Nanoparticles in Lustre Reconstructions

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\textbf{ABSTRACT}

It is increasingly apparent that the spatial distribution of Ag and Cu nanoparticles in lustre glazes is an important factor in determining the colour displayed by the decoration. Using STEM-EDX of cross sections, this distribution can easily be imaged, as is demonstrated in two modern reconstructions of lustre decorations from Granada, Spain. On the nanoscale, the difference in colour can be related to a different spatial distribution of the Ag and Cu particles, with the brownish gold variant consisting of a top layer of Ag nanoparticles with an underlying layer of Cu nanoparticles while in the yellowish golden lustre Cu specks are unevenly dispersed.

\textbf{INTRODUCTION}

A lustre layer is a decorative layer applied to a white opaque glaze for pottery that is famous for its metallic sheen. It has been applied to embellish ceramics since its invention in the 9th century A.D. in Iraq and then was spread all over the Mediterranean basin [see e.g. 1, 2].

Lusteware is effectively a multi-layered structure. On a macroscopic level the base is formed by the ceramic body. This is covered by a thick white layer (about 200 µm thick), opacified by large (i.e. between 150 nm and 300 nm diameter [3]) crystals of SnO\textsubscript{2}. In the upper regions of this white glaze, nanoparticles constituting the lustre layer are present. As will be demonstrated, the lustre layer can in itself have a nanoscopically layered structure.

Nanoparticle colours in historic context can also be seen in stained-glass windows. Ag nanoparticles in a glass matrix display a surface plasmon resonance (SPR) frequency around 410 nm, that can be seen as a yellow colour, for example, in stained-glass windows. Cu nanoparticles have an SPR frequency of about 560 nm, which is used, for example, in the red glass areas of stained-glass windows. In lustre layers, both types of particle are present simultaneously. This, in combination with a higher particle density produces new effects and different colours than in the transparent stained-glass windows.

It becomes clear that the colour of a lustre decoration layer depends on more parameters than only the quantitative composition of elements or element ratios [4]: it also depends on the micro- and nanostructure of the lustre layer, which can be revealed by TEM. The systematic investigation of the relationship among the fabrication parameters, the resulting nanoparticle distribution and the resulting colour is an ambitious, yet essential, project for the future. As a first step towards the realisation of such an endeavour, this contribution reports the results obtained in two reconstructions of lustre ware made by a modern potter in Granada, Spain, who works in the traditional way. The two ceramic vessels have slightly different colours. The respective micro- and nanostructure of fragments of these vessels will be compared with that of ancient material, as reported in literature. Both examples have been investigated with a wide array of techniques [5] and the preliminary Conventional Transmission Electron Microscopy
(CTEM) results were presented during the E-MRS Spring Meeting 2003 [3]. Here, the results of Scanning Transmission Electron Microscopy (STEM) investigations are reported adding essential information to achieve a fundamental understanding of the structure and appearance of the lustre glazes.

EXPERIMENTAL DETAILS AND SAMPLES

The distribution of Cu and Ag nanoparticles is clarified by recording energy dispersive X-ray analysis (EDX) maps with an Oxford EDX detector attached to a JEOL 3000F TEM-STEM apparatus, operated at 300 kV. A 0.5 nm analytical probe was used with the High Angle Annular Dark Field (HAADF) detector. Cross section samples of the lustre layer are prepared by ion milling, with an Ar+ beam of 5 kV and an incidence angle of 8°. The samples were glued to Cu and Mo supports.

The objects investigated have a slightly different colour. The first fragment (of which sample 1 was taken) displays a yellowish golden lustre layer. The second fragment (sample 2) is rather brownish-gold, a colour that is comparable to that of polished Cu metal, according to the similarities of the diffuse reflectance spectra [5]. In fragment 1, the Ag/Cu ratio determined by Rutherford Back-Scattering is 1.47 and in fragment 2 it is 1.36 [5].

RESULTS AND DISCUSSION

On a microscopic level, using CTEM, both materials at first glance display the same general microstructure shown in Fig. 1. From the surface down, a transparent particle-free layer can be seen, and underneath a very dense nanoparticle top layer of about 300 nm thickness. The dense top layer has in fact a density gradient with a maximum close to the surface. Under this first dense top layer of nanoparticles there is an area with less but slightly larger nanoparticles. The number of nanoparticles slowly decreases at larger distances from the surface. In sample 1 the particles present a noticeable density until about 2 µm deep. In sample 2 the number of particles diminishes distinctly from about 3 µm under the surface. In both samples the mean particle size is almost the same throughout the entire lustre layer. For sample 1 this is (11.0 ± 2.3) nm and for sample 2 (13.8 ± 2.0) nm. Particles larger than 20 nm are rare.

