XAFS-Investigation of CuO-based engobes – the system CuO-Al_2O_3-SiO_2 at temperatures from 850°C-1150°C

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For the majolica [1] of the Italian renaissance two techniques were used: engobe-painting and glaze-painting. An engobe is defined as a homogeneous mixture of clay and water, which is fired at temperatures ranging from 800 °C to 900 °C. It's characteristics are high porosity and a rough surface. A glaze is a homogeneous mixture of different glass-forming substances which melt at temperatures of 900 °C to 1200 °C. The surface of a glaze is very smooth and the porosity is small. In both cases, the addition of small amounts of metal oxides (e.g. CuO) to these mixtures leads to colored substances (e.g. $CuAl_2O_4$ or CuO in a solid solution). The aim of this investigation is to look at some majolica ceramics (14^{th}-17^{th} century, Montelupo) and to find out more about the firing conditions that were used and the way in which copper(II)oxide CuO was applied onto the ceramics. This is done by analyzing new CuO-based engobes that we prepared under defined conditions and by comparing these engobes and a glaze to the majolica ceramics [2].

The engobes were prepared by mixing kaolin with 7% CuO. The samples were calcined in air at different temperatures [3]. Cu*K*-XAFS spectra were recorded at beamline X1 in transmission at 77K (DORIS III operating at 4.445 GeV, injection current 144 mA, Si(111)-double-crystal monochomator). The spectra were energy calibrated, background corrected and normalized. After conversion into k-space, the EXAFS signal was extracted by using a cubic-spline fit and Fourier transformation was applied. The spectra processing was performed with the program WinXAS [4].

The XANES spectra of the CuO-engobes in comparison to CuO and the partially inverse spinel $CuAl_2O_4$ can be seen in Fig. 1. The edge position of 8.992 keV of the CuO-engobes is in good agreement with the value of 8.991 keV for CuO and $CuAl_2O_4$, so that it can be concluded that all Cu in the samples is in the oxidation state +2. The Cu*K*-XANES spectra can furthermore be divided into the pre-edge peak **A** at 8.975 keV, a shoulder **B** at 8.984 keV, and a region **C** around the white line. Since about 65% of the Cu ions in the spinel $CuAl_2O_4$ occupy tetrahedral sites [5], the dipole-forbidden $1s \rightarrow 3d$ transition **A** is comperatively strong in the spectrum of $CuAl_2O_4$. The engobes that were prepared at 850 °C and 950 °C show a very small pre-edge peak, indicating that at least part of the Cu is in tetrahedral sites. The shoulder **B** can be assigned to a dipole-allowed $1s \rightarrow 4p$ transition and is visible in the CuO spectrum. The area **C** is a diagnostic feature to differentiate between $CuAl_2O_4$-type and CuO-type. The shape **C** of the spectra of

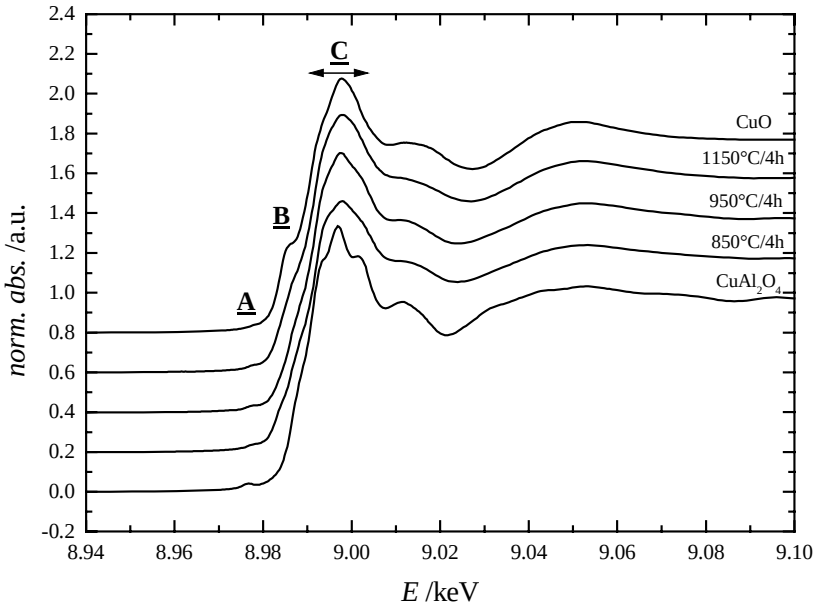

Fig. 1: CuK-XANES of CuO, $CuAl_2O_4$ and three CuO-based engobes burned at three different temperatures.

