MICROSTRUCTURAL CONTROL OF SINGLE-FIRED CERAMIC TILE BODIES

M.M. JORDAN, A. BOIX and T. SANFELIU
Applied Mineralogy and Crystallography Research Group Universitat Jaume I, Castellon, Spain
J. Ma. RINCON and M. ROMERO
Lab. of Glass-ceramics
Inst. E. Torroja de Ciencias de la Construcción, CSIC, Madrid, Spain

ABSTRACT

After defining the main differences among: aspect, texture, microstructure and structure of ceramic tiles, the paper discusses the importance of appropriately controlling tile microstructure. This is the factor that most influences the technological properties, and in particular the mechanical properties. The microstructure of floor and wall tile bodies was examined with a view to optimizing the glaze/body interphase in order to improve the wettability between both tile parts, by means of the following microscopy techniques:

Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and a new microscopy technique: Atomic Force Microscopy (AFM) derived from *Tunnelling* Microscopy (STM). The study details the results obtained on using TEM, SEM and AFM microscopy to examine surface and fracture areas of porous, single-fired, white-firing ceramic bodies.

1. INTRODUCTION.

Though porcelain tile production is increasing, stoneware products obtained by fast single firing still have the largest share in production, the body or substrate being the determining factor in the mechanical and technological properties of the resulting ceramic tiles. Thus, flexural strength and water absorption are controlled mainly by the body characteristics. The most important characteristic of the body with respect to final tile properties is the «microstructure» of the fired body, namely: phase composition and their interrelationships (crystalline, glassy and porous), which make up the body. The geometrical interphase relationships are also essential for defining the final microstructure. However, the terms: microstructure, aspect, texture and structure are often confused by researchers and technicians in industry.

On considering the magnification scale of a product, the order from lower to higher is:

aspect---> texture---> microstructure--->structure

The first concepts relate to the external appearance, colour, decoration and extrinsic characteristics of the material, but the term «microstructure» indicates the intrinsic material characteristics related to composition and technological properties. The term «structure» is a concept that goes further and should not be applied to traditional ceramic products (as multiphase materials), but rather is only meaningful with regard to single phases, whether glassy or crystalline.

Though different methods are available for improved microstructure control such as: X-ray diffraction, porosimetry, etc., the only methods directly allowing these characteristics to be visualized is MICROSCOPY, in its widest sense.

As grain and phase sizes are nowadays smaller as a result of improved raw materials processing techniques, Optical Microscopy has become inadequate for in-depth control of ceramic microstructures, including the most traditional ones. Therefore, Electron Microscopy in all its forms is currently the best method for suitable quality control of microstructure in such materials and their by-products (1).

The research presented here is part of an ongoing, systematic investigation into the application of different electron microscopy techniques, such as:
Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and new microscopy techniques, such as Confocal and Atomic Force Microscopy (AFM), for controlling various typical substrates or bodies used in ceramic floor and wall tile manufacture in Castellón.

Studies have been published on microstructural determinations in ceramic tiles (2) (3) (4), but the great value of the above-mentioned methods for enhanced microstructural control has not been sufficiently emphasized or recognized. Pragmatic technicians in the ceramic industry have for some time considered these methods to be instruments that are only used for pure scientific research, whereas they are viewed as ideal tools for better microstructural control of materials in technologically advanced countries. Moreover, such instruments are now more much cost-effective with shorter pay-back periods than in the past, as well as being relatively inexpensive compared to other capital investments that are usually required, and are certainly a mainstay for laboratories involved in quality control, or research and development.

2.MATERIALS AND METHODS.

The microstructure of the final surface and fracture area of a white-firing, single-fired ceramic body (150 x 150 x 5 mm) was investigated by SEM and Energy Dispersive X-Ray analysis (EDX), as well as by transmission electron microscopy by the carbon and triafol-carbon replica methods. The SEM/EDX procedure was run on a Hitachi/ Kevex 8000 configuration. Samples were used with and without chemical etching by hydrofluoric acid (HF 15 %) for 60 s. The Bradley method of replication by carbon evaporation was also used (5). After several tests, the triafol-carbon double replica was observed to yield the best results for these types of porous products. For the TEM investigation, a Philips 300 transmission instrument was used. The resulting data from the examination of the porous character of these materials have been summarized in Table I.

TABLE I. Several types of observations of microstructure carried out on porous fast firing substrates

	sample	without etching	with etching
SURFACE	SEM	X	//////
	TEM	//////////	X
FRACTURE	SEM	X	////////
	TEM	X	X

3.RESULTS AND DISCUSSION.

3.1. Surface microstructure

Figure 1 shows surface micrographs of a fired body, obtained by SEM and TEM microscopy. A high percentage of irregularly shaped and sized pores can be observed of about 5 μm at lower magnifications. The microstructure is layered with weathered-looking material over the layered grains, indicating poor surface cohesion on this scale. The microstructure shows low sintering at lower magnifications. However, at higher TEM magnifications, there are large tabular crystals of wollastonite and rounded primary mullite crystals starting their crystallization, embedded in an incipient amorphous matrix. This phase comes from the feldspar components, which would be in an intermediate glassy/ amorphous state.