For sample 1, the “very small” particles between 0 nm and 5 nm occur throughout the first dense layer to a depth of about 1.4 µm. When their number diminishes, the “large” particles (larger than 15 nm) increase in number, a clear indication for “Ostwald ripening”, where larger
particles grow at the expense of smaller ones. A similar conclusion can be drawn for sample 2, though the lack of “very small” particles below 300 nm points to a longer process of “Ostwald ripening”. The particles display spherical and cubo-octahedral shapes while some of the very small ones are multiply twinned with a five-fold symmetry axis, common in particles grown in an isotropic matrix [6].

In order to investigate the spatial distribution of the particles throughout the material, various TEM modes can be used [3]. Individual particles can be identified structurally using lattice imaging by High Resolution TEM (HRTEM) and analytically investigated by Electron Energy Loss Spectroscopy (EELS), which clearly indicates that the nanoparticles are metallic Ag and Cu. This was confirmed by selected area electron diffraction and EDX analyses of larger areas.

In the present work EDX-elemental maps were made with STEM. It was also attempted to visualise the nanoscopic structures with Energy Filtered TEM (EFTEM), but this was not very successful. The Ag M\textsubscript{4,5} edge is closely surrounded and partly overlapped by the Ca and O edges. This makes the choice of the energy windows and the image treatment less straightforward. Mappings were recorded for both samples and at various magnifications, both in the optimum electron transparent areas and also in slightly thicker areas.

**Sample 1, golden lustre**

![Figure 2.](image)

**Figure 2.** (a) Z-contrast overview image of the area in the maps, i.e. the upper area of sample 1, (b) Ag L\textalpha map, (c) Cu K\textalpha map (enhanced contrast), (d) Na K\textalpha map, (e) Ag L\textalpha map of another region (f) Cu K\textalpha map corresponding to (e), with profile through one of the bright specks.

In sample 1 in general the STEM-EDX maps confirm the distribution of the elements as found by the other TEM modes. This material has a dense top layer consisting of Ag nanoparticles as seen from Figure 2b. In most of the cross section only a very small amount of Cu can be distinguished from the background by enhancing the Cu map as shown in Figure 2c. However, in some regions larger Cu particles are found but they do not seem to be associated with a specific depth in the sample as seen in Figure 2f. These specks have sizes between 50 nm and 100 nm, and perhaps, may be linked to the inhomogeneities that were observed by High
Resolution SEM (HRSEM) of a plan-view sample of this material [5]. These inhomogeneities are a surface feature and form conglomerations of 300 nm to 500 nm, scattered over the surface. In the areas where these Cu specks can be found, a small amount of Cu can still be seen deeper into the material (see Figure 2f). The line profile across the image in Figure 2d shows that the sodium content diminishes when moving closer to the surface, which is expected because of the ion-exchange mechanism when heating the pottery.

**Sample 2, brownish golden lustre**

![Ag Lα map, Cu Kα map, Z-contrast image](image)

**Figure 3.** (a) Ag Lα map, (b) Cu Kα map, (c) Z-contrast image, corresponding with (a) and (b) taken in sample 2.

In this sample Ag particles occur in the dense top layer and Cu particles are primarily present in the region under the first concentrated layer (Figure 3). To obtaining the lustre layer, the glass is fired only once, during which some phase separation must take place internally. In some historic samples similar phase separation has been observed [1,7] although it has never been described as a nanolayered structure.

Figure 4 shows a superposition of the Ag (red) and Cu (blue) elemental maps (green is oxygen). When zooming in on the cases where the Ag and Cu maps coincide, particles consisting of Cu and Ag become apparent. Although it is difficult to completely rule out the possibility of overlapping particles the right particle in Figure 4f clearly gives the impression that Cu and Ag remain separated on either side of the particle. It could therefore be that either a Cu or a Ag particle in the intermediate area between the Ag and Cu layers in sample 2 has served as an “impurity” onto which a particle of the other type (they both have an fcc crystal lattice), started
to grow. Inhomogeneous partly Cu-partly Ag particles synthesized in a silica matrix by the sol-gel technique are reported in literature, for example by De et al. [8].

