USE OF THE HTK-XRD HIGH-TEMPERATURE CAMERA FOR THE STUDY OF THE EVOLUTION OF CRYSTALLINE PHASES IN CERAMIC GLAZES

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1. INTRODUCTION

The X-ray diffraction technique under non-ambient temperature conditions (HTK-XRD) [1] is a widely used technique in the study of multiple processes that need to be researched *in situ*, such as solid-state reactions, crystalline transitions, and thermal expansion. This technique has had a limited application in the field of ceramic glazes, however, basically for two reasons: because of the low sensitivity of the detectors and the fluxing character of these materials. Nonetheless, the introduction of instrumental improvements in the field of (position sensitive) X-ray detectors and changes in the design of high-temperature cameras have enabled new analysis methodologies to be fine-tuned for studying ceramic glazes, simulating industrial firing cycles.

2. OBJECTIVE AND MOTIVATIONS

This work addresses the study *in situ* of crystalline phase evolution with temperature in an industrial glaze using X-ray diffraction with a high-temperature camera (HTK-XRD). In addition, the results obtained with this HTK-XRD method were compared with those obtained with traditional methods (fusion buttons and tiles subjected to industrial firing cycles).

3. METHODOLOGY AND MATERIALS

A Bruker Theta-Theta model D8 Advance X-ray diffractometer coupled to an Anton Paar HTK 1200N camera, with Bragg-Bentano geometry and Göbel mirror, was used for crystalline phase analysis. The experimental measurement conditions are detailed in table 1.



Figure 1.

A standard industrial glaze composition used in glazed stoneware tile manufacture was selected to obtain matt glazed surfaces.

Tube	Voltage	Intensity	Diverg.	Range	Cte t	Step	V _{heating}	ΔT	Tmax
	(kV)	(mA)	slit	(20)	(s)	(20)	(°C/s)	(°C)	(°C)
Copper	40	45	0.50	19-48	0.25	0.02	0.5	100	1140

Table 1. Measurement conditions.

To compare the methods, fusion buttons were prepared and heat treated in a laboratory kiln to maximum temperatures of 400°C, 600°C, 800°C, 900°C, 1000°C, 1100°C, and 1140°C. The glaze composition was also applied on to a stoneware tile body and heat treated in an industrial kiln to a peak temperature of 1140°C. The crystalline phases were quantified by complete fit of the diffractogram using the Rietveld method and corundum as an internal standard [2].

4. **RESULTS AND DISCUSSION**

The HTK-XRD technique has enabled the evolution of the crystalline phases to be followed *in situ* (figure 1) with sufficient resolution for their subsequent quantification. The phenomenon of clay mineral (kaolin) dehydroxylation, and feldspar, quartz and zircon dissolution at temperatures above 900°C, as well as the crystallisation and devitrification of calcium phases, were observed. There was a displacement of the diffraction angles throughout the thermal cycle owing to the thermal expansion of the materials, which affected the structural parameters of each crystalline phase and, therefore, the position and shape of the peaks. This phenomenon needs to be taken into account in the quantification, it being more intense in the crystalline phases that display greater expansion, such as quartz or wollastonite.



Figure 1. Evolution of the crystalline structures of the test glaze with HTK-DRX (2 Theta=26-31°).

Table 2 details the percentage by weight of the crystalline phases for the three tested methods after cooling, when the test glaze was subjected to a thermal cycle resembling the industrial cycle to a peak temperature of 1140°C.



Crystalline phase	W (*)	An	Со	ZrSi	Q	Geh	F.V.
Fusion Button	<1	45±4	10±1	5±1	1±0,5	2±1	37±4
HTK-DRX	9±2	24±5	8±2	5±2	1±0,5	1±2	52±5
Industrial tile	3±1	24±2	10±2	6±1	<1	<1	56±4

(*) (W: Wollastonite (CaSiO₃); An: Anorthite (CaAl₂Si₂O₈); Co: Corundum (Al₂O₃); ZrSi: Zircon (ZrSiO₄); Q: Quartz (SiO₂); Geh: Gehlenite (Ca₂Al₂SiO₇); F.V. (Glassy phase)

Table 2. Crystalline phases (% by weight) after the thermal cycle (1140°C).

Good correlation is found between the results obtained with the HTK-XRD technique and those displayed by the tile after industrial firing. Significant differences are observed between the results obtained with the fusion buttons for the calcium phases, which are probably due to the difference in cooling and in quantity of material, which favours bulk crystallisations.

5. CONCLUSIONS

The HTK-XRD technique allows the evolution of crystalline phases to be studied *in situ* during the heat treatment of a glaze, when it is still partly molten.

At the same time, it allows reversible processes that occur at high temperature to be studied, such as allotropic transformations (e.g. α - β of quartz).

The quantification of crystalline phases from diffractograms obtained with HTK-XRD is more complex due to the thermal expansion of the crystalline structures, which affects the lattice parameters of the crystalline structures. After the necessary mathematical adjustments have been made, however, satisfactory results are obtained.

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