STUDY OF DEVITRIFICATION IN A ZIRCONIUM FRIT BY HIGH-TEMPERATURE X-RAY DIFFRACTION

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1. INTRODUCTION

X-ray diffraction (XRD) is the most suitable technique for studying the transformations involving crystalline phases which arise at high temperatures,. The traditional method consists of allowing transformation to proceed to a certain degree (at a given temperature and time), subsequently quenching and analysing by XRD.

X-ray diffraction in a high-temperature chamber is a modification of the technique that allows in situ analysis of these transformations. It has been shown to be very suitable for studying reactions between solids, especially when phases are formed in the reaction, which are only stable at high temperatures, and can be used for the study of crystallisation in melts[1].

In this work, the sequence was studied of the phases that devitrify on subjecting a so-called "zirconium white" frit to non-isothermal heat treatment at a constant heating rate. The resulting data were compared with the findings from a previous study[2] in which the conventional heat treatment method was used, followed by quenching and XRD analysis of the sample at room temperature.

2. MATERIALS AND PROCEDURE

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[1]. D.D.L. Chung, et al. *X-ray diffraction at elevated temperatures: a method for in situ process analysis*. New York: VCH, 1993.

[2]. Escardino, A; Moreno, A; Amorós, J.L, et al *Study of crystalline-phase formation in white zirconium glazes*. In: IV World Tile Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996.

A standard "zirconium white" frit was used, which was subjected to non-isothermal heat treatments at a constant heating rate in the high-temperature chamber of an XRD instrument.

3. RESULTS AND DISCUSSION.

Figs. 1 and 2 plot the variation with temperature of peak intensities d=3.164 Å of monoclinic ZrO_2, d=2.960 Å of tetragonal ZrO_2 and d=3.300 Å of zircon, obtained in the high-temperature chamber (Fig. 1) and by the traditional method (Fig. 2).

It can be observed that for the zirconium oxides, the curves obtained by the two methods exhibited similar trends. The results did not fully coincide as in the high-temperature study, a smaller sample mass was analysed, so that lower values were found for the diffracted intensity. The results also exhibited a shift to slightly lower temperatures for the high-temperature chamber analysis.

However, zircon evolution only obeyed this trend at temperatures below 1100°C, whereas beyond this value the results were inverted. While traditional XRD revealed dissolution of this crystalline phase (reduction in peak intensity), peak intensity was observed to rise in high-temperature analysis, which might in a first approximation be associated with a rise in the content of this crystalline phase.

Previous papers[2], [3] have shown that at high temperatures, the crystals partially dissolve in the melt. A series of experiments was therefore conducted to justify the above results.

A consolidated layer of frit was applied to an inert body and fired in a traditional kiln at temperatures of 1100 and 1300°C. The fired specimens were analysed by XRD from the glazed surface (sample resembling the one in the high-temperature chamber), and after milling (conventional method).

The following table sets out the zircon peak intensity values obtained:

Intensity of zircon peak d_{200}= 3.300 Å (counts)			
Sample treated at 1100°C		Sample treated at 1300°C	
surface	powder	surface	powder
344	413	452	322

Zirconium silicate dissolution was only detected in the milled samples. Electron microscopy revealed that at 1300°C, the surface area covered by zircon crystals had decreased with regard to the sample at 1100°C. However, the crystals were needle-like and their longest axis was oriented parallel to the glazed surface, thus favouring diffraction in some planes compared to others, which the peak corresponding to these planes (d_{200}= 3.300 Å) recorded as a rise in intensity.

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[2]. Escardino, A; Moreno, A; Amorós, J.L, et al *Study of crystalline-phase formation in white zirconium glazes*. In: IV World Tile Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996

[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, Department of Chemical Engineering, 1994. Doctoral dissertation.

On milling the sample, the orientation stemming from crystal growth in the melt was broken up, which then yielded the most representative intensity values of the relevant phase proportion. The crystalline phases of other systems in which no preferential orientations occur have been shown to yield equivalent results on using high-temperature and conventional XRD techniques.

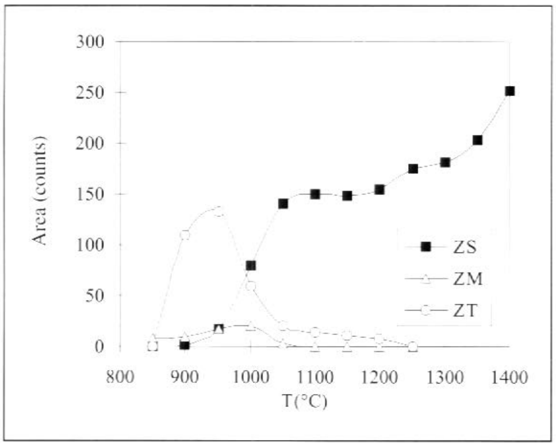

Figure 1. *Variation of the zirconium silicate, monoclinic zirconia and tetragonal zirconia content. Method: High-temperature chamber. Heating rate = 2.5°C/min.*

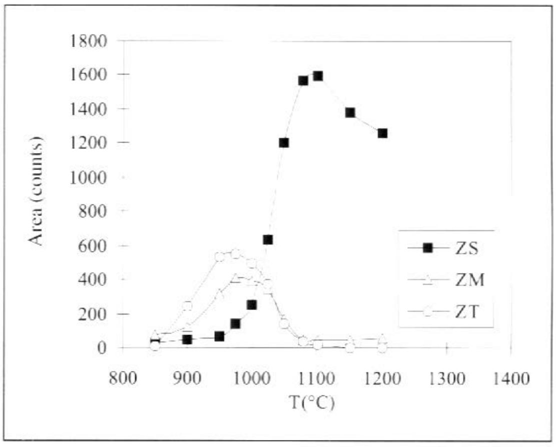

Figure 2. *Variation of the zirconium silicate, monoclinic zirconia and tetragonal zirconia content. Method: Powder chamber. Heating rate = 2.5°C/min.*