CRYSTALLINE GLAZES

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1. FRITS, GLAZE COMPOSITIONS AND FIRED GLAZE COATINGS

Ceramic frits are glasses that are prepared from raw materials of a crystalline nature by melting them at temperatures round 1500°C, with subsequent quenching in air or water so that they will keep their glassy structure.

Frits are used, alone or mixed with other constituents of a glassy or crystalline nature, to obtain the glaze coatings found in glazed ceramic floor and wall tile. On milling the mix, henceforth called the glaze composition, it is applied to a (fired or unfired) ceramic body, where it forms a consolidated layer of particles. In firing, the layer melts and undergoes certain transformations that convert the melt on cooling into the glaze coating of the tile.

The application of the glaze particles to the body, before firing, is usually carried out by either of two procedures: a wet or a dry method. In the wet method, the glaze composition (frits and additives) are milled to a particle size that is normally below 40μm, in a ball mill with water. The resulting suspension is then applied to ceramic bodies, coated beforehand with engobe. Part of the water contained in the applied suspensions is evaporated and part is absorbed by the body, leaving behind a consolidated layer of particles. In the dry method, the frit (in the form of more or less sphered particles, flakes, or granules made up of particle agglomerates), is applied to the previously engobed ceramic body, onto which another "base glaze" layer is often applied. This layer sometimes contains an organic adhesive, which serves to fix the frit particles or granules deposited on top.

The glaze coating is the fair face of the tile, which remains visible after tile installation. It must therefore possess certain technical and aesthetic characteristics that match its service application. The requirements set for floor tile glazes, in which technical characteristics are more important, differ from those set for wall tile glazes, where the prevailing interest lies in the aesthetic properties of the glaze [1][2][3][5][6].

2. OPAQUE GLAZE COATINGS

Opaque glaze coatings have found widespread acceptance in the ceramic tile market, particularly where (glossy or matt) white glaze coatings are involved, which are typically used in wall tiling.

2.1 CAUSES OF OPACITY IN GLAZE COATINGS

Glaze opacity stems from the scatter of incident light at the micro-heterogeneities within the glassy phase. As a result of this scatter, the intensity of the light that is transmitted through the glaze layer decreases, yielding opacity. The micro-heterogeneities involved may be crystalline phases or immiscible glassy phases within the major glassy phase (they may at times be trapped gases).

Opacity is directly related to the degree of scattering that incident light undergoes when it strikes the inclusions dispersed within the major glassy phase, and depends upon their number and size, on their optical anisotropy (birefringence), and upon the differences between their refractive indices [2][3][4]. Thus, the greater the number of dispersed inclusions, and the greater the difference between their refractive index and that of the major glassy phase, the more intense will glaze opacity be in principle, as long as these inclusions are larger than the visible light wavelength.

Fig. 1 schematically illustrates the mechanism that gives rise to opacity in ceramic glazes.

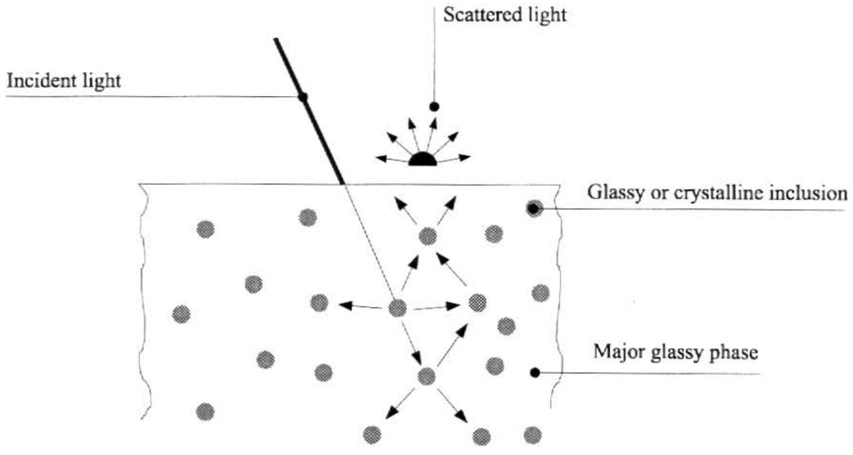


Figure 1. *Schematic of the mechanism yielding opacity in ceramic glazes.*

2.2 METHODS USED FOR PRODUCING OPACITY IN CERAMIC GLAZES

The procedures normally employed in glazed ceramic tile manufacture for obtaining opaque glazes are based on introducing or producing solid or glassy (immiscible and disperse) micro-heterogeneities within the major glassy phase, with a different refractive index to that of the glassy matrix.

i) Opacity produced as a result of the immiscibility of two glassy phases

When certain frits start melting in the heating step of the firing cycle, incidental compositional changes arise, which may yield immiscibility phenomena in the melt, as a result of which one of the liquid phases is dispersed in small droplets within the other, a situation that is maintained on quenching the melt. The dispersed droplets, whose refractive index differs from that of the major glassy phase, produce glaze opacity.

The size of the droplets of glassy phase is closely related to the degree of glaze opacity. When the dispersed droplet size exceeds a bounding value, glaze transparency decreases, and a progressive opalescence arises, appearing first as a bluish colour, then becoming white as droplet volume grows [4][7][8][9].

The opacity that arises as a result of glassy-phase immiscibility is usually less intense than that caused by the presence of crystalline phases within a major glassy phase, a subject dealt with below, because in the former case, the difference between the refractive indices of the immiscible phases is smaller.

ii) Opacity produced by dispersed crystalline phases within a glassy phase

It is useful to distinguish between glaze coatings whose opacity arises, wholly or partly, as a result of the presence of crystalline particles or aggregates, which have not fully fused during the firing cycle of the glazed tile, and fired glaze coatings whose opacity is solely due to the presence of crystalline phases produced by devitrification of the frit during firing.

In the former case, opacity is obtained by operating in such a way as to leave small particles of unmelted crystalline materials dispersed within the major glassy phase when firing ends, and whose refractive index differs from the glassy matrix. These are obtained from frits mixed with crystalline aggregates such as corundum, zircon, quartz, rutile, etc., of suitable particle size. This kind of glaze is usually employed for coating ceramic flooring, owing to the presence of the crystalline particles that they contain, which bestow very good mechanical properties on such tile. At times, some crystalline phases may also be found, stemming from the devitrification of the starting frit, together with particles of unmelted crystalline materials.

In the latter, opacity is produced by causing crystalline phases to form as a result of frit devitrification in firing. The glazes obtained by this procedure are preferentially used to coat wall tile, because of their aesthetic characteristics (whiteness index, surface texture, gloss, etc.). Among such glazes, the so-called "zirconium whites" particularly deserve highlighting because of their widespread use in glazed tile manufacture. These are fabricated from frits containing up to about 14 wt% zirconium silicate. This percentage is the maximum proportion, a bound imposed by the solubility limit of zircon (used as a raw material) in the melt in fritting kilns, at the standard operating temperature (round 1500°C). In such glazes, it has been observed that zircon is the crystalline phase which produces opacity, while in some cases the presence of diopside crystals (magnesium and calcium silicate) has also been detected, owing to the fact that the starting frits usually contain a certain amount of MgO and CaO, which, because of their rearrangement or reaction with SiO_2, can produce structural units of $MgSiO_4Ca$ that give rise to diopside crystal formation [10-17].

3. SUITABILITY OF THE TERM "GLASS-CERAMIC" FOR QUALIFYING GLAZES WHOSE OPACITY IS DUE TO THE PRESENCE OF DISPERSED CRYSTALLINE PHASES WITHIN THE GLASSY PHASE

Of late, the term "glass-ceramic" has been increasingly used to extol the characteristics of certain heterogenous crystalline glazes that are being offered as a novelty in the glazed ceramic tile market. In view of this situation, we feel that it would be useful to set out a few considerations aimed at establishing the degree of accuracy or appropriateness with which this term is being used, and determining whether it would also be applicable to other polycrystalline glazes that have been widely used for quite some time in the tile branch, and which to date have not been deemed worthy of this qualification.

The concept, glass-ceramic material, will therefore first be introduced, subsequently followed by a comparison of its characteristics (properties and formation process), with those of crystalline glazes available in the marketplace, to allow drawing the appropriate conclusions.

KINGERY, BOWEN and UHLMANN, in their work *Introduction to Ceramics* [18], define glass-ceramic materials as "materials that are produced by controlled crystallization of appropriate glasses. They consist of a large proportion, typically 95 to 98 vol%, of very small crystals, generally smaller than 1μm, with a small amount of residual glass phase making up a porefree composite".

Other definitions of "glass-ceramic material" have been found in the literature [19][20]. They all coincide with the former as to the following features: a) they are polycrystalline solids that are fabricated by controlled crystallization of glasses; b) it is convenient for the crystals formed by devitrification to be uniformly sized; c) they are pore -or void- free solids; d) they are formed or moulded in the glassy phase (in the molten state), before crystalline-phase formation or devitrification occurs, which arises subsequently with heat treatment.

There are various discrepancies among authors, both with regard to the minimum proportion of total volume occupied by the crystalline phases, which some authors set as low as 40-50% (the remainder being glassy phase), and in respect of maximum crystal size, which in some cases [20], may reach 10 μm. Figs. 2 and 3 show microphotographs of different glass-ceramic products, taken from the literature [19][20]. They exhibit the compact polycrystalline structure of these materials, the typical size and uniformity of the crystals, as well as the low proportion of glassy phase.

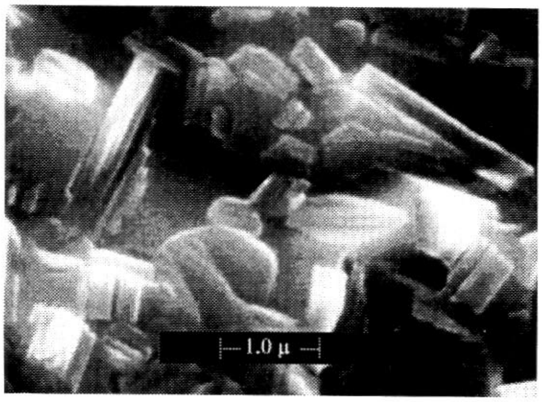


Figure 2. *Microstructure of DICOR® glass ceramic.*

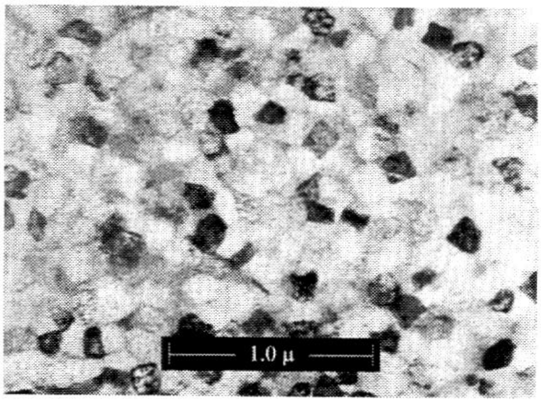


Figure 3. *Submicrostructure in a Li_2O-Al_2O_3-SiO_2 glass ceramic*

With regard to the formation process of a glass-ceramic, it can be said that this is quite complex, and generally arises according to the following four-step sequence [21][22][23][24]: a) starting with a given glass, a disperse amorphous phase usually forms (on heating or cooling), which is typically quite unstable and rich in one or two key oxides (e.g. ZrO_2 o TiO_2), while being structurally incompatible with the host glass; b) primary crystalline nuclei are formed either by heterogeneous nucleation at the phase boundaries or homogeneous nucleation within the major glassy phase; c) a metastable crystalline phase nucleates heterogeneously at the primary nuclei and generally grows at the expense of the major glassy phase, constituting a metastable solid solution in the form of very small-sized granules; d) the metastable solid phase becomes a definitive stable crystalline structure (also in granular form) by isochemical phase transformations (allotropic changes), as a result of reactions between metastable phases or because of exsolution (exit of some elements from within the metastable phase granules outwards into the glassy phase).