![Image]

**Figure 4.** (a) Overview Z-contrast image of a mixed area in sample 2, (b) Ag Lα map, (c) Cu Kα map. Detail of (a) showing particles with Ag on one side (d) and Cu on the other (e), (f) Z-contrast image of detail in (a).

**Effects on the colour**

Both materials can effectively be described as a nanolayered structure; sample 2 displays a layer of Ag nanoparticles on top of a layer of Cu nanoparticles, while sample 1 seems to display mainly two thin layers of Ag nanoparticles (possibly due to temperature variations during firing), which are sometimes intermixed with Cu specks. The difference in nanoscopic layout of the samples has its effects on the resulting colour of the material. A sample that consists of a top layer of Ag nanoparticles will clearly display the colour caused by these nanoparticles, namely golden. When this layer contains unevenly distributed Cu specks, a red light is returned in local areas. To the eye, these local areas will get intermixed with the main golden colour resulting in a somewhat pale orange or gold. In sample 2 the upper Ag-containing layer returns a golden
colour, but everywhere throughout the material there is also an underlying Cu layer, which adds a red hue to the gold, resulting in a brownish gold colour throughout the material. Still, as mentioned by Tsuji et al. (2002) [9], still more experimental studies are desired on optical absorption properties for multicomponent nanoparticle-glass composites because of the difficulty in theoretical prediction of such complex systems with many unknown factors.

**Comparison with literature on ancient lustre glazes**

The first TEM observations of the lustre layers of genuine historic materials were done on plan-view specimens. The first report of cross-section samples was by J. Pérez-Arantegui et al. (2001) [1]. The results reported deal mainly with a red Cu-rich lustre layer and are thus different from the samples studied in this contribution. It can be seen, however, that the local arrangement of both types of particles shows some similarities with what is seen in sample 1, although in ref. [1] an inhomogeneous distribution of Ag specks in a predominantly Cu-rich area was seen. Also, the areas involved are larger than what is seen in 1, namely Ag-rich zones of 5 µm to 100 µm. A comparable situation was observed in Colomban and Truong (2004) [10], where the Ag/Cu ratio was very inhomogeneous over the sample surface. In Borgia et al. (2002) [7], the nanoscopic build-up of golden coloured lustre layers is shown. It can be seen that the Ag particles occur close to the glaze surface and that the Ag penetration gradient is less profound than the Cu one, though it does not show the level of phase separation as seen in sample 2. Borgia et al. also state that the Ag and Cu are well separated, while in our samples, possibly composite particles have been observed. Also Padovani et al. [11] indicate that in a red lustre elemental Cu can be found deeper in the material than in the golden lustres.

The most remarkable difference between the present samples and the historic samples as reported in the above-cited articles and also in Padeletti and Fermo [2], is that in the historic samples the upper layer consists of particles that are clearly larger than the particles deeper inside the material. In this top layer the particles can easily reach dimensions of 50 nm or even larger, while in the present samples these sizes are very rarely observed. Larger particles induce a red shift in the SPR frequency. In samples 1 and 2 the same overall effect is reached by having a very densely packed top layer. Indeed, when the interparticle distance is reduced, a red shift in the SPR frequency can be seen [12]. The difference in ranges of particle sizes between the historic and the modern material indicates that the manufacturing procedures and/or equipment used by the modern potters is different from that applied by their historic colleagues. More work on both reconstructions and historic samples is needed to determine which factors are most important.

**CONCLUSIONS**

A lustre decoration layer owes its colour to a complex interplay of the nanoparticles present, here metallic Ag and Cu, which can be distributed over the material in various ways. Sample no. 1 is mainly golden because of the presence of a thin Ag nanoparticle containing layer. In sample no. 2 this golden colour is modified by the red colour caused by the underlying layer of metallic Cu nanoparticles, resulting in a brownish golden colour.

The particles have sizes between 5 nm and 15 nm. Smaller particles occur only at the very top of the samples. Areas where particles display “Ostwald ripening” processes are recognised.
Comparison of these modern samples with results on historic samples show that the latter consist of a top layer of larger particles. It is therefore suggested that the manufacturing process used in the modern reproduction attempts is still different from the ancient one used in historic times.

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REFERENCES