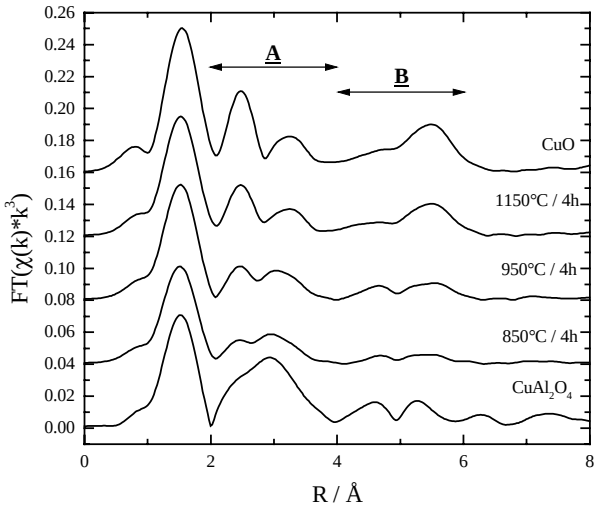

Fig. 2: Cu*K*-EXAFS-spectra of CuO, $CuAl_2O_4$ and three CuO-based engobes fired at different temperatures

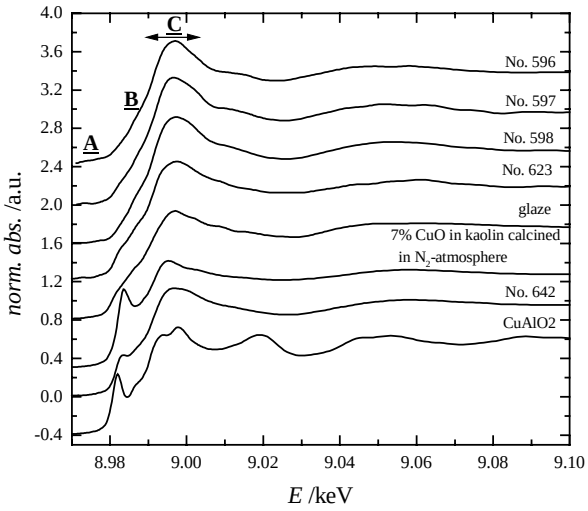

Fig. 3: Cu*K*-XANES-spectra of some majolica ceramics (No. 596, 597, 598, 623,642), of delafossit $CuAlO_2$ and of an egobe fired under reductive conditions

the CuO-engobes burned at 850 °C and 950 °C show some resemblance to the spectrum of the spinel $CuAl_2O_4$ whereas the spectrum of the engobe fired at 1150 °C is similar to the spectrum of CuO. It seems that only in the temperature range from 850 °C to 950 °C a $CuAl_2O_4$-spinel-type phase is formed.

This can also be proved by comparison of the Cu*K*-EXAFS spectra of the engobes with the reference materials (Fig.2). The second shell (area **A**) of the Fourier transform (FT) of CuO shows two separate signals resulting from Cu and O backscatterers, respectively. The first peak has more intensity than the second. In contrast the spinel $CuAl_2O_4$ shows only one broad signal including Cu, O and Al backscatterers. The FTs of the engobes calcined at 850 °C and 950 °C show similarities to the FT of $CuAl_2O_4$; the FT of the engobe fired at 1150 °C is comparable to that of CuO. Obviously, by calcination of the engobes at temperatures of 950 °C and below, a spinel phase is formed. At temperatures of 1150°C and above, the CuO-engobes consist of small CuO-clusters solved in a glass-like matrix of Al_2O_3-SiO_2.

The Cu*K*-XANES spectra of the majolica ceramics are shown in Fig.3. They are compared to an engobe prepared in N_2 atmosphere, a glaze and the delafossite-type compound $CuAlO_2$. The edge position of the engobe prepared in N_2 atmosphere and of the majolica ceramic No. 642 is at 8.987 keV. This agrees with the edge position of $CuAlO_2$, where Cu is in an oxidation state of +1. The other majolicas and the glaze contain Cu in the oxidation state +2. The majolica No. 642 was fired under reductive conditions, whereas the other majolica were calcined at high temperatures while being exposed to air. The glaze has a slight shoulder in the region of **B** as has the sample No. 623. The regions **C** of samples No. 596, No. 597 and No. 598 are very similar. Sample No. 623, however, looks more like the glaze. Cu*K*-EXAFS spectra of the majolica ceramics could not be evaluated because of a bad signal-to-noise-ratio.

References

[1] F. Berti, *The Montelupo Ceramics, From Sixtheenth to Eighteenth Centuries*, Ed. Electra-Milano, 1986.

[2] H.-J. Wölk, B. Hoffmann, Jahrestagung der Archäometrie u. Denkmalpflege, Wien 1997.

[3] B. Spandl, Untersuchung von Engoben auf Kaolin/Kupferoxid-Basis unter Berücksichtigung didaktischer Gesichtspunkte, *Wissenschaftliche Hausarbeit zur ersten Staatsprüfung für das Amt des Studienrats*, Berlin, 2000.

[4] T. Ressler, *J. Phys. IV* **7**, 269 (1997).

[5] R. F. Cooley, J. S. Reed, *J. Am. Ceram. Soc*. **55**, 395 (1972).