Taking the above into account, it may be stated that there is a certain structural analogy between the two types of glazes whose opacity is due to the presence of dispersed crystalline phases (defined above) within a glassy phase and glass-ceramic materials, bearing in mind that they are all vitreous-crystalline solids.

However, the proportion of crystalline phases in the glazes that we are dealing with is usually lower than the minimum limit of 40%, previously set for glass-ceramics. Figures 4 and 5 depict the photographs of the glaze coatings of two industrially produced floor tiles, one of them containing unfused crystalline particles and the other, having zircon crystals formed by frit devitrification. It can be qualitatively observed that the crystalline phase percentage is of the order of at most 20-30 vol% in both cases.

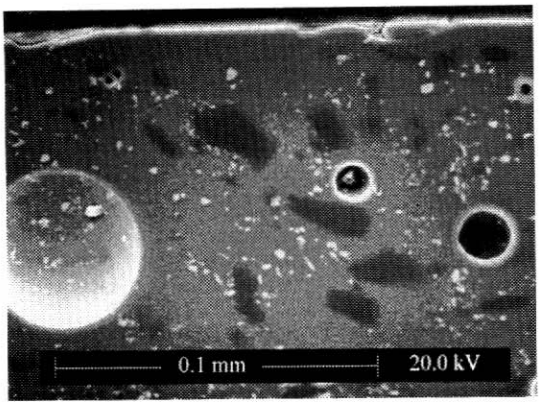


Figure 4. *Micrograph (SEM) of the cross-sectional area of a glaze containing unmelted crystalline particles (taken from an industrial floor tile).*

Figure 5. *Micrograph (SEM) of the cross-sectional area of a white zirconium glaze (taken from an industrial wall tile)*

The fact that the crystalline glazes used in the ceramic floor and wall tile industry have such a low crystalline-phase proportion is partly due to the procedure used in firing glazed tile, and therefore in producing these glaze coatings. Thus, if the proportion of crystalline phases in the glaze became greater than the indicated amount, the viscosity of the whole layer of crystals and glassy phase might rise excessively, during the heating step of the firing cycle, hindering the sintering process that takes place in parallel or sequentially with the devitrification process, as set out below. This would give rise to glazes of a commercially unacceptable quality, since they would have a rough, matt surface, with open pores.

In glazes whose opacity is due to the presence of unmelted crystalline aggregates left on firing the glazed tile, there are also other important differences with regard to glass-ceramics: a) They are materials with inner porosity in the range 8 to 16% (Fig. 6); b) Most (or all) the crystalline aggregates that they contain have not been formed by devitrification of a glass but are particles of crystalline materials (zircon, corundum, or quartz) that were mixed with the starting frits and did not fully dissolve in the glassy phase that formed during the firing of the ceramic tile; c) Some of these crystalline aggregates have sizes that considerably exceed 10μm (Fig. 4). Thus, we consider that glazes possessing such characteristics cannot be called glass-ceramics.

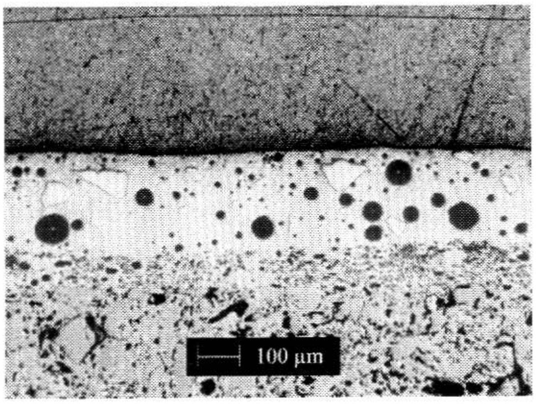
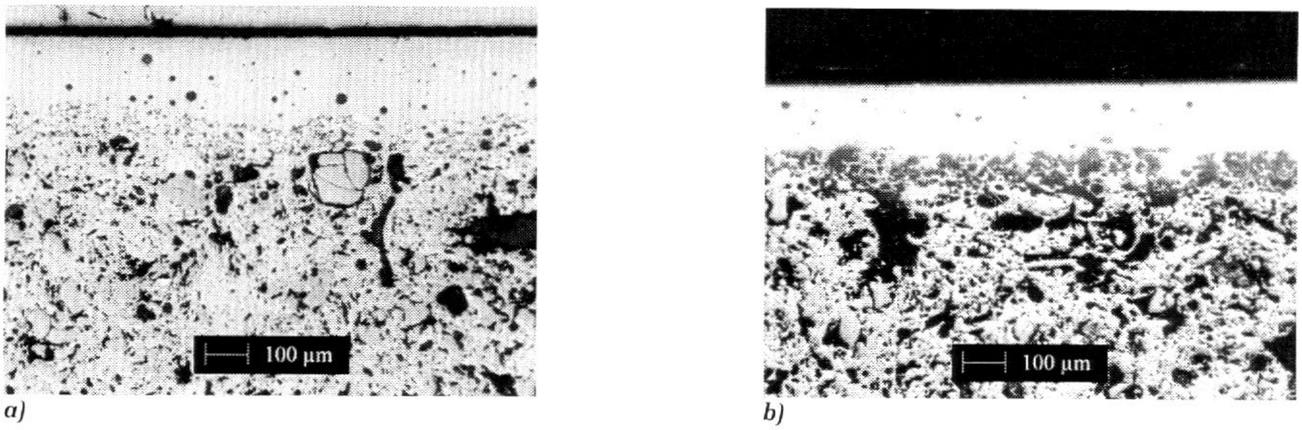


Figure 6. *Micrograph (optical microscopy) of the cross-sectional area of a glaze containing unmelted crystalline particles (taken from an industrial floor tile).*

However, glazes whose opacity is due to the presence of crystals formed by devitrification of a homogeneous starting glass (frit), as in the case of the white zirconium glazes containing zircon crystals or that of the glaze known commercially as CER-GLASS, presented at CEVISAMA-1994 [23], containing diopside crystals, are in many ways similar to glass ceramics, because: a) They possess very low inner porosity (between 1.0 and 2.5%), which, as may be observed in the photographs of Fig. 7 corresponding to a white zirconium glaze and to CER-GLASS, is considerably lower than that exhibited by the other types of glaze (Fig. 4); b) Most of the crystals that they bear are smaller than 10μm, as can be observed in Figs. 5 (zircon crystals), 8 (diopside crystals), and 9 (gahnite crystals); c) Crystalline-phase formation is quite similar to that of the glass-ceramics.

As far as this last similarity criterion is concerned, on studying the process involved in obtaining opaque glazes from zirconium frits or from frits based on other, different, oxide systems, it has been observed that stages (c) and (d), described above for glass-ceramics, are strictly followed. Thus, in accordance with stage (c), metastable precursor crystalline phases form, of the solid solution type, which grow from the micro-heterogeneities existing at the frit particle surface (heterogeneous nucleation), and which act as "active centres" or crystallization nuclei; and in accordance with stage (d) final crystalline structures are formed as a result of the transformation of metastable precursor phases, or by their interactions or reactions with some other glassy-phase constituents.



a) *b)*

Figure 7. *Micrograph (optical microscopy) of the cross-sectional area of: a) CER-GLASS; b) white zirconium glaze*

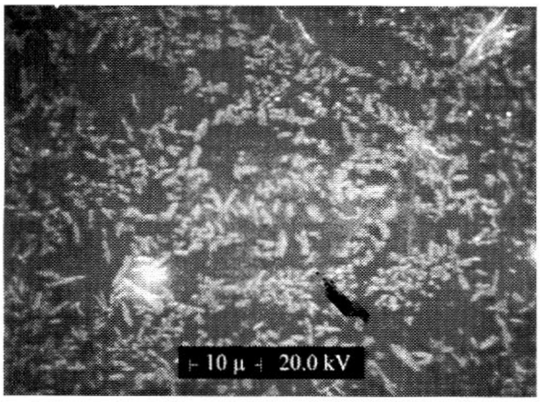


Figure 8. *Micrograph (SEM) of the cross-sectional area of a glaze containing diopside crystals (of an industrial-size tile coated with CER-GLASS)*

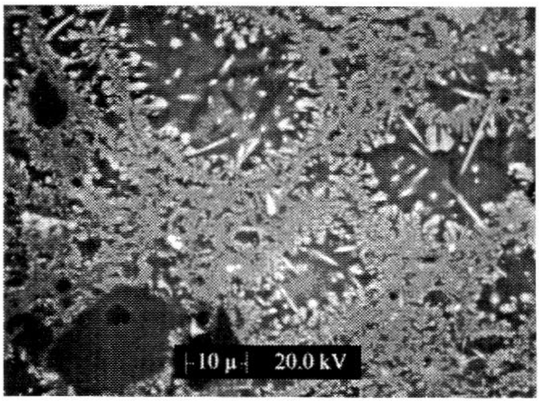


Figure 9. *Micrograph (SEM) of the cross-sectional area of a glaze containing gahnite crystals (taken from an industrial floor tile).*

Taking the formation process of white zircon glazes as an example of this behaviour, we have observed (Fig. 10) that when test specimens made using zirconium frit particles sized below 40µm are heat-treated under isothermal conditions, a metastable solid solution forms first, probably a calcium zirconate, with a tetragonal zirconium oxide crystalline structure, which is transformed (by calcium exsolution) into monoclinic zirconium oxide. Parallelly, diopside crystals are formed (petedunite has also been detected at certain temperatures, when Zn is present). Finally, these crystals are transformed into zircon (zirconium silicate) by reaction with SiO_2 [26]. The same crystalline-phase formation sequence could be observed on heat treating identical test pieces at a constant rate of heating, a heating method that is more like the one that the tile undergoes in the heating step of the firing cycle for glazed tile. Fig. 11 shows that as temperature rises, the solid solution with a tetragonal zirconium oxide crystalline structure and monoclinic zirconium oxide that first arise, progressively turn into zircon, which is the sole crystalline phase to survive at the peak firing temperature interval in the firing cycles usually employed in the ceramic floor and wall tile industry (from 1110 to 1140 °C). Thus, for test specimens made using frit particles sized below 40µm (standard size interval used on applying the glaze composition as a slip or aqueous suspension), it has been observed [10], that the sole crystalline phases remaining in the interval 1110 to 1140 °C are zircon and some diopside, as the XRD diagrams show in Fig. 12.

