

Lustre is a typical decoration of Medieval and Renaissance pottery of the Mediterranean basin characterized by brilliant metallic reflections, iridescence and *"cangiante"* effects (see Fig. 1). As recently found, it consists of a very thin layer of silver and/or copper nanoparticles dispersed within the white surface of a tin-opacified lead glaze[1].

The manufacturing technique of lustre is originally Islamic. It was first developed in Mesopotamia, during IX century, then the technique moved to Egypt during the Fatymid period and from Egypt diffused throughout the Mediterranean basin together with the spread of the Islamic culture (X-XIII century). In Europe, the manufacture of lustre was particularly developed in

FIGURE 1 - Two Umbrian lustre plates. On the left: "S. Antonio Abate", Maestro Derutese (first half of the XVI century). Museo Regionale della Ceramica di Deruta; on the right: "Pico, Circe and Canente", Mastro Giorgio Andreoli da Gubbio (1528). Museo Comunale di Gubbio.

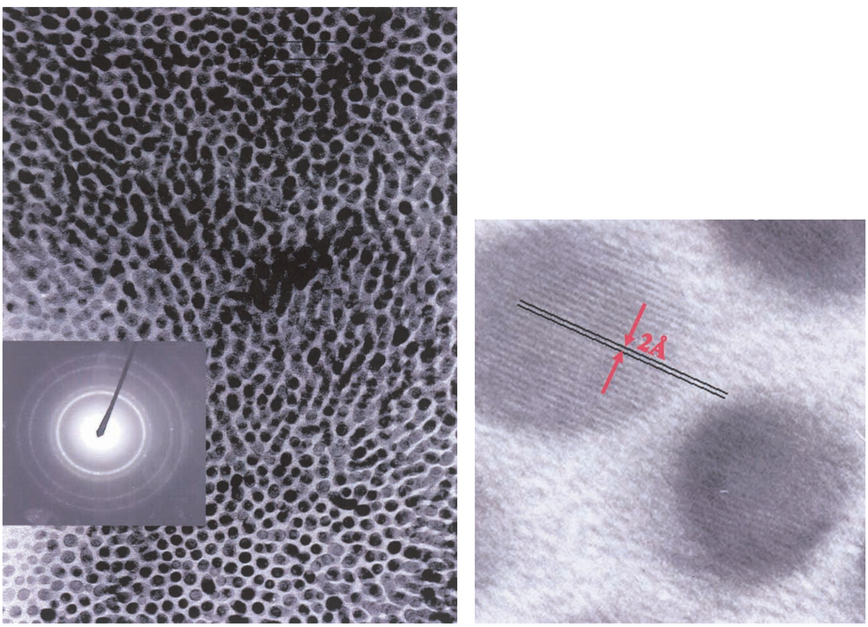

FIGURE 2 - A TEM image of the copper nanoparticles distributed in the glaze surface of gold lustre. The insertion reports the corresponding Cu X-ray diffraction pattern. On the right, a magnification of one Cu nanoparticle (diameter ~ 7 nm) is shown with the indication of the Cu lattice fringes.

Spain, near Valencia, from XII to XV century and then in Italy, in Deruta and Gubbio, during the XV and XVI century[2]. The preparation of the Renaissance Italian lustre decoration was described by C. Piccolpasso in *I Tre Libri dell'Arte del Vasaio (1557)*[3]. Lustre was obtained by putting a mixture of copper and silver salts and oxides, together with vinegar, red ochre and clay, on the surface of a previously glazed pottery. Then, the whole system was heated to about 600 °C in a reductive atmosphere, produced by the introduction of smoking substances in the kiln.

Studies by Scanning and Transmission Electron Microscopy (SEM and TEM) and by Rutherford Back-Scattering (RBS) technique clearly demonstrated that lustre decorations at the glaze surface appear as an inhomogeneous distribution of silver and/or copper nanoparticles in the glassy matrix of the glaze[1,4-6], although the distribution may be homogeneous in some regions (Fig. 2). Visible reflectance spectra recorded on a large number of samples clearly showed that lustre chromatic effects depend on the properties of the nanoparticle colloidal dispersion. Indeed, surface plasmon resonances (SPR),

