



## SOME ASPECTS OF CRYSTALLIZATION MICROSTRUCTURE ON NEW GLASS-CERAMIC GLAZES

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### ABSTRACT

The nucleation and crystallization of thin layers of glasses (glazes) over ceramic substrates during the fast firing of tiles for pavements and wall tiles has been a topic of great interest for tile and ceramic paving industries in recent years. Here a wide range of glass-ceramic compositions having different types of crystallization microstructure has been investigated. Based on observations by scanning electron microscopy and energy-dispersive X-ray microanalysis, several aspects of nucleation and crystallization of these new types of glass-ceramic glazes are presented and discussed. © 1998 Elsevier Science Ltd

**KEYWORDS:** A. glasses, A. oxides, C. differential scanning calorimetry (DSC), C. electron microscopy, C. X-ray diffraction

### INTRODUCTION

For many years, ceramists have known that certain glaze compositions are susceptible to large visible crystallization effects when they are applied as coatings on decorative ceramic wares [1]. Similarly, in the past there have been glassy beads that were not amorphous, but opaque or opalescent due to crystallization in either the bulk or surface, giving rise to different heterogeneity colors and appearances similar to those of natural stones [2]. Both controlled nucleation and crystallization of glasses have been widely developed since the

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1960s, due to the wide interest in the production and commercial exploitation of glass-ceramic products in domestic and technological applications [3]. Not much investigation, however, has been devoted to the production of glass-ceramics in thin layers, although surface crystallization phenomena in glasses have been investigated [4,5]. However, these latter studies have focused more on associating surface crystallization with defects in conventional glasses or as an intermediate stage in the bulk crystallization of glass-ceramics.

In recent years, there has been a growing interest in ceramic glazes and frits for developing new glaze compositions that can be crystallized in order to improve the mechanical and chemical properties of fast-fired glazed tiles. Nucleation and crystallization of thin layers of certain glasses covering ceramic substrates (glazes) to obtain high-performance glass-ceramic coatings [6,7] are scientific and technological challenges due to the difficulties of controlling crystal growth homogeneously. Therefore, the aim of this research has been to explore the capabilities of commercial and other new glass-ceramic compositions for use as glass-ceramic glazes and to show and discuss the different crystalline microstructures that can be obtained in these special glass-ceramics.

## EXPERIMENTAL

Several parent glasses from a wide range of compositions in the CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system, the Li<sub>2</sub>O–ZnO/BaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system, and the G–C commercial systems based on spodumene, cordierite, nepheline, and leucite were melted and water quenched to obtain powdered glasses (or frits). The glasses/frits obtained were subsequently applied to stone-ware tiles ( $\alpha = 7.41 \times 10^{-6} \text{ C}^{-1}$ ), as is usual in the production of ceramic pavements. An industrial fast firing to 1100°C for 30 min. was used, during which the (nucleation + growth) stages were accomplished in the thin layer of glassy coating (approx. 0.3 mm). In some cases, a complementary (nucleation + growth) thermal treatment was carried out, in order to recrystallize the residual glassy phase remaining after the fast-firing cycle. In these cases, the temperature used for the additional thermal treatment was that of the main DTA (digital thermal analysis) exothermic crystallization peak (DTA conditions: heating rate of 10°C/min. and cooling rate of 30°C/min.). The final result were tiles with glass-ceramic glazes containing several volume percent of crystals.

The mineralogical composition of crystalline phases was determined by reflection X-ray diffraction (XRD) from the sample surface, using a Philips instrument under the normal operation conditions used in powder XRD analysis. In order to identify the different microstructures of the experimental glazes, both the surface and sections of tiles were observed by scanning electron microscopy (SEM)/energy-dispersive X-ray analysis (Zeiss DSM-950 with Tracor configuration, working at 20 kV accelerating voltage).

## RESULTS AND DISCUSSION

After melting the original compositions, the glasses were obtained by quenching in ambient temperature water to give frits. XRD analysis was performed in order to assess the noncrystalline character of these parent glasses. DTA experiments at a heating rate of 10°C/min. were carried out to determine the relative tendency for devitrification at high temperatures. As an example, Figure 1 shows the DTA curves for the N2 (feldspar composition) and C2 (cordierite original composition) glasses. It was found that there was a wide range of thermal