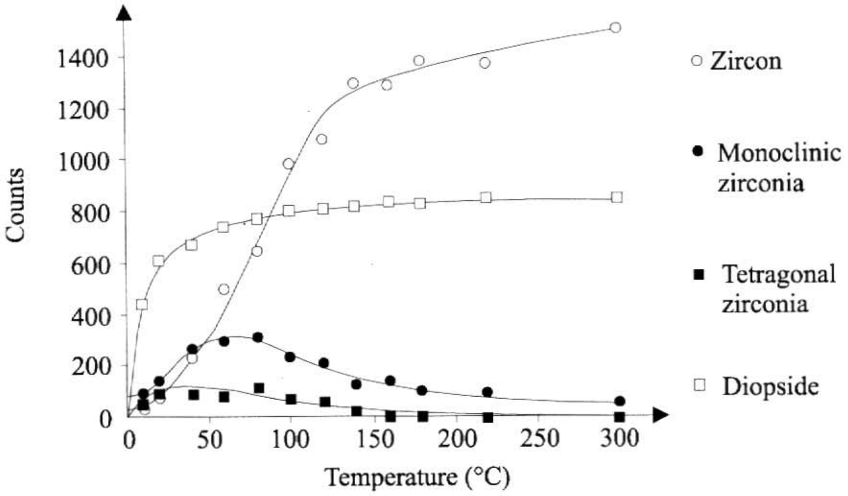


Figure 10. *Counts of the maximum intensity peak of the devitrifying crystalline phases v. dwell time. T=950°C (zirconium frit).*

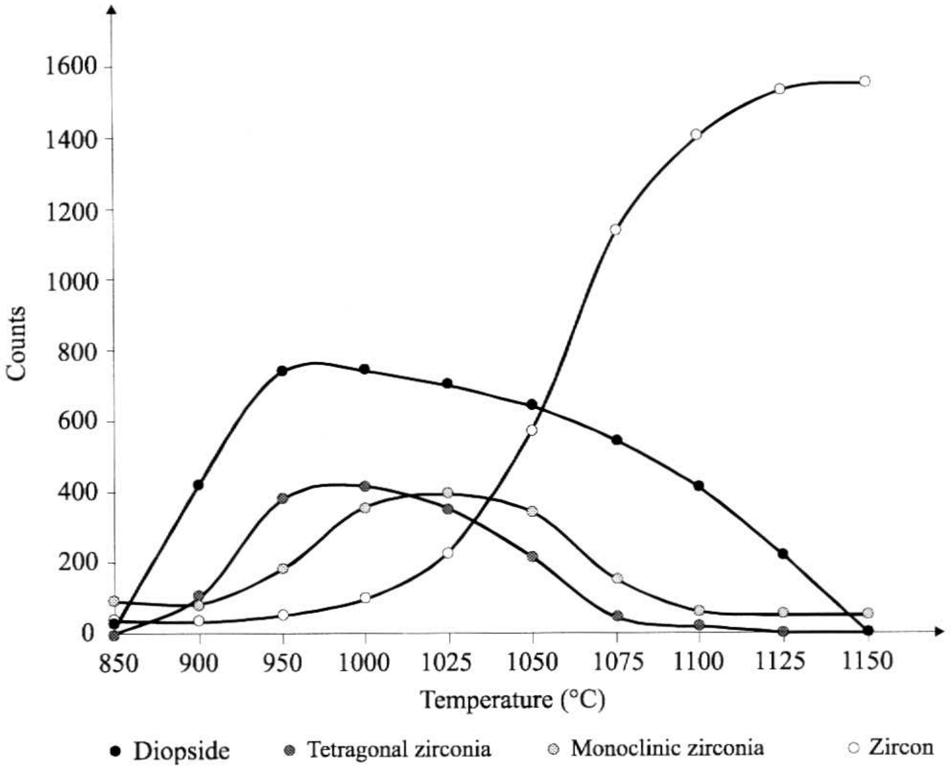


Figure 11. *Counts of the maximum intensity peak of the devitrifying crystalline phases v. temperature. Heating rate=5°/min. (Zirconium frit)*

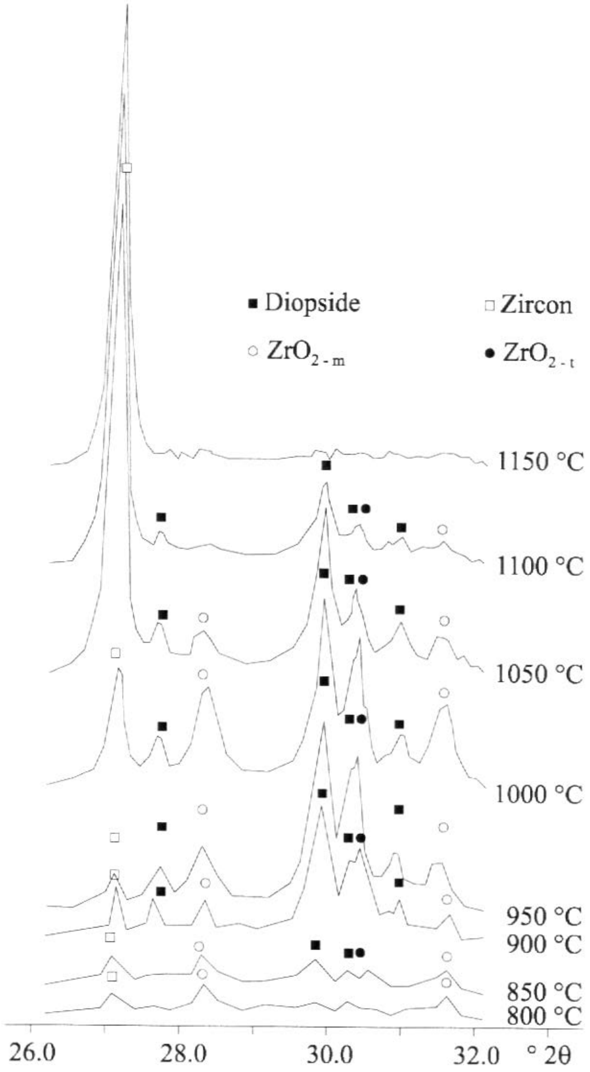


Figure 12. *Crystalline phases identified at different peak firing temperatures. Heating rate=5 °/min. (Zirconium frit)*

It may be inferred from the above, that there are only two differences worth mentioning between the opaque glazes obtained by crystalline-phase devitrification of frits and glass-ceramic materials: namely, the proportion of crystalline phases that they contain (below 40%) and their porosity (from 1.0-2.5%). However, the process that yields both is quite alike, i.e. the way in which the different stages unfold, which give rise to a final polycrystalline solid from a glass, by heat treatment.

We are thus left in doubt concerning which term should really be used for classifying glazes obtained by frit devitrification: are they glass-ceramics or just crystalline glazes? Faced with this doubt, we have decided to use the second expression in the title and throughout this conference, while awaiting a definitive conclusion in this regard.

Finally, to round off the reflections set out in this section, I believe it is important to point out that among all the heterogeneous glaze coatings commonly used in tile manufacture, white zirconium glazes lie closest to the glass-ceramic concept, since they possess very low inner porosity (≈1.5-2 vol%), and are polycrystalline solids in which the existing crystalline phases (normally sized below 10μm) are formed by devitrification of the starting frit during tile firing, while following, as described above, the characteristic process stages that yield glass-ceramic materials.

4. FACTORS INFLUENCING THE QUALITY OF CRYSTALLINE GLAZES

The quality of a glaze is defined by its aesthetic and technical properties, within the constraints of the glazed tile's prospective service function: i.e. for use as wall cladding or flooring.

Its most important aesthetic properties are its whiteness index or colour, gloss, and surface texture (smooth or rough).

As far as the technical properties are concerned, a distinction needs to be made between mechanical and chemical properties. The principal mechanical properties to be considered in a glaze are: wear resistance, scratch hardness, microhardness, impact resistance, and toughness. Particularly worth highlighting among the chemical properties are: resistance to chemical attack (acids and alkalis), and stain resistance.

Some factors are set out in the following, which can impact the quality of crystalline glazes, and the respective properties that may be affected are detailed.

i) Starting frit composition and particle-size distribution

The starting frit composition defines the nature of the crystalline phases that will arise during devitrification. It shall therefore be selected according to the targeted aesthetic and technical characteristics of the glaze coatings, while keeping their coefficient of linear thermal expansion at round $65 \cdot 10^{-7} °C^{-1}$, so that it will be sufficiently close to that of the red- or white-firing bodies, commonly used in industry, in order to keep deformations from arising in the tile as a result of glaze-body mismatches.

On the other hand, once the set of oxides has been chosen, which is to make up the frit, as well as the respective oxide proportions that will allow the frit to meet the requirements indicated in the previous paragraph, its composition may need to be slightly adjusted to obtain the appropriate sintering curve (Section 5) in respect of body to be used (red- or white-firing), the firing procedure to be employed (single- or twice-firing), or the type of product sought (floor or wall tile). Thus, for instance, in the case of porous, single-fired wall tile, the sealing temperature of the molten glaze (temperature at which the layer becomes impermeable), shall exceed 960°C or 980°C respectively, according to whether the body is white- or red-firing. This requirement need not be complied with if the same product (porous wall tile) is processed by twice firing, since on applying the glaze layer to a fired body (first firing), frits or glazes that have considerably lower sealing temperatures can be used for the second firing. Section 5 sets out the convenience of having a suitable frit sintering curve that will yield appropriate devitrification (producing opacity) and the targeted surface texture, on reaching the standard peak firing temperature interval used in ceramic tile manufacture (1110-1150°C).

The particle-size distribution of the starting frit particles is very important since on raising frit mean particle size, the temperature interval at which devitrification arises shifts towards the higher temperature region [10], as well as lowering crystallization intensity, as may be observed in Fig. 13, which shows the DTA diagram corresponding to samples of an industrial zirconium frit with different particle-size distributions.

