APPLICATIONS OF RAMAN SPECTROSCOPY TO THE STUDY OF CERAMIC GLAZES

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ABSTRACT

In this study, Raman spectroscopy has been used to monitor the devitrification process in ceramic glazes. The study specifically addresses the devitrification of titanium oxide in so-called "lustre" glazes obtained by applying a Ti precursor followed by heat treatment at low temperature. Aspects are examined, such as the influence of Ti precursor concentration, heat-treatment temperature and penetration into the glaze layer.

1. INTRODUCTION

In this study Raman spectroscopy has been used to monitor the devitrification process in films that contain dissolved Ti, applied by screen printing onto already fired base glazes, which are then subjected to heat treatment. Raman spectroscopy is the measurement of the wavelength and intensity of inelastic light scattering by the molecules of the solid. When electromagnetic radiation reaches a material, a great amount of the radiation is observed to continue in its initial direction, but there is also a small part of the radiation that is scattered in any other direction. The light scattered by interaction with the molecules of the solid (transparent or opaque), in values that can reach 4000 cm^{-1} with regard to the original radiation, is the so-called Raman scattering, which has been used in this study. The most typical applications of Raman spectroscopy are found in the determination of materials structure as well as in the qualitative and quantitative analysis of multicomponent systems [1], [2], [3].

2. EXPERIMENTAL

In this study we have used a base glaze for porous single firing with a tendency to devitrify zirconium silicate in small proportions. Films containing dissolved Ti were applied by screen printing onto this already fired glaze, then subjecting both to heat treatment (820 °C for 5 minutes). As an application in the form of a thin layer is involved, the devitrified anatase is assumed to react with the base glaze and diffuse inwards into this layer during heat treatment. Films with a different Ti content (A<B<C) were deposited with a view to determining how this parameter influenced the diffusion of anatase into the glaze.

In order to study the effect of anatase diffusion into the glaze layer during heat treatment, the samples were analyzed by confocal Raman spectroscopy. The essential characteristic of a confocal image system is that the illumination zone and the detection zone are always confined in a same point of the specimen at any time. If the point is so small that its liits are imposed by diffraction, the resolution obtained in this case is greater than that obtained in a conventional system. The lateral resolution can approach the theoretical maximum, increasing the conventional resolution 0.7 times. However, the fundamental and distinctive property of the confocal image is that only what is focused is detected. The out-of-focus areas of the sample appear black and do not contribute to the formation of the image.

The light source used has been a laser beam, since it allows obtaining images with high resolution and sensitivity when working with fluorescent probes. We used a Bruker FRA 106/S Raman spectrophotometer. The frequencies analyzed were between 1050 and 100 cm^{-1}. Exposure time was 10 s and 5 accumulations. Laser power was 28 mW and the lens 100x.

3. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra made for the film with the smallest Ti content. These spectra display the characteristic peaks of the base glaze and some small peaks are observed on these stemming from the devitrified anatase. The frequencies at which the anatase peaks appear are at 144, 400, 515 and 640 cm^{-1}.

Figure 1 also shows how the anatase Raman signal decreases with the glaze depth in which the Raman beam has been co-focalized.

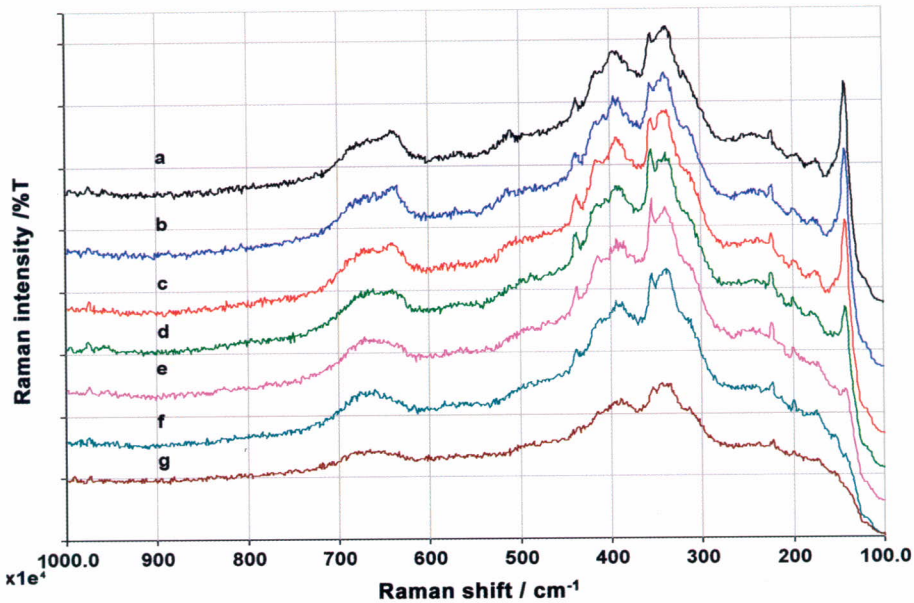

Figure 1. FT-Raman spectra of the screen printing film with the smallest Ti content at the following depths in micrometers: (a) 0; (b) 0.5; (c) 1; (d) 2; (e) 3; (f) 5; (g) 10.

Figure 2 depicts the Raman spectra obtained as a function of the film with the largest Ti content. In these spectra, a very intense Raman signal is observed, particularly for the band with the greatest intensity which appears at about 144 cm^{-1}. This signal even exceeds the base glaze peaks.