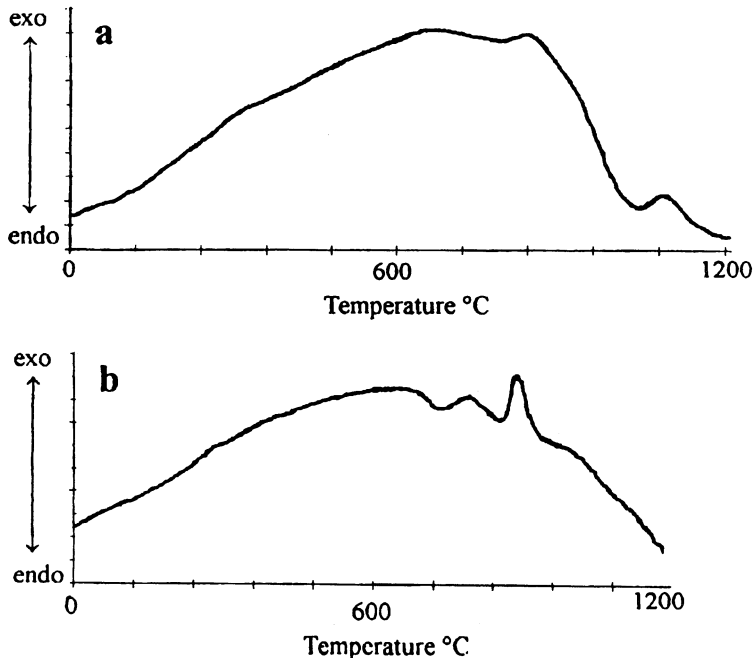


FIG. 1

DTA curves obtained from (a) original N2 and (b) C2 glasses quenched in water.

behavior among the glassy compositions studied here [8]. As was expected, the feldspar composition produced a very stable glass with respect to nucleation and crystallization, whereas the cordierite glass showed two exothermic peaks at 800 and 920°C due to the precipitation of  $\alpha$ - and  $\mu$ -cordierite phases.

The difficulty of crystallization made it necessary to introduce some nucleating agents [9,10] into several of the glassy compositions considered here, mainly in the case of the most thermally stable glassy frits. Table 1 gives the glaze systems investigated, together with the crystalline phases precipitated after fast thermal treatment at 1000°C for 30 min.

TABLE 1  
Glass Frits and Crystalline Phases Obtained After Blade Deposition and Fast Firing Over Ceramic Substrates of Earthenware Tiles

Composition system	Main crystal phase	Microstructure
Li <sub>2</sub> O-CaO-MgO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	spodumene	rounded crystallites
	cordierite	dot crystals
	diopside	square/rounded crystals
	diopside + anorthite	elongated and prismatic crystals
G-C commercial systems	cordierite	grained crystals
	spodumene	prismatic crystals
Li <sub>2</sub> O-ZnO/BaO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	nepheline/celsian	needle crystals
Li <sub>2</sub> O-K <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	leucite	as whiskers 1-2 $\mu$ m crystals

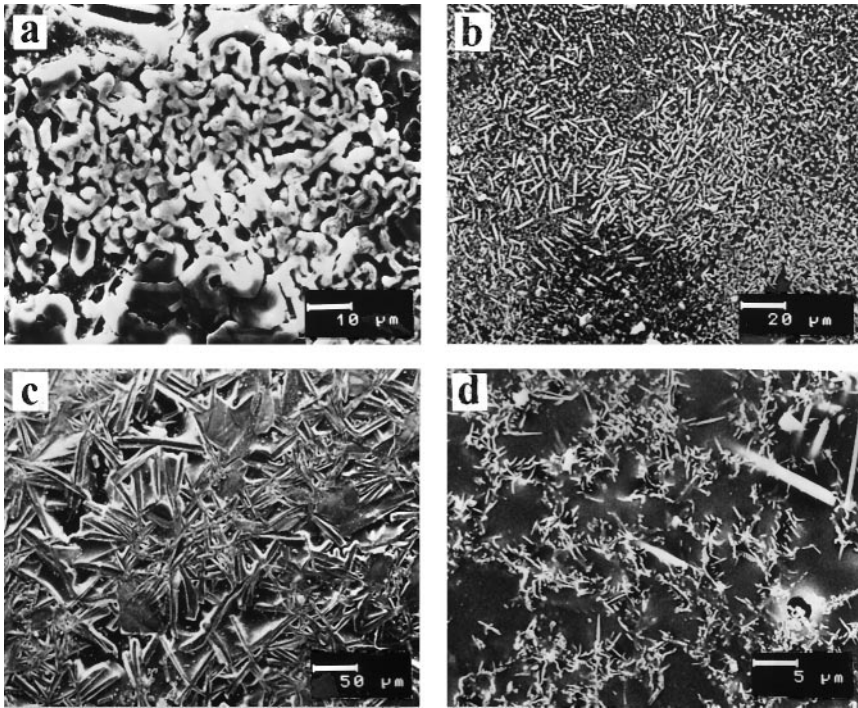


FIG. 2

SEM micrographs from glass-ceramics glazes of (a) spodumene, (b) cordierite, (c) nepheline, and (d) leucite.