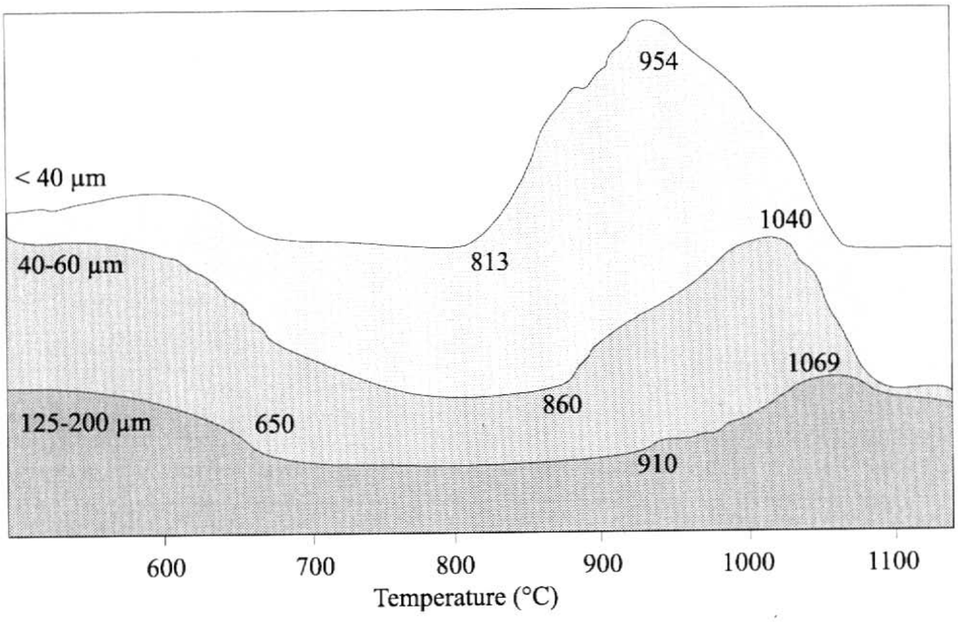


Figure 13. *DTA curves corresponding to different particle-size fractions of a zirconium frit. Heating rate 10°C/min.*

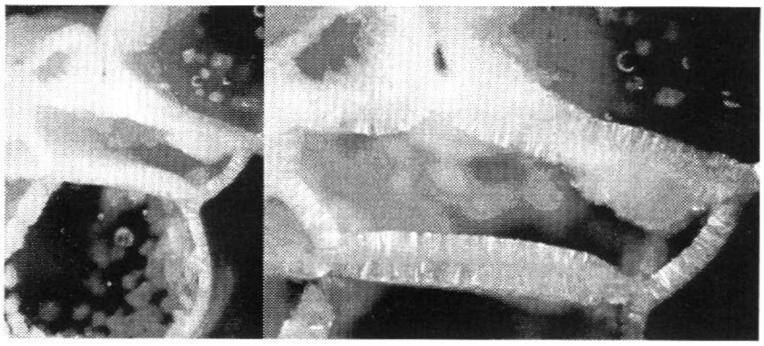
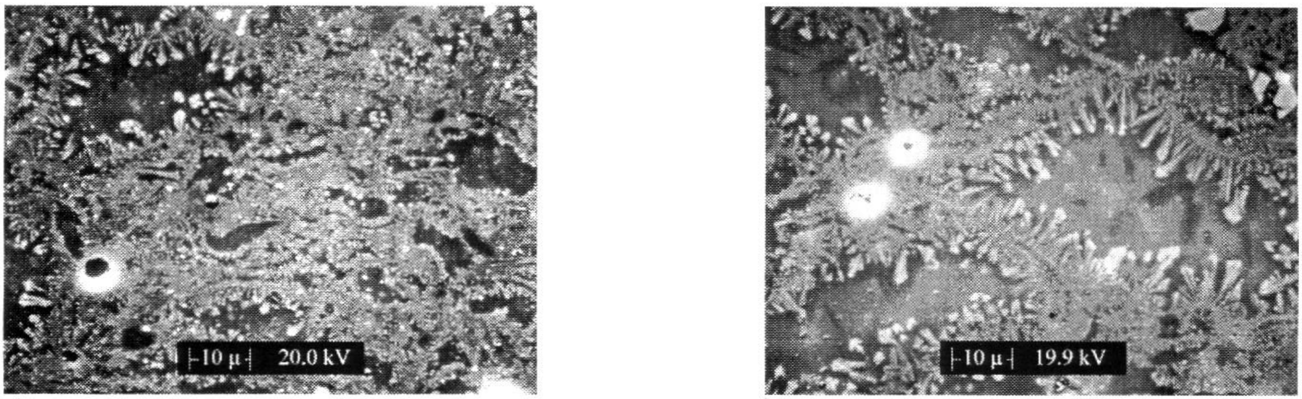


Figure 14. *Diopside crystal growth from the surface of the frit particles inwards.*

This outcome can be explained by making the assumption that when frit particles undergo heat treatment, nucleation is heterogenous and takes place at the surface, so that crystals grow from the particle surface inwards, as may be observed in Fig. 14, which corresponds to diopside devitrifying frit particles. Consequently, the smaller the starting frit particle, the greater will crystal density be in the resulting final glaze, as the photographs in Fig. 15 reveal, in which the results obtained are compared on subjecting test specimens formed using differently sized particles, corresponding to a gahnite devitrifying frit, to the same heat-treatment cycle. This phenomenon has also been observed in industrial practice. Thus, when zirconium frit granulars (with particle sizes ranging from 1 to 3 mm) are applied, glazes are produced with a much lower whiteness index than when the same frit is applied (by the wet method), with a particle-size below 40μm, after both have undergone the same firing cycle. This is because the resulting crystal density in the fired glaze coating is considerably lower in the former than in the latter case.

On the other hand, frit particle-size distribution is closely linked to the sintering phenomenon that arises in firing, concurrently (parallel to, or sequentially) with crystalline-phase formation, and which, as will be seen further on, must occur at the right moment, in order to obtain a glossy or matt glaze, with a smooth surface, without any open pores.



a) b)

Figure 15. *Influence of the particle size of a gahnite-devitrifying frit upon resulting crystal density.*

ii) Glaze application technique

The glaze application procedure (dry or wet method) can affect the opacity of the resulting glaze, to the extent that frit particle size does, as indicated previously. Thus, on using the dry method, mean frit particle size tends to be considerably larger than when using an aqueous suspension (in this case, mean particle size typically lies below 40μm).

When glaze is applied by the wet method, the fact that the aqueous glaze suspension is applied by spraying or by curtain glazing may influence the resulting surface texture of the glaze. In the former case (airbrushing or discing), when the targeted glazes are systems that have high viscosity in the melt, as is the case with crystalline glazes, not very smooth surfaces are obtained, which may affect their final gloss. However, if the suspension or slip is applied by curtain glazing (waterfall-curtain or bell glazing), a smooth glaze coating is usually produced, which enhances gloss.

iii) Nature, size and closeness of the crystals that devitrify in firing glazed tile

These factors condition glaze opacity, its coefficient of thermal expansion, its hardness (Mohs and Vickers), as well as its abrasion resistance.

a) Opacity

Glaze opacity depends on the difference between the refractive index of the crystals present and that of the residual glassy phase. It will therefore be highly influenced by the refractive index of the devitrifying crystalline phases, which depends on their nature, since the refractive index of the residual glassy phase varies only slightly with its composition (between 1.5 and 1.6).

It has been shown in white zirconium glazes [26] that the whiteness index, which is closely related to opacity, rises with the zircon crystal content, tending asymptotically to a peak value that arises when this crystal mass fraction in the glaze is about 16% (Fig. 16).

On the other hand, opacity appears to peak when mean crystal size is the same as the incident light wavelength.

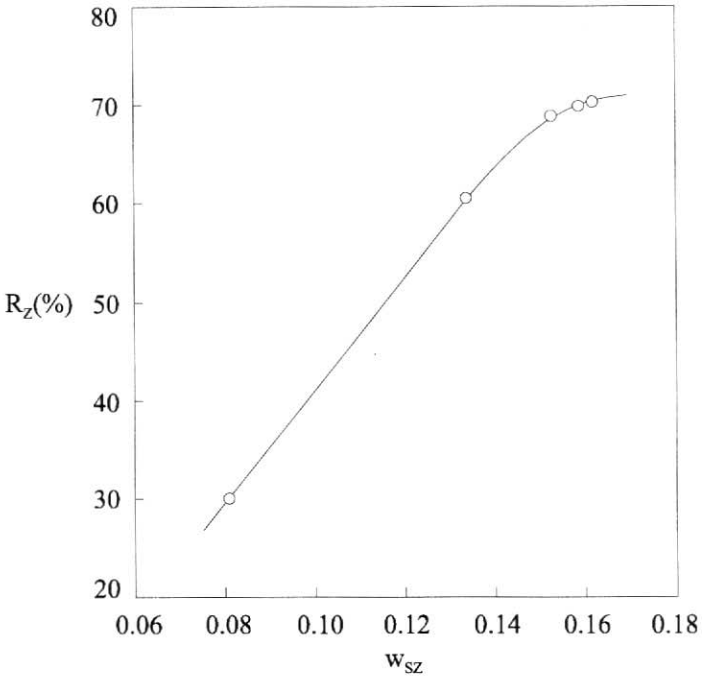


Figure 16. *Variation of the degree of whiteness (R_z)*(*) *with the zircon crystal mass fraction. (White zirconium glazes)*

b) Coefficient of thermal expansion

This property depends on the nature and proportion of the crystalline and glassy phases that are present. Some authors [14] suggest that the coefficient of thermal expansion of a vitreous-crystalline material is an additive property, so that it can be computed quite closely from the corresponding values of this property in the glassy phase and in the crystals, by applying the law of mixes.

c) Mohs hardness and Vickers microhardness

Mohs hardness and microhardness of the glaze are influenced by the respective values of these properties in the devitrifying crystalline phase (therefore depending upon its nature) and on the closeness of the crystals in the glaze (the closer the crystals are to each other, the better will the glaze be able to withstand scratching or indentation by a pointed solid). Thus, in gahnite devitrifying glazes (hardness 7.5-8), it has been shown (Fig. 17) that microhardness increases as the mean intercrystal spacing decreases [27].

(*) R_z = Percentage reflectance to the blue filter (450nm) using a sample of $BaSO_4$ as a reference (R_z=100).