3.2. Fracture microstructure

Figure 2 shows the observations carried out at lower magnifications by SEM and at higher magnifications by TEM on the fracture surface without chemical etching. A continuous porous microstructure can be seen, interconnected by solid bridges. In spite of this very porous microstructure, the non-porous areas are well sintered as is shown in the TEM-replica micrographs. There are ovoidal, square-shaped or pseudo-hexagonal crystallizations embedded in a continuous matrix. As phase separation was not clear, etching was carried out to remove amorphous phase, thus enhancing the contrast of more rounded crystallizations as Figure 3 shows. With respect to the microstructure obtained by HF-etching, a composite microstructure was observed by TEM, similar to cement/aggregate mixes. In this case, the wollastonite phase was embedded in an amorphous phase separated in very small phase-separated droplets. These droplets could be primary mullite seeds that were not well developed, though they were uniformly distributed throughout the material.

The above observations have been complemented by those shown in Figure 4, obtained by Atomic Force Microscopy (AFM). AFM is a non-destructive technique which allows the observation at high resolution levels of materials at room temperature and pressure (6). Its basic principle is the use of the atomic scale forces between the sample surface and the atoms from the apex of a very sharp tip, carried by a cantilever. The cantilever deflections are measured by two photodiodes. Thus, the tridimensional microstructure or roughness determinations can be produced by using low and high voltages applied to a piezoelectric ceramic sensor. It should be highlighted, that this is the first time that a tile body has been observed by AFM. Therefore, much work must be carried out in order to become more familiar with the capabilities of this novel method for microstructure control of ceramics.

The capacity of this technique for obtaining tridimensional views is shown in Figure 4.

Due to the high roughness of fracture there was a drag force on the tip giving rise to low resolution in this case. Experiments are currently being performed by the «tapping mode» method with the aim of suppressing this effect. Nevertheless, these first observations allow identifying the ovoidal crystallizations embedded in the amorphous matrix and the micro-droplet microstructure detected by transmission electron microscopy.

4. CONCLUSION

New views of the microstructure of white ceramic tile bodies obtained by fast single firing, used in floor and wall tile manufacture, have been obtained by electron microscopy techniques, which now can be considered not only as research tools, but also as very valuable instruments for quality control of ceramic microstructures. In this case, primary mullite formation and very fine partly reacted, rounded quartz grains were observed in an amorphous phase. First observations by AFM were carried out and, in spite of the need for more research in this field, this new microscopy technique, which has been derived from Scanning Tunnelling Microscopy, opens up promising applications in ceramics.

Acknowledgements

Many thanks are due to L. Vazquez from the Inst. de Ciencia de Materiales, CSIC, Universidad Autonoma de Madrid for valuable help in obtaining the AFM micrographs. Thanks are also due to the Servicio de Microscopía Electrónica del Centro de Ciencias Medioambientales del CSIC, Madrid and by the Servei de Microscopia de la Universitat de València.

REFERENCES.

1. J. Ma RINCON,Analytical electron microscopy as quality control, Tile and Brick Intern.6(1990)4,24-27.

2. P. K. CHU, Microstructure of complex ceramics. In: Ceramics Microstructures. Ed.R. M. Fulrath and J. A. Pask. John Wiley, 1966, NY, pp.829-862

3. A. GARCIA-VERDUCH, J. Mª. GARCIA and F. J. GOMIS, Microestructura de una porcelana triaxial, Bol. Soc. Esp. Ceram. Vidr.6(1967)43-65.

4. M. J. ORTS, A. ESCARDINO, J. L. AMOROS and F. NEGRE, Microstructural changes during the firing of stoneware floor tiles, Applied Clay Science 8 (1993)193-205

5. D. E. BRADLEY, Formvar- C replica methods. In: Techniques for electron microscopy, Blackwell Scientific Publications, Oxford, 103-105 (1961)

