ZIRCONIUM SILICATE OPACIFICATION MECHANISM IN CERAMIC ENGOBES

A. Moreno; E. Bou; M. J. Cabrera; P. Quereda

Instituto de Tecnología Cerámica (ITC)
Asociación de Investigación de las Industrias Cerámicas (AICE)
Universitat Jaume I. Castellón. Spain.

INTRODUCTION

Ceramic engobes need to exhibit high whiteness and opacity to allow optimum development of subsequent glaze applications. This is achieved by including zirconium silicate or zircon in the engobe composition, a raw material that is widely used as an opacifier in the field of ceramic frits and glazes[1]. Recent hikes in zircon prices have led to a search for alternative materials that yield similar products. The preliminary step, however, to seeking new raw materials is understanding the mechanism whereby zirconium silicate acts as an opacifier in glazes and engobes.

EXPERIMENTAL, RESULTS AND DISCUSSION

Firstly, the relationship that exists between engobe opacity and zirconium silicate content was determined. This was done by selecting a standard industrial engobe (A), containing 16% zirconium silicate, and preparing another engobe (B), which contained the same constituents (in identical proportions) as the former, however without any zircon.

These two engobes were applied to ceramic bodies that were then fired at different peak temperatures. The fired, zircon-free engobe layer was observed to be less opaque, yielding a lower whiteness index at all the tested temperatures. Thus for instance at 1140°C, engobe A exhibited values of 90.05 and 77.5 respectively for chromatic coordinate L^* and I_b (whiteness index), whereas zircon-free engobe B yielded 78.02 and 72.2 for the same parameters.

---

[1]. PARMELEE, C.W. *Ceramic glazes*. 3rd ed. Boston: Cahners Books, 1973.

Having established a relation between zircon proportion and engobe opacity, a study was undertaken of the mechanism that gave rise to this effect.

From a general point of view, engobe opacification by adding zircon might be due to different mechanisms. It might arise if the added zirconium silicate particles themselves were to be insoluble in the glassy phase that is produced in firing, and then remain dispersed in this glassy phase. Opacification might on the other hand be due to the devitrification in the firing cycle cooling step, of zirconium silicate that had previously dissolved in the glassy phase[2], [3].

Engobe composition A was used to determine which of these two mechanisms produced opacification. The experiments described below were run on three test specimens made from this composition. One was kept unfired and referenced A-C. Of the other two test specimens, one was subjected to a firing cycle with a peak temperature of 1140°C and conventional cooling (A-1140), whereas the other underwent the same heat treatment and T_{max}, followed by quenching (A-1140-S). These last two test specimens were intended to allow studying the possible effect of the cooling cycle on zirconium silicate devitrification, as cooling by quenching would impede such devitrification (if this were to take place during the cooling step).

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were run on these specimens, yielding the results detailed below[4].

In test specimen A-C, the crystalline phases identified by XRD were kaolinite, illite, quartz, feldspars and zirconium silicate. In specimen A-1140, the following crystalline phases were identified: quartz, feldspars, and zirconium silicate. A comparison of these findings revealed that in firing, the clay mineral (kaolinite and illite) disappeared, the feldspars and quartz partially dissolved (the peak intensities corresponding to these phases in the fired specimen diffractograms decreased), while the zirconium silicate peak exhibited a slight increase. In order to better examine zirconium silicate behaviour, the test specimens were studied by XRD in the diffractogram range in which the zirconium silicate maximum intensity peak was located, subsequently determining peak area. The data obtained are reported in Table 1.

Specimen	Peak area (counts)
A-C	2187
A-1140	2661
A-1140-S	2711

Table 1. *Silicate zirconium peak area.*

It can be observed that the number of counts found for test specimens A-1140 and A-1140-S are practically identical, since the difference between both lies within the method's margin of statistical error. This allows inferring that zirconium silicate did not devitrify in cooling, and hence that the added zircon remained undissolved in the glassy

---

[2]. TAYLOR, J.R.; BULL, A.C. *Ceramic glaze technology.* Oxford: Pergamon Press, 1986.

[3]. MORENO, A. *Estudio de la formación de fases cristalinas en vidriados blancos de circonio. Factores que influyen sobre su índice de blancura.* Castellón: Universitat Jaume I, 1994. Tesis Doctoral.

[4]. *The X-ray identification and crystal structures of clay minerals.* Edited by G. Brown. London: Mineralogical Society, 1972.

phase. These data agree moreover with the results obtained in the engobed specimens, in which the cooling cycle was observed not to affect the whiteness of the engobe layer.

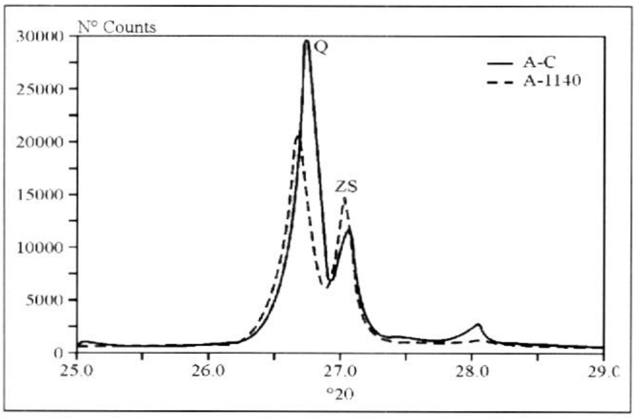

Figure 1. *Zirconium silicate peak in specimens A-C and A-1140.*

It can be observed in Fig. 1, in which the diffractograms corresponding to fired specimens A-C and A-1140 have been superimposed, and from the values detailed in Table 1, that zirconium silicate peak intensity increased in firing. This rise occurred because in the unfired specimen, zirconium silicate was only detected in the starting composition as a crystalline aggregate, whereas in the fired specimen, the zirconium silicate was also measured which devitrified from the dissolved zircon (2.47%) contained in the starting frit.

Finally, specimens A-C and A-1140 were examined by scanning electron microscopy. In specimen A-C, zircon particles corresponding to the added zirconium silicate were detected as crystalline aggregates which remained as such in the fired sample, keeping their sharp edges, thus indicating that they underwent no changes during firing. In the fired specimen, needle-like zirconium silicate crystals were also observed, which stemmed from the devitrification of the frit contained in the starting engobe.

CONCLUSION

The opacity and whiteness of the studied engobe were fundamentally due to the presence of unmelted zircon crystalline aggregates and to the presence (in minor proportions) of zirconium silicate crystals that devitrified in firing.