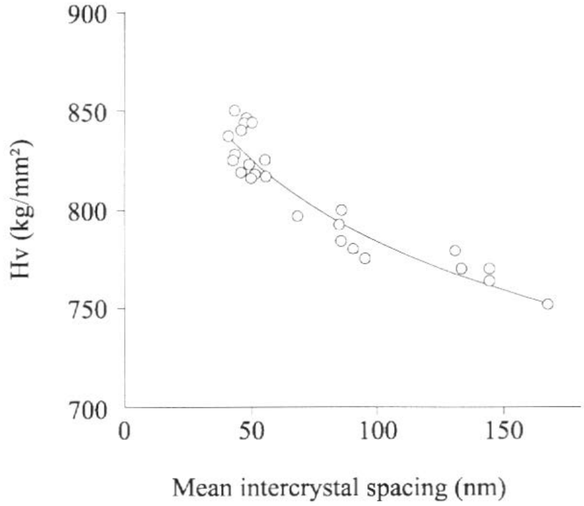


Figure 17. *Relationship between Vickers microhardness and mean intercrystal spacing in a gahnite devitrifying glaze.*

iv) Properties of the residual glassy phase

As a crystalline glaze is a composite material in which a glassy phase that remains after crystallization bonds the devitrified crystals, its properties must be influenced by both the properties of the crystals that have formed and those of the residual glassy phase.

The properties of the glassy phase that remains after crystallization must therefore influence the values of the different glaze properties, such as: opacity; gloss and surface texture; toughness, abrasion resistance and resistance to chemical attack [3].

a) Opacity

This property is hardly affected by the refractive index of the residual glassy phase since, as already mentioned above, this glaze property generally varies within very narrow bounds (1.5-1.6). However, in the few cases in which the refractive index of the crystalline phase of the glaze lay below that of the residual glassy phase, glaze opacity was enhanced by adding some lead to the starting composition, which raised the refractive index of this glassy phase, increasing the difference with that of the crystalline phase.

b) Surface texture (roughness and open pores) and gloss

In firing glazed tile, the viscosity of the residual glassy phase (or rather, of the whole made up of crystals and glassy phase) must be appropriate, both within the carbonate breakdown temperature interval, so as to avoid the defect known as pinholing, and within the peak firing temperature interval, to achieve proper maturing of the glaze (absence of open pores), thus producing a smooth, and glossy surface if so desired. The viscosity of the residual glassy phase can be modified by varying the proportion of certain starting frit oxides, which by not intervening in the crystallization process, remain fully contained in the glassy phase, changing its composition and hence its viscosity.

c) Toughness and abrasion resistance

It has been observed [28] that these two properties are directly related. Consequently, it will be convenient to obtain crystalline glazes of high toughness in glazed tile, in which high abrasion resistance is sought.

In glass-ceramics, it has been shown that when the coefficient of thermal expansion of the crystals exceeds that of the residual glassy phase, intergranular fracture is encouraged and the material's toughness is enhanced. Thus, these conclusions should be borne in mind if improved wear resistance of a crystalline glaze is targeted.

d) Resistance to chemical attack

This property depends almost exclusively upon the composition of the residual glassy phase. In order to obtain maximum resistance to chemical attack, it is advisable for the remaining glassy phase not to contain excessively high concentrations of alkali metal oxides such as Na_2O or K_2O [3].

v) Addition of crystalline aggregates that remain unmelted in firing

This type of heterogeneous glaze has already been mentioned above. As indicated, such glaze is typically employed for coating floor tiles, since adding particles that do not melt completely in firing enhances the mechanical properties of the glazed tile, particularly its resistance to wear by friction and scratch hardness, as a result of the high hardness of the particles that come to form part of the glaze (zircon, corundum, quartz, etc.). The presence of such particles, however, does involve a drawback, namely, an increase in the inner porosity of the glaze layer (Fig. 4).

5. IMPORTANCE OF AN APPROPRIATE MATCH OF THE DEVITRIFICATION AND SINTERING PROCESSES OF THE FRIT PARTICLES IN THE HEATING STEP OF THE FIRING CYCLE.

During the heating step of the firing cycle for glazed tile, the initially stiff frit particles soften and then partially fuse. Consequently, the consolidated layer that forms from these particles and other additives (glaze composition), which is initially quite porous, gradually densifies by a laminar flow mechanism, in which highly viscous liquid phase arises, stemming from frit fusion (vitrification process). As the frit particles soften, a simultaneous devitrification process (nucleation and crystal growth) occurs in the glaze layer. Both processes (vitrification and devitrification) together should yield a compact layer of crystalline glaze, with very low sealed porosity, on reaching the peak firing temperature interval.

The following will attempt to set out how the devitrification process impacts the development of the overall sintering process, which yields the crystalline glaze. This will be done by comparing how the overall sintering process develops on using frits that do not devitrify during heat treatment, with how this process evolves with frits that devitrify one or more crystalline phases. This comparative study will be made by using the representative diagram of temperature (T) versus the linear shrinkage (LS) that a test specimen, formed from frit particles (by casting), undergoes on subjecting it to heat treatment in a hot-stage microscope.

i) Sintering of test specimens formed from frit particles that do not devitrify in firing

Fig. 18 shows how the linear shrinkage of a test specimen, made using a non-devitrifying frit (F1), evolves with temperature. The resulting curve exhibits the characteristic sigmoid shape of materials having an exclusively glassy nature.

For values of $LS<0.15$, increasing temperature raises test specimen shrinkage and sintering rate (curve slope) as porosity decreases owing to the progressive softening and partial fusion of the frit particles, which cause the pores to gradually close.

For values of $LS>0.15$, shrinkage continues as temperature rises but the shrinkage rate decreases little by little, until finally cancelling out, when densification peaks. The behaviour of the material during this second step is the result of two concurring, opposite effects. On the one hand, the capillary pressure that arises in the pores or existing interparticle voids, as a result of the presence of a highly viscous liquid phase that partially fills these voids, acts as a driving force encouraging densification of the material. On the other hand, the expansion of occluded gases within the pores, or gases that are released as a result of the breakdown of certain oxides contained in the frit when the temperature is raised, tend to increase the size of the trapped bubbles or raise their number, producing higher sealed porosity, and making the test specimen expand.

Finally, beyond the temperature at which densification peaks, there is only a gradual swelling of the test specimen (LS falls), owing to the effect of the second phenomenon mentioned above, since the phenomenon that produced shrinkage has virtually ceased. It can be inferred from the plot in Fig. 18, that in the case of the studied frit (F-1), the glaze will mature well in the temperature interval 750-800°C.

ii) Sintering of test specimens formed from frit particles that devitrify in firing

When a devitrification process arises concurrently with the process that produces densification on heating the test specimen, as set out above, the crystalline phases that form and grow in the frit particles produce a structure that is capable of slowing down and even partially or wholly detaining the sintering process, in the latter case impeding the completion of the sintering process in a firing cycle of the kind typically employed in tile manufacture. To illustrate this, three example specimens will be used, corresponding to three frits that behave differently during heat treatment.

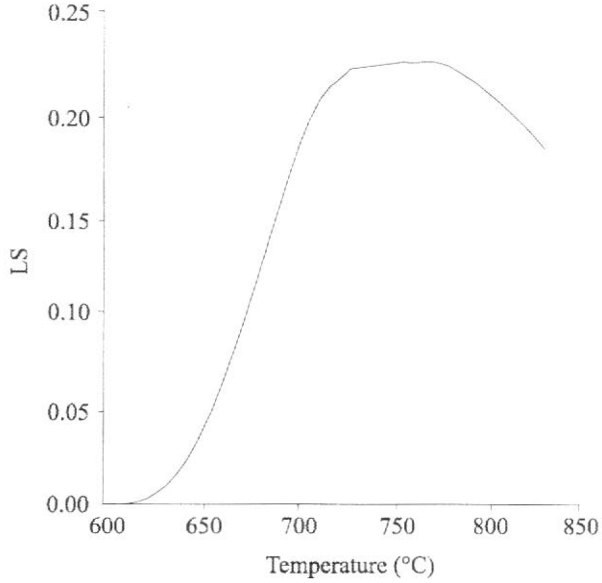


Figure 18. LS-T curve of frit F-1

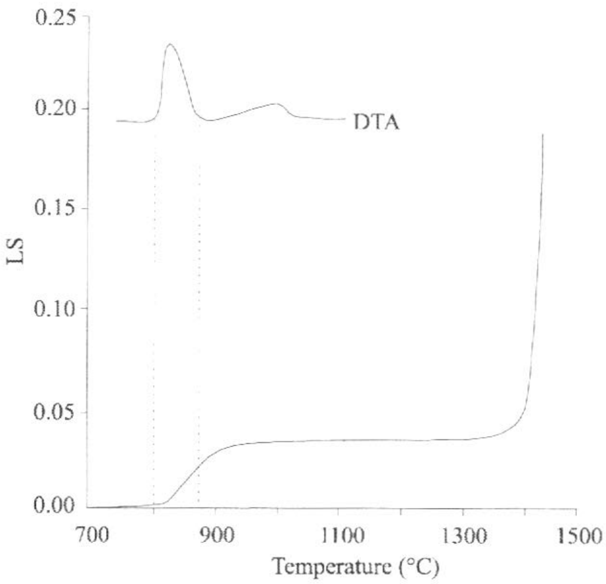


Figure 19. *LS-T curve and DTA diagram of frit F-2*

Fig. 19 depicts the LS-T diagram corresponding to a test specimen made of frit (F2) particles, which starts devitrifying a considerable proportion of crystals at a relatively low temperature, when the particle grouping making up this specimen is not as yet very compact (shrinkage has hardly been initiated). It can be observed, that at the outset the densification rate grows as described previously, up to 850°C. Beyond this temperature the densification rate decreases, until cancelling out at round 950°C, because the arising crystalline phases have formed a structure that ends up arresting shrinkage, mainly as a result of frit particle deformation. Above 1380°C, shrinkage starts again, as the progressive dissolution of previously formed crystals reduces the space that they occupy, and raises the existing liquid-phase proportion, reaching a high sintering rate. This last curve segment is similar in shape to the one corresponding to the plot shown in Fig. 18. In order to verify whether the momentary freezing of the sintering process was due to crystalline-phase formation, the plot representing linear shrinkage of the test specimen versus temperature was superimposed in Fig. 19 on the DTA diagram corresponding to a sample of the same frit, with an analogous particle-size distribution, making the abscissa axis scale (temperature) coincide. It can be observed that the exothermic peak, representing crystallization, initiates at 800°C and reaches its maximum at 850°C, the temperature at which, as indicated, the sintering process starts slowing down. Using this frit, temperatures exceeding 1400°C would be needed to obtain discrete glaze maturing, according to the plot in Fig. 19.

Figs. 20 and 21 show plots of the LS-T curves, and the respective DTA diagrams corresponding to two other different frits, referenced F-3 and F-4 respectively, in which the crystallization interval appears with quite different linear shrinkage values, even though both frits start sintering at virtually the same temperature (around 750°C), as a result of having similar viscosities in the molten state.