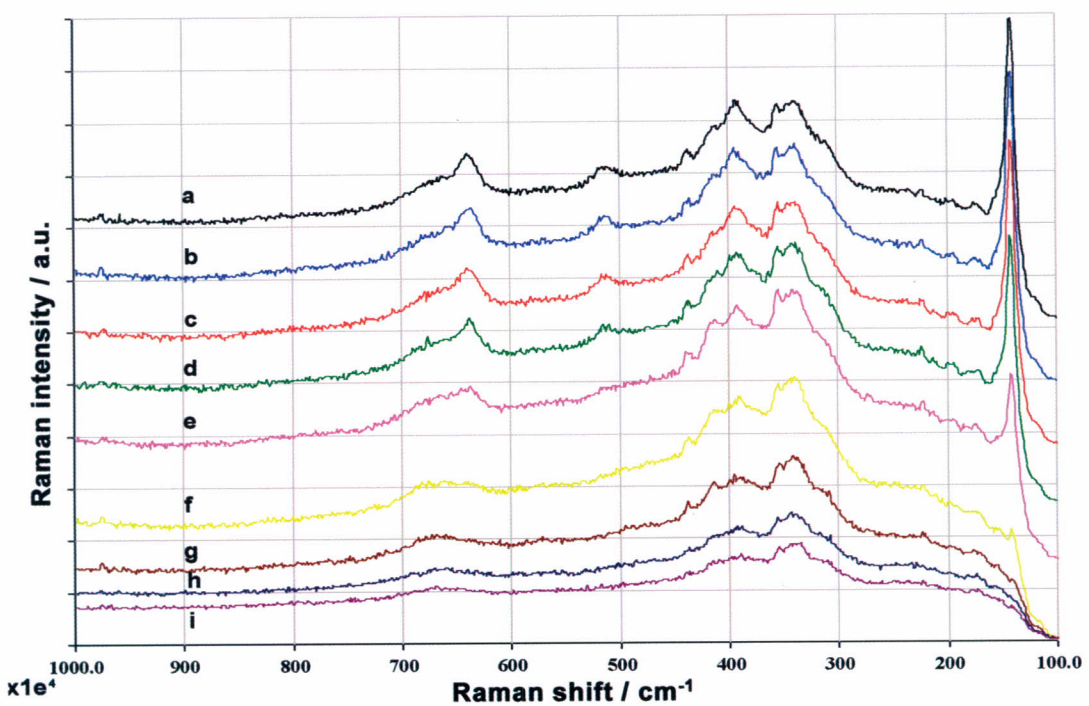

Figure 2. FT-Raman spectra of the screen printing film with the largest Ti content at the following depths in micrometers: (a) 0; (b) 0.5; (c) 1; (d) 2; (e) 3; (f) 5; (g) 10; (h) 15; (i) 20.

From the Raman signals and the depths studied by the confocal technique, the depth has been evaluated to which the anatase diffuses into the base glaze with heat treatment. Figure 3 shows the results obtained.

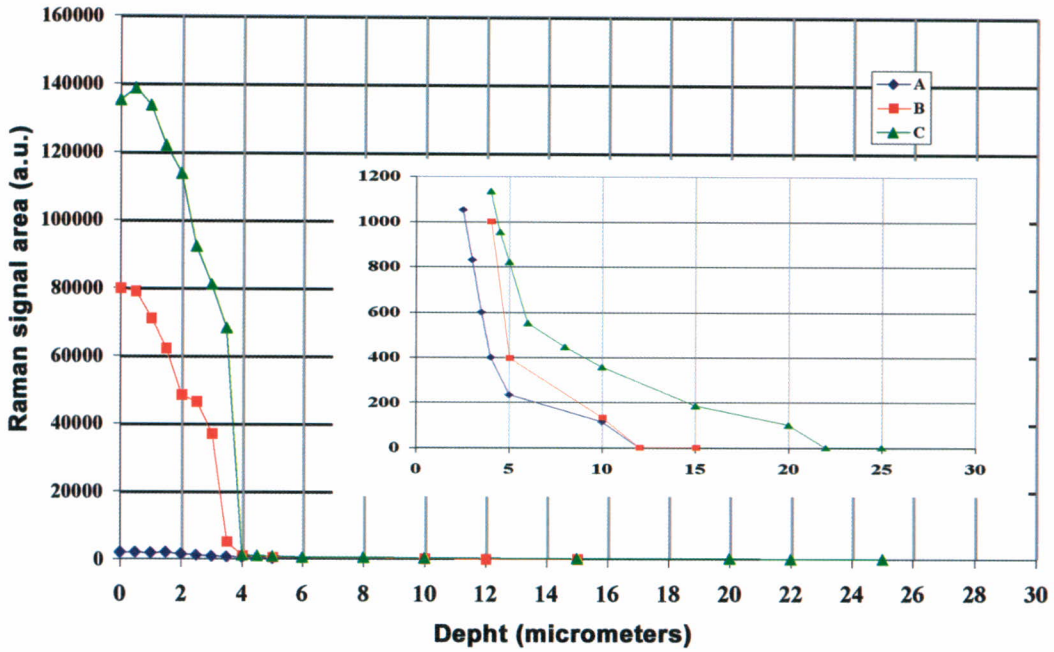

Figure 3. Diffusion depth of anatase into the base glaze

Figure 3 shows that the anatase concentration in the film, as well as its diffusion into the base glaze, is a function of the quantity deposited in the initial layer. For samples A and B, the maximum depth reached was 10 micrometers, while for sample C (with the largest concentration) the depth reached was slightly over 20 micrometers. On the other hand, in the outermost layer, the anatase concentration was practically constant up to 1.5 micrometers, while the concentration decreased after this thickness as a result of the diffusion effect.

4. CONCLUSIONS

The present study shows that confocal Raman spectroscopy is a useful tool for determining the diffusion of anatase into ceramic floor and wall tile glazes. This technique enables determining the quantity anatase that is present (when quantifying this), as well as the anatase diffusion depth into the glaze when the system has been fired.

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