6. Y. MARTIN, C. C. WILLIAMS and J. WICKRAMASINGHE, J. Appl. Phys.61 (1989)4723

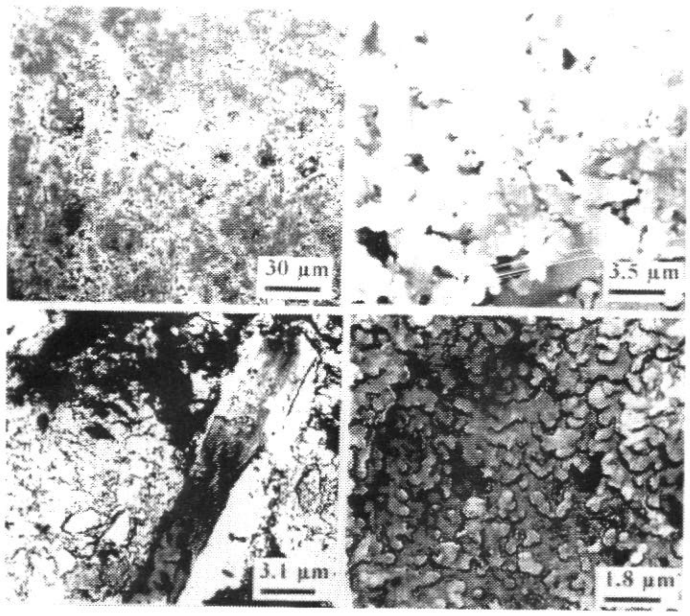

Figure 1.- Electron micrographs from the surface of a white, fast-fired substrate: a) and b) SEM and c) and d) TEM

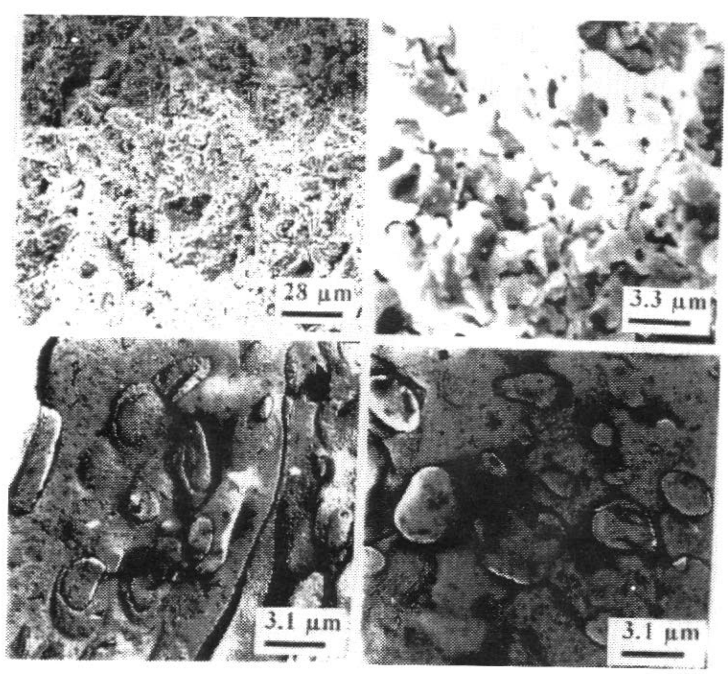

Figure 2.- Electron fractographs obtained from a white, fast-fired substrate: a) and b) SEM and c) and d) TEM

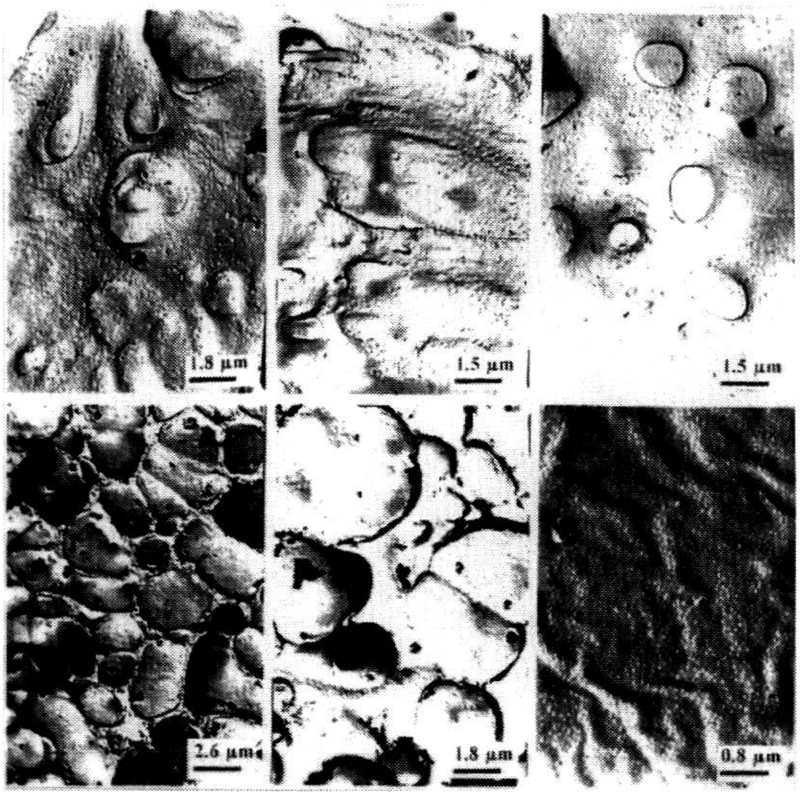

Figure 3.- Several areas observed by transmission electron microscopy (carbon-replica) from a white, fast-fired substrate