In frit F-3 (Fig. 20), devitrification starts at around 700°C (DTA diagram), even before the test specimen starts shrinking, which commences at 750°C and slowly increases up to 920°C. From this temperature on, shrinkage and densification rates rise rapidly, and maturing takes place at 1100-1120°C. In view of the linear shrinkage percentage reached at peak densification, it would appear that an important part of the crystalline phase that has formed dissolves within the residual glassy phase (with low viscosity) above 950°C.

In frit F-4 (Fig. 21), devitrification starts at around 775°C (DTA diagram), a temperature at which shrinkage of around 0.02 has been reached. At 825°C, shrinkage starts slowing down, almost stopping at about 870°C, when the test specimen has practically achieved peak densification. The maturing temperature needed for producing a considerable proportion of crystalline phase in the glaze would lie at around 900°C, i.e. about 200°C lower than in frit F-3, even though the optimum maturing interval would practically range from 900 to 1050°C.

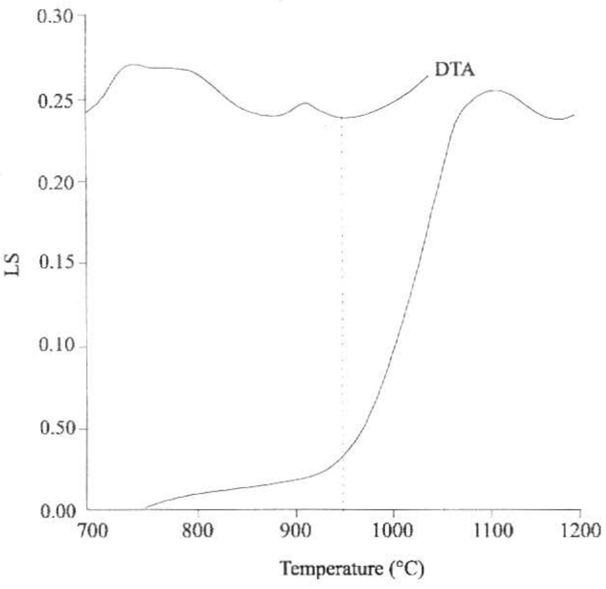


Figure 20. *LS-T curve of frit DTA diagram of frit F-3*

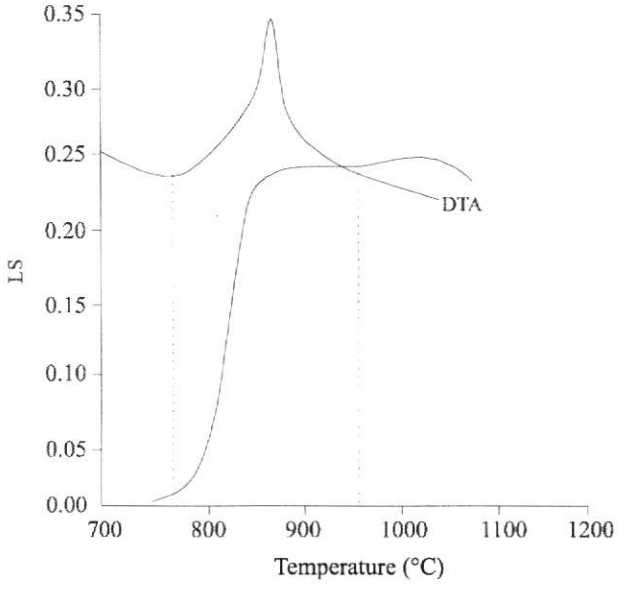


Figure 21. *LS-T curve and DTA diagram of frit F-4*

The foregoing thus allows inferring that devitrification always impacts the evolution of the sintering process of a glaze with a vitreous-crystalline nature to a greater or lesser extent. Therefore, to obtain a quality glaze, it is advisable to select a suitable frit composition so that: a) the consolidated layer will start sintering at the right moment; b) there will be enough open porosity to allow any gases that the body may release in firing (due to oxidation of organic matter or carbonate breakdown) to be outgassed through the glaze layer at temperatures ranging from 800 to 950°C (in single firing); c) the sought crystal percentage (with the right size) will devitrify; d) appropriate maturing will take place at the standard peak firing temperature interval used (1110-1150°C).

In the examples considered, frits F-1 (Fig. 18) and F-4 (Fig. 21) could be used for twice firing, since both would produce pinholing in the glaze, if they were to be used in porous single-fired wall tile manufacture. However, frit F-3 (Fig. 20) could be used for single firing, if residual glassy-phase viscosity at 1100°C were sufficiently low to fill the porous structure resulting from devitrification, since the consolidated layer would conserve a highly porous structure ($LS<0.05$) in the outgassing temperature interval (800-950°C). Frit F-2 (Fig. 19) could not be used to obtain a good glaze coating for wall or floor tile, because it would be quite porous at 1110-1150°C, and have a very matt and perhaps rough glaze surface, with open pores, as a result of not having matured at these temperatures.

Of the last three studied frits, frit F-4 most approaches what would be desirable behaviour in a frit to be used for producing crystalline glazes, if only a suitable match of the devitrification-densification processes is considered. In fact, as Fig. 21 shows, when devitrification starts, densification has almost ended. This means that the frit particles have softened and deformed, fitting together better, and reducing intergranular voids. Highly viscous liquid phase has thus already segregated when crystals start forming and growing. Consequently, on reaching maximum shrinkage (almost flat stretch of the curve), the crystals that have formed are surrounded by a residual glassy phase of low effective viscosity, forming the matrix that will contain them. When the whole is cooled, a smooth glaze coating is obtained, which is more or less glossy depending upon the viscosity of the residual glassy phase at peak firing temperature in the firing cycle used.

The use of frit F-4 in porous, single-fired wall tile manufacture could give rise to pinholing owing to its low sealing temperature, which lies at round 840°C (Fig. 21). To suppress such pinholing, it would be necessary to slightly modify its composition in order to shift the LS-T curve towards higher temperatures, delaying the sintering start or making the curve slope smaller (or both actions together), so that shrinkage at 950°C would be round 0.10-0.12 (instead of 0.23), which would assure holding a sufficiently open or porous structure in the glaze layer, thus allowing the gases released by the body to be outgassed through the glaze layer.

6. CONVENIENCE OF HAVING A REPRESENTATIVE KINETIC MODEL OF CRYSTALLIZATION

In order to suitably develop controlled devitrification, the thermodynamics and kinetics of the process must be known. The former allows determining within which bounds the phenomenon may arise, and the latter the rate at which it will occur.

Whether it will be thermodynamically possible for the phenomenon to take place (i.e. crystalline phases that may devitrify, and maximum obtainable crystalline-phase proportion), within the selected temperature interval, may be derived from the corresponding phase-equilibrium diagrams. Bearing in mind that ceramic frits are made up of several constituents, the previously required data are only obtainable, in an approximate fashion, from ternary or quaternary diagrams (should such exist), of the major oxide proportions found in the starting frit. Once it has been established that a given crystalline phase can devitrify, in order to obtain fuller and more precise data, the equilibrium of the whole oxide system involved must be studied, at the temperature and compositional interval within which devitrification is to occur.

It is indispensable to know the rate at which crystalline phases can devitrify of frits based on a certain oxide system, as well as their dependence on composition and temperature, in order to anticipate the degree of crystallization that will be attained on using these frits when they undergo a certain heat-treatment cycle. Starting out with a thermodynamically suitable composition for obtaining a given crystalline phase, when equilibrium is reached, is of itself not enough. It is necessary for the crystallization process to unfold at an appropriate rate so that during the firing cycle, throughout which temperature and the frit dwell times in the kiln vary, the necessary crystalline phase proportion will devitrify to obtain the sought effect. This must all take place without jeopardising the proper development of the almost simultaneously occurring sintering process, as set out in Section 5.

In order to possess information on the degree of crystallization advance with time and temperature, it is necessary to carry out a set of experiments, using the selected frit, at the same time modifying the value of both operating variables by testing constant-rate heating cycles, using different rates in each cycle. This should be repeated with other frits whose composition is quite similar to, though differing slightly from that of the standard or reference frit, in order to study the influence of frit composition on the degree of crystallization advance. The resulting data allow empirically predicting the final degree of crystallization which will be obtained, in an approximate fashion, on subjecting a frit like the studied ones to a given firing schedule.

Thus, if the experimental data could be expressed in one or more equations that relate the degree of crystallization to temperature and dwell time of a frit made up of a certain oxide system, furthermore keeping in mind the influence of this frit composition, it would afford much greater flexibility in calculating the degree of crystallization that could be expected under different operating conditions.

On analogy with a chemical system, the devitrification rate (or crystallization rate) must, in the main depend upon the composition (oxide system and oxide proportions contained in the frit) and operating temperature, without excluding the possible influence of any other variable, taking into account the fact that devitrification is a heterogeneous transformation, which will be effected, in practice, using a bed of small frit particles. However, the kinetic model that represents the crystallization rate must account for the mechanism through which this arises, and the controlling process step or steps involved (incorporation at the crystal-glass interface of the corresponding structural units, their diffusion through the glassy phase, reaction of glassy-phase constituents with crystalline phases or intermediate solid solutions, etc.). Bearing in mind that systems are involved in which the devitrifying crystalline phases (intermediate or final) have a composition that differs from that of the starting frit, mass transfer through the residual glassy phase or the crystals that form (within the frit particles) may be crystallization-rate controlling [18].

It would therefore be convenient to put forward a kinetic model, which was, to start with, as simple as possible, as long as it was sufficiently representative, yielding an equation of the form:

crystallization rate = f(temperature, composition)

Subsequently, as a consolidated frit layer on a ceramic body behaves as an independent physico-chemical system when it undergoes heat treatment in a kiln, the mass conservation equation can be applied, since an intermittent reaction (or transformation) system is involved, with a view to obtaining a differential equation that will relate the degree of arising crystallization advance to temperature and dwell (or firing) time of this layer. Integrating this differential equation, by means of a suitable method, will enable predicting the variation in the degree of crystallization with time and temperature, and hence throughout a known firing cycle, for the studied frit, if the values of the different parameters of this equation have been determined experimentally beforehand.

The following sections set out how the data is obtained, which will allow proposing and verifying the effectiveness of a kinetic model representing crystalline phase devitrification of a given frit. The method involved will then be applied, as an example, to a simple oxide system that devitrifies one sole crystalline phase, to make the train of reasoning easier to follow.

7. NATURE OF THE DEVITRIFYING CRYSTALLINE PHASES AND SEQUENCE OF FORMATION

To enable a kinetic model to be put forward, which will allow deriving a representative equation or set of equations of the devitrification rate, it is first of all necessary to know the nature of the devitrifying crystalline phase or phases and the order in which they appear and disappear (on turning into others or because they dissolve in the residual glassy phase), when there are several crystalline phases.

i) Nature of the devitrifying crystalline phases

In order to determine the nature of the crystalline phases that devitrify during heat treatment of a frit, the following steps were taken. Test specimens were formed by casting from a frit with a previously chosen particle-size distribution.