As can be seen in Figure 2, the crystallization microstructure of the surface of these glass-ceramic glazes is different depending on the crystalline phase and composition of the original glassy matrix. When the microstructure of the cross section of the glaze/substrate interface is observed by SEM, it can be seen that a high volume of crystallization produces many bubbles and coarse crystallization in some thin layer glazes. Therefore, in those cases where there was a high tendency to crystallize, it was necessary to dilute the original frits with some commercial boro-zinc silicate frits, which likewise were phase separated [10]. This enabled the crystallization process to be better controlled, as can be observed in the SEM micrograph shown in Figure 3.

This dilution allowed a reticular crystalline microstructure embedded into the residual glassy original phase to be obtained, which, in principle, may allow the abrasion and hardness properties of the glaze surface to be improved. In the case of the spodumene glaze, the dilution allowed the precipitation of crystals between the cracks produced by the different expansion coefficient of the spodumene glassy matrix and the solvent frit (Fig. 4). This type of nucleation of crystals associated with the cracks and interfaces agrees well with the models of surface nucleation recently developed by Schmelzer *et al.* [5].

The crystallization mechanisms in this case are different from those in bulk glasses because three different nucleating interfaces must be considered; *viz.*, air/surface of glaze, substrate/glaze interface, and frit/frit interface. Nucleation and growth of crystals in this case share some aspects of the processing of sintered powdered glasses. A wide range of

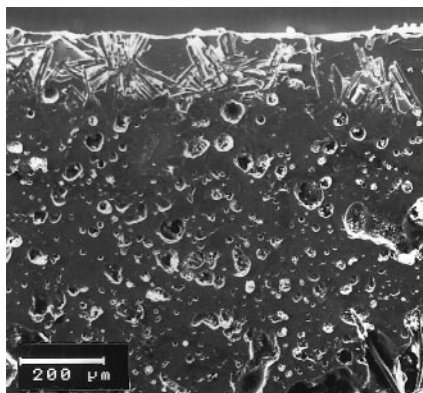


FIG. 3

SEM micrograph obtained from a perpendicular cross section of the nepheline glass-ceramic glaze diluted with a commercial frit.

crystallization microstructures has been achieved by this processing, depending on the original glass composition. However, the very short time for the growth step makes it difficult to obtain high percentages of volume crystallization. Crystals ranging in size from less than 1 μm to elongated crystallites larger than 20 μm precipitated in the glassy matrix of the coating were obtained.

Compatibility between glaze and ceramic substrates was excellent in all cases investigated, due to the close similarities in  $\text{Al}_2\text{O}_3/\text{SiO}_2$  and alkaline/alkaline-earth components. Otherwise, a very thin layer of melted glass was observed by SEM and even optical microscopy at the substrate interface.

Based on our previous research, we consider that classical theories of nucleation and crystallization of glasses must be adapted to the case of crystallization of thin glass-ceramic layers over ceramic substrates obtained from clay mixtures. This is because of the strict conditions for achieving homogeneous crystal precipitation in the fast-firing conditions and

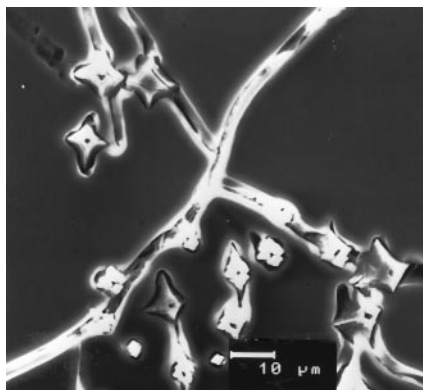


FIG. 4

Nucleation of spodumene star crystals, or incipient dendrites, in the S2 glaze composition.

also because of the complexity associated with the several types of interfaces involved in these glass-ceramic coatings.

### CONCLUSION

In spite of the difficulties in finding glass compositions able to crystallize over a very narrow range of temperature and time (1100°C, 30 min.) and with a thermal expansion coefficient matching that of red and white ceramic substrates, there are several possibilities for transferring the knowledge of nucleation and crystallization to develop new improved glass-ceramic glazes. The interphase and/or surface crystallization phenomena have, in this case, a special importance due to the high ratio of interface-to-bulk crystallization. Controlling nucleation and crystallization at these interfaces to obtain a critical volume fraction and size of crystals in very thin layers should allow, in the near future, improvement of the physical and technological properties of this new family of glass-ceramics.

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