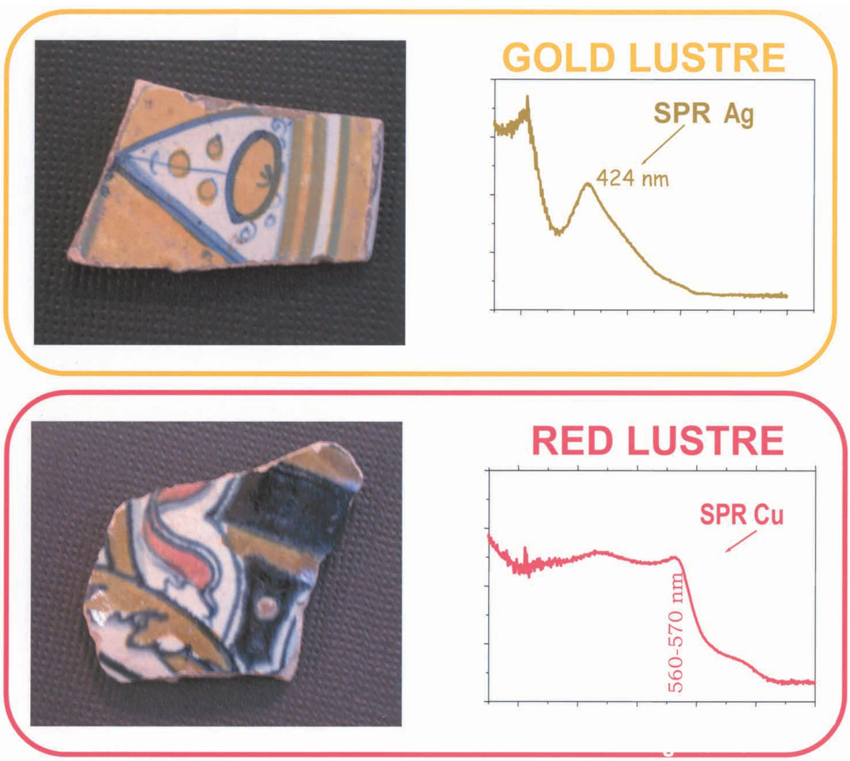

FIGURE 3 - Reflectance adsorption spectra of gold and red lustres showing the Surface Plasmon Resonances (SPR).

typical of silver and copper nanocluster dispersions in a transparent medium, have been observed for lustres of different colours (Fig. 3).

However, many questions regarding composition, structure and optical properties of the decoration are still open. For example, no information are available on state and chemical environment of silver and copper in the lustre glaze. Therefore, in the effort of better understanding these aspects, an EXAFS study on original samples of gold and red lustre is discussed.

2. DISCUSSION

The study of the local environment of copper and silver atoms in original Italian Renaissance samples of gold and red lustre confirms that gold and red chromatic effects can be mainly attributed to silver and copper nanoparticles, respectively. However, it has been found that in gold lustre almost all silver present in the glaze is reduced to metallic nanoparticles, while copper is largely in the oxidised Cu^{+} and Cu^{2+} forms.

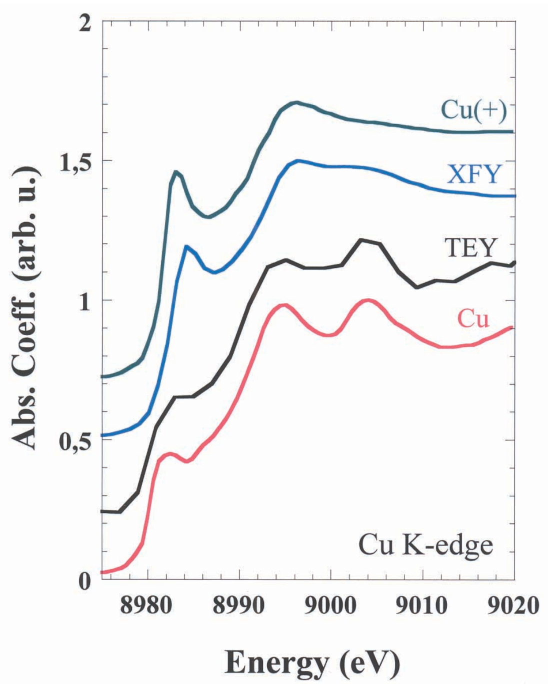

FIGURE 4 - Comparison between EXFAS spectra for a red lustre collected in fluorescence (XFY) and total electron yeld (TEY) mode, together with the standards Cu and Cu_2O (see text).

Correspondingly, in the case of red lustre, where silver is not present, copper is only partially reduced, being largely present in the oxidation state Cu^{+}.

This result well explain why previous attempts to put in relation elemental Cu/Ag composition ratio with lustre colour did not produce any significant conclusion: only the fractions of reduced silver and reduced copper are mainly responsible of the colour, and this fraction can be low and variable case by case, according to the reductive conditions and temperature produced in the kiln by ancient masters.