These test specimens underwent heat treatment at a constant heating rate up to different temperatures, within a preset interval, which typically lay in the range 750-1200°C. On reaching the set temperature, the frits were quenched to freeze the devitrification process.

X-ray diffraction (XRD) was used to determine the nature of the existing crystalline phases in the resulting test specimens, which was morphologically confirmed by observation using scanning electron microscopy (SEM) together with energy-dispersive X-ray analysis (EDX).

The XRD diffractograms depicted in Fig. 12 may serve as an example. They belong to different test specimens, formed using particles of a frit of the kind that is commonly employed for producing glossy, white zirconium glazes. These specimens were heat treated at a heating rate of 5°C/min, up to different temperatures. The diffractograms permit the identification of the crystalline phases arising in each specimen. On the other hand, Fig. 22 shows a photograph of the cross-sectional area of a test specimen formed using particles of the same frit, treated at 900°C for 320 min. In this photograph several areas have been highlighted to better appreciate the crystalline phases that formed, whose nature was identified by EDX, confirming the XRD outcomes. The identified crystalline structures were: tetragonal zirconia, monoclinic zirconia, zircon and diopside. However, the frits that are available in the market for producing glossy, white, zirconium glazes contain what is perhaps one of the most complicated oxide systems, in respect of the devitrifying crystalline phases.

The frits made up of other oxides, such as the ones that we are working with, only tend to devitrify one or two crystalline phases, of which one is usually a precursor of the other. Thus, in systems just comprising $MgO-SiO_2-CaO$, only diopside crystallizes $MgCa(SiO_3)_2$ [30]. If they also contain ZnO, petedunite may crystallize $CaZn(SiO_3)_2$ as well. In $SiO_2-Al_2O_3-ZnO$ systems, gahnite has been detected (Al_2O_4Zn), and sometimes a β-quartz crystalline structure, together with cristobalite and α-quartz [31]. On using $Mg_2Al_4Si_{11}O_{30}$ compositional systems, α-cordierite and β-quartz formations were detected [32].

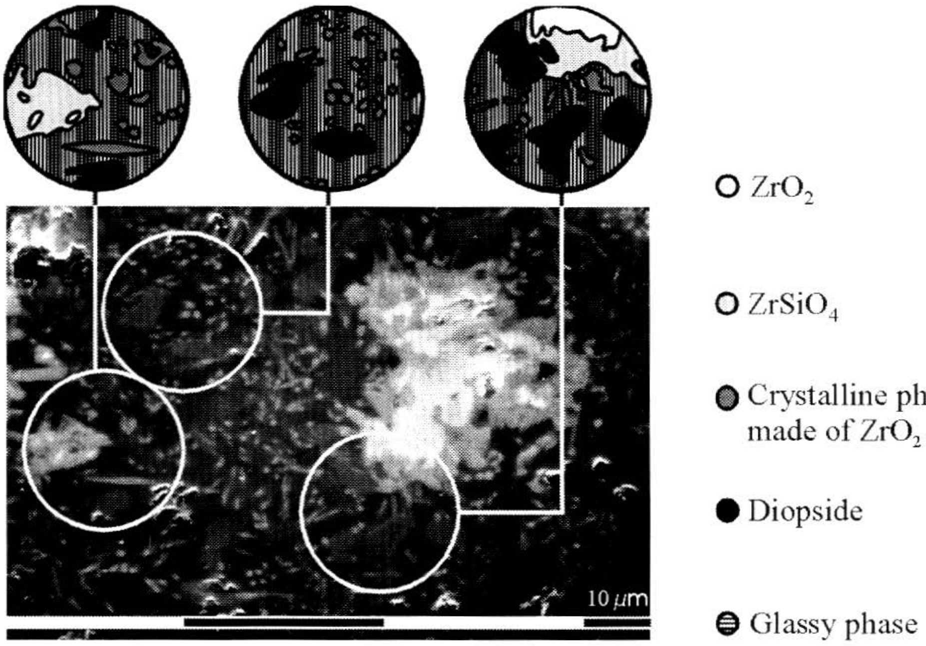


Figure 22. *Nature of the devitrifying crystalline phases in a zirconium frit.*

A very important point that deserves highlighting is the fact that in crystalline glazes, which are used for coating ceramic floor and wall tile, the crystalline phases that are really of interest are the ones that survive at the standard peak firing temperatures used in glazed tile manufacture (1100-1150°C), since these are the phases that will be found in the resulting tile glazes, thus providing such glazes with their aesthetic or technical properties. As may be observed in Fig. 12, in the case of the zirconium frit to which we have been referring, at temperatures above 1100°C, only zircon and some diopside remain. In the other three oxide systems mentioned, the only crystalline phases that have been observed to survive above 1100°C are diopside [30], gahnite [31] and cordierite [32] respectively.

ii) Sequence in which crystalline phases arise

The operating method that was proposed in the previous section for detecting the devitrifying crystalline phases can provide sufficient data to determine whether these will arise sequentially or in parallel, when several devitrify at the same time. To do so, the data must be plotted in the form "number of counts of the maximum intensity peak of each crystalline phase" versus "temperature". Comparing the shape of the resulting curves with the ones that are obtained for parallel or consecutive irreversible chemical reactions can provide a qualitative orientation with regard to the set of transformations that occur in the crystallization system being studied, and the order in which the transformations take place.

In $Mg_2Al_4Si_{11}O_{30}$ compositional systems, a metastable solid solution has been observed to form first, with a β-quartz crystalline structure, having the same composition as the starting frit or glass. This solid solution, as a result of the exsolution of part of the SiO_2 that it bears, is transformed into cordierite ($Mg_2Al_4Si_5O_{18}$), which is the sole crystalline phase left at 1150°C [32].

In certain frits made up of the oxide system SiO_2-Al_2O_3-ZnO, the formation of a solid solution with a β-quartz structure has been observed (Fig. 23), which then appears to yield gahnite. Moreover, at slightly higher temperatures, an α-quartz structure forms, which would appear to be a cristobalite precursor. In other frits based on the same system, with a slightly different composition, only gahnite was observed to form.

Finally, in the oxide system involved in the industrial zirconium frit studied (Fig. 11), petedunite forms (if there is Zn) as well as diopside, arising parallel to the sequential crystallization of tetragonal zirconia, monoclinic zirconia, and zircon, which takes place in this order.

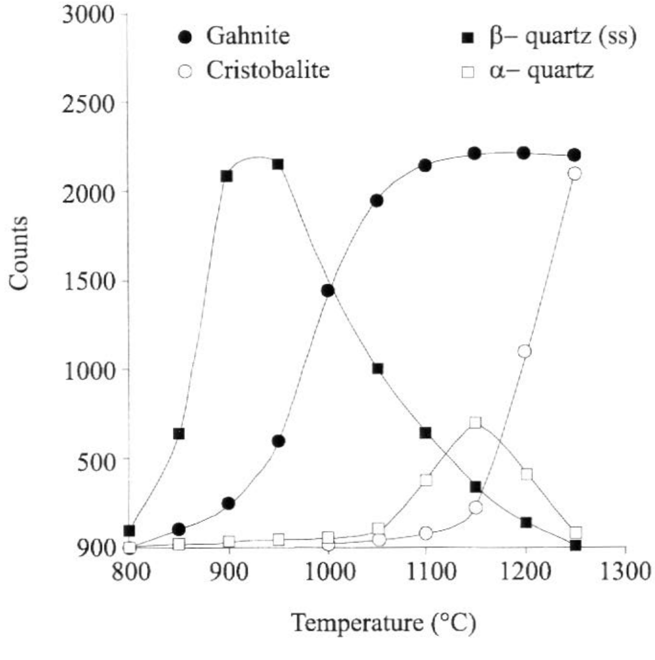


Figure 23. *Variation of the number of counts of the maximum intensity peak with temperature (system SiO_2-Al_2O_3-ZnO with TiO_2).*

iii) Using the experimental data to derive a kinetic model of crystallization

It is clear, that the fewer the number of devitrifying crystalline phases, the simpler will the kinetic model be, which is to be used in attempting to reproduce the behaviour of the system. The simplest case is that of systems in which just a single crystalline phase arises directly from the glassy phase, such as in the ones made up of MgO-SiO_2-CaO, which only devitrify diopside [30]. This simple system will be used in Section 8 to illustrate the operating method. In this system, both the starting assumptions and the interpretation of the results are much simpler than in a system in which several crystalline phases devitrify simultaneously, where, in order to interpret the results, certain simplifications are needed in order not to excessively complicate the resulting kinetic model.

It should be borne in mind that in the case of crystalline glazes, which are to be used in glazed tile manufacture, the point at issue is the prediction of the degree of crystallization, which the surviving crystalline phase or phases will achieve at 1110-1150°C, since they will produce the sought-after (aesthetic or mechanical) effect in the glaze. Thus, when quite a complicated system is involved, without wishing to lessen the importance of any intent aimed at trying to establish what may actually be occurring and subsequently attempting to interpret this in the most accurate possible way, our objective, if such an interpretation should threaten to become too complicated, must be to try and solve the problem, perhaps less accurately, but more simply and effectively, so as to derive one or more mathematical equations that will allow reproducing the degree of crystallization of the major, experimentally observed, arising crystalline phases, with time and temperature.

8. PROPOSED KINETIC MODEL AND DERIVATION OF A CORRELATION BETWEEN THE DEGREE OF CRYSTALLINITY, HEAT-TREATMENT TIME AND TEMPERATURE

The shape and position of the curves found on plotting the "Number of counts of the maximum intensity peak" corresponding to the crystalline phase or phases that devitrify versus "time" (at constant temperature), or versus "temperature" (at constant-rate heating), yield data on the complexity of the crystallization process. The less complicated the crystallization process is, the simpler will the kinetic model be, which will need to be tested in order to attempt to interpret the experimental data.

The methodology to be followed is set out below for obtaining a mathematical equation that will relate the amount of devitrifying crystalline phase, heat-treatment time and temperature.

To illustrate the method, the oxide system MgO-SiO_2-CaO will be used, which just devitrifies a single crystalline phase (diopside), so as to obtain a simple kinetic model that will yield a relatively simple algorithm, and make the discussion easier.

i) Experimental phase

Using test specimens formed by casting, with the set sized particles of the selected frit, several series of experiments are required at constant temperature and constant rate of heating.

The findings in both cases are then plotted in the form: "Number of counts of the maximum intensity peak" (XRD), or any other magnitude that represents the amount of arising crystalline phase, versus "treatment time" or dwell time of the test specimen (in the series carried out at constant temperature), or versus "temperature" (in the series performed at a constant rate of heating).