The lustre effects is produced even if the reduction to metal particles involved only the very minor fraction of the ions close to the glaze surface. The comparison of the results obtained on a red sample by measuring the X-ray absorption probing ~30 μm of the glaze or, alternatively, the first 150 nm, demonstrates that the layer of metal nanoparticles producing a good lustre effect can be very small compared to the whole layer containing ions, so small to be hardly detectable by EXAFS in fluorescence mode (see Figure 4).

The large presence of silver and copper ions in the glaze is compatible with the previously suggested mechanism of lustre formation involving a first step, where a migration of copper and silver ions occurs from the paste of the original lustre recipe into the glaze. The migration is probably occurring through an ion-exchange with the glaze alkali ions. According to this mechanism, the ion penetration into the glaze matrix is followed by the reduction to silver and copper nanoparticles, produced by the reductive atmosphere created in the kiln. After the first nucleation, the crystal growth could regarded as a spontaneous process due to the supersaturation of the elemental concentrations in the region where clustering occurs [7,8].

REFERENCES

1. J. Pérez-Arantegui, J. Molera, A. Larrea, T. Pradell, M. Vendrell-Saz, I. Borgia, B.G. Brunetti, F. Cariati, P. Fermo, M. Mellini, A. Sgamellotti, C. Viti, J. Am. Ceramic Soc. 84 (2001) 442.
2. A. Caiger-Smith, *Lustre Pottery. Technique, Tradition and Innovation in Islam and the Western World*. (Faber & Faber, London, UK, 1985).
3. C. Piccolpasso, *I Tre Libri dell'Arte del Vasaio, 1557* (Edizioni all'Insegna del Giglio, Firenze, 1976).
4. I. Borgia, B. Brunetti, I. Mariani, A. Sgamellotti, F. Cariati, P. Fermo, M. Mellini, C. Viti, Appl. Surf. Science 185 (2002) 206.
5. G. Padeletti, P. Fermo, Appl. Phys.A 76 (2003) 515
6. S. Padovani, C. Sada, P. Mazzoldi, B. Brunetti, I. Borgia, A. Giulivi, A.Sgamellotti, F. D'Acapito, G. Battaglin, J. Appl. Phys. 93 (2003) 158.

7. A. Miotello, G. De Marchi, G. Mattei, P. Mazzoldi, A. Quaranta, Appl. Phys. A 67 (1998) 527.
8. A. Miotello, G. De Marchi, G. Mattei, P. Mazzoldi, A. Quaranta, Appl. Phys. A 70 (2000) 415.

Discussion

L.L. HENCH: Please, comment on the early history of the discovery of lustre glazes and how the process was discovered.

A. SGAMELLOTTI: The lustre is an Islamic technique, but no precise information are available on the discovery of the process. Probably analogous techniques were already utilized by the glass makers.

G.L. MESSING: Can you comment on how artisans in the Renaissance period were able to control the reducing atmosphere to obtain the best lustres?

A. SGAMELLOTTI: The reductive atmosphere was produced by the introduction of smoking substances in the kiln.
Documents report the use of broom wood in Deruta

J. LAFAIT: Surface plasmon phenomenon is not enough by itself to explain iridescent effects in lustres. Interference phenomena need to be involved in the explanation. What's your opinion?

A. SGAMELLOTTI: Certainly the interference phenomena play a relevant role in the explanation of iridescences. We are currently carrying on a research along this direction in collaboration with the "National Institute of Applied Physics" in Florence (INOA).

S. BAIK: 1. How did they control the nanoparticle size and interparticle distance?
2. Can you reproduce the process to give such colors nowadays?

A. SGAMELLOTTI: Concerning the first question, the conditions of the lustre process were based on the great experience of the master artisans.
Nowadays some artisans are able to reproduce the colours of lustres following the antiques recipes: there are some relevant differences e.g. the kilns are electrical, the silver salts and oxides are not prepared by calcination, as in the old time. Today it is easer to control the many variables of the process and therefore the reproducibility is higher. However it remains extremely difficult to reach the high level of the creations of the great Renaissance Masters.

J. LIS: Can you compare the ancient lustre techniques with more modern lustre technologies used in porcelain and tiles industries starting from XVII's to our times (techniques, multicolour effect, etc..)?

A. SGAMELLOTTI: The modern lustre technologies, used in the industry, are completely different from the old ones since the decorations are directly applied above the glazed surface: but I do not know the details of the industrial process.