As an example, Figs. 24 and 25 depict the plots found on applying the method described to test specimens formed from frit particles based on the oxide system MgO-SiO_2-CaO, which devitrifies diopside [30].

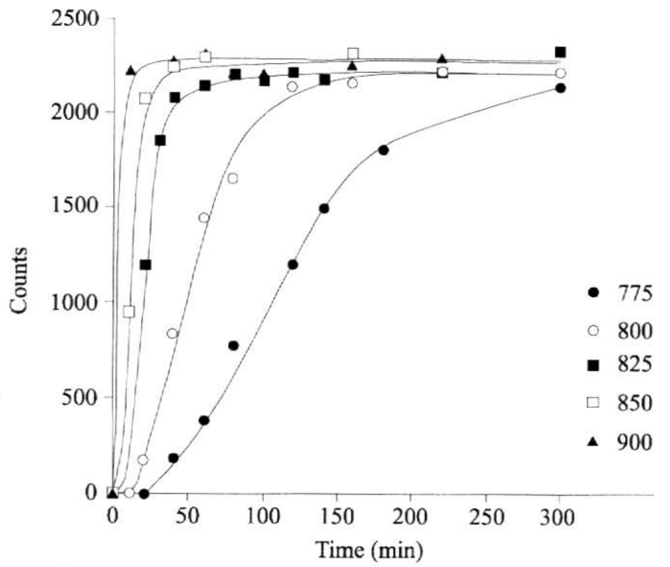


Figure 24. *Variation of the number of counts of the diopside maximum intensity peak with dwell time.*

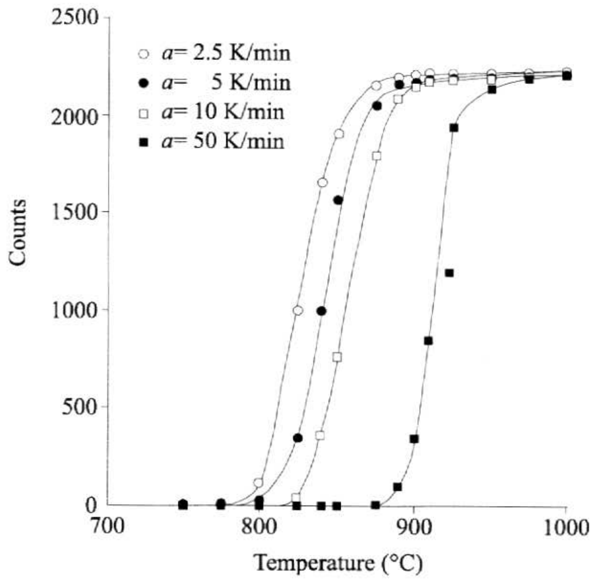


Figure 25. *Variation of the number of counts of the diopside maximum intensity peak with temperature.*

ii) Proposed kinetic model

In view of the shape of the curves obtained, a kinetic model must be proposed, which is based on logical assumptions. In the case of the oxide system MgO-SiO_2-CaO, several different models were tested, which yielded good results. Of these, one has been chosen, based upon the assumption that the crystallization rate is controlled (as it is the slowest step) by diffusion of the structural unit $MgCa(SiO_3)_2$, from within the glassy phase to the crystal-glass interface. The formation of a structural unit (A_u) within the glass and its inclusion in the crystal, once it has reached the crystal-glass interface, are steps that unfold more quickly than the mentioned diffusion.

In accordance with this assumption, the crystallization rate, in respect of a single crystal, may be expressed by an equation of the form:

$$r_u = S_c \cdot \psi_u = S_c \frac{D_{ef}}{\delta_{ef}}\left(c_u^v - c_u^{ve}\right) \qquad \frac{molA_u}{min \cdot m^2} \tag{1}$$

where:

S_c = Crystal surface area (crystal-glass interface area)(m^2)
Ψ_u = Mass flow density (mol A_u/min.m^2)
D_{ef} = Effective diffusivity of A_u through the glassy phase (m^2/min)
δ_{ef} = Thickness of the hypothetical laminar film (m)
c_v^u = Mean concentration of A_u within the glassy phase (mol A_u/m^3)
c_u^{ve} = Concentration of A_u in the glassy phase at the glass-crystal interface (mol A_u/m^3)
r_u = Crystallization rate, in respect of a single crystal (mol A_u/min)

Making the following assumptions:

a) r_u has the same value, at each instant, for all the crystals present, which therefore grow uniformly.

b) The number of growth nuclei or active centres (n*) is constant, as nucleation has been observed to be heterogeneous, and take place at the surface, in this system.

c) S_c is proportional to the power 2/3 of the crystal volume.

d) Test specimen volume hardly varies during devitrification (see Figs. 19, 20 and 21).

and applying the mass conservation equation to the whole test specimen, relative to the structural unit A_u contained in the glassy phase of the specimen, during its heat treatment, keeping in mind that a closed (intermittent) system is involved, and assuming that the number of counts (α_c) measured by XRD is proportional to the number of moles in the structural unit that has crystallized, which thus yields the equation:

$$\frac{d\alpha_c}{dt} = K \cdot \alpha_c^{2/3}\left[\alpha_c^e - \alpha_c\right] \tag{2}$$

where:

α_c = number of counts that correspond to the diopside maximum intensity peak.
α_c^o = number of counts that correspond to the diopside maximum amount obtainable at each temperature, which will correspond to crystallization equilibrium for this glass-crystal system, at each temperature.
t = time during which the test specimen undergoes heat treatment.
K = constant that includes several magnitudes and depends upon temperature.

iii) Calculation of K and α_c^e at each temperature

On integrating the foregoing differential equation by the Runge-Kutta method of order 4, using computational iteration, different values of K are tested, as the approximate value of α_c^e is known, which lies close to the experimentally obtained maximum value, in each series of constant temperature experiments. Suitable values of K and α_c^e are found when the integrated curve coincides with the experimental points (Fig. 26). These trials are repeated for each isothermal series of experiments run, obtaining the corresponding value of K and α_c^e at each of the tested temperatures.

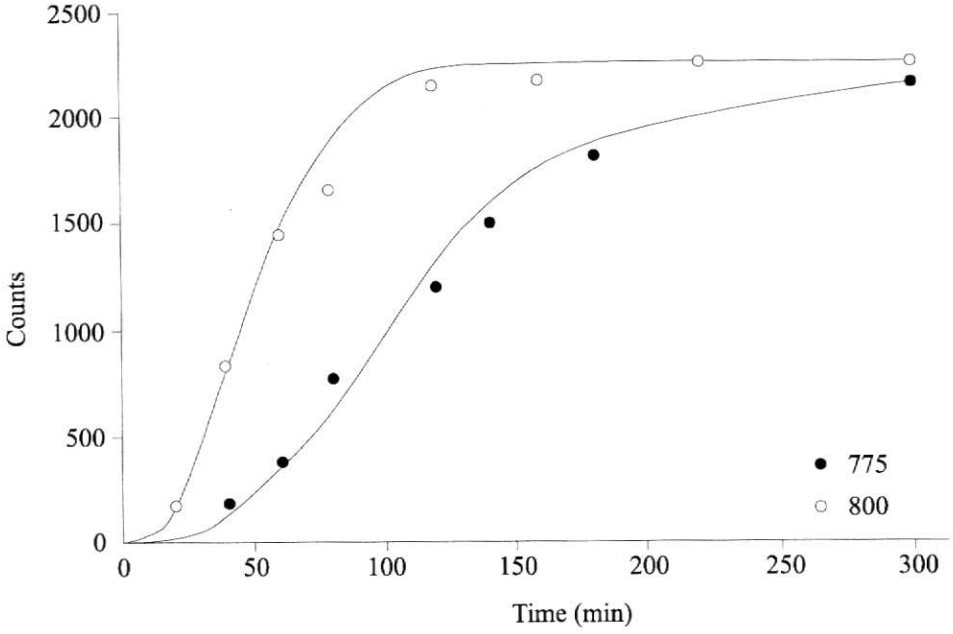


Figure 26. Fit of the proposed model to the isothermal experiments.

The values of K are then fitted to an Arrhenius-type exponential equation:

$$K = A\exp\left[-\frac{E}{R\,T}\right] \tag{3}$$

If a satisfactory fit is found, the proposed model is likely to be suitable, since it has been adapted to the outcomes of the isothermal series of experiments carried out at different temperatures. The values of parameters A and E can then be calculated.

It should also be attempted to obtain a correlation between α_c^e and T, which can be introduced into Equation (2).

iv) Confirmation of the effectiveness of the model. Application to the data obtained in the series of experiments at a constant rate of heating.

Equations (2) and (3) yield an equation of the form:

$$\frac{d\alpha_c}{dt} = A \cdot exp\left[-\frac{E}{R\,T}\right] \alpha_c^{2/3}\left[\alpha_c^e(T) - \alpha_c\right] \tag{4}$$

Before using this equation to predict the variation in the degree of crystallization of the crystalline phase (diopside) with temperature and time, through a firing cycle of the kind typically used in ceramic tile manufacture, its effectiveness in reproducing the outcomes of the series of experiments performed at different heating rates should be validated. In order to integrate Equation (4), variable T, which appears in this equation, must be set as a function of the test specimen's kiln dwell time (t). The relationship that exists between both variables is of the form [10]:

$$T = T_0 + a \cdot t + \Delta T \tag{5}$$

where:

T = Temperature of the test specimen (K)
T_0 = Temperature recorded by the thermocouple located inside the kiln when the test specimens are put in the kiln, at the start of each series of experiments (K).
a = Heating rate used in each series of experiments (K/min).
t = Time elapsed from placing the test specimen inside the kiln to withdrawing it.
ΔT = Mean value of the difference between test specimen surface temperature and the temperature measured by the thermocouple located inside the kiln (K). This is experimentally determined.

Equations (4) and (5) yield:

$$\frac{d\alpha_c}{dt} = A\cdot\exp\left[-\frac{E/R}{T_o + a\cdot t+\Delta T}\right]\alpha_c^{2/3}\left[\alpha_c^e(T)-\alpha_c\right] \qquad (6)$$

where A and E have been determined from the results of the isothermal series of experiments and T_0 and ΔT have been experimentally measured. With regard to $\alpha_c^e(T)$, if an equation of $\alpha_c^e=f(T)$ can be obtained, which can be substituted into Equation (6), taking into account Equation (5), so much the better. Otherwise, the maximum value of α_c^e found in isothermal testing is used.

Integrating this equation, for the values of the tested heating rates (*a*) in the nonisothermal series of experiments, at boundary conditions ($t=0$; $\alpha_c=1$), yielded the curves depicted in Fig. 27, where they are compared with experimental data [30]. The results match well, which substantiates the validity of the method proposed, and therefore also of Equation (6) for predicting how the degree of crystallization will evolve with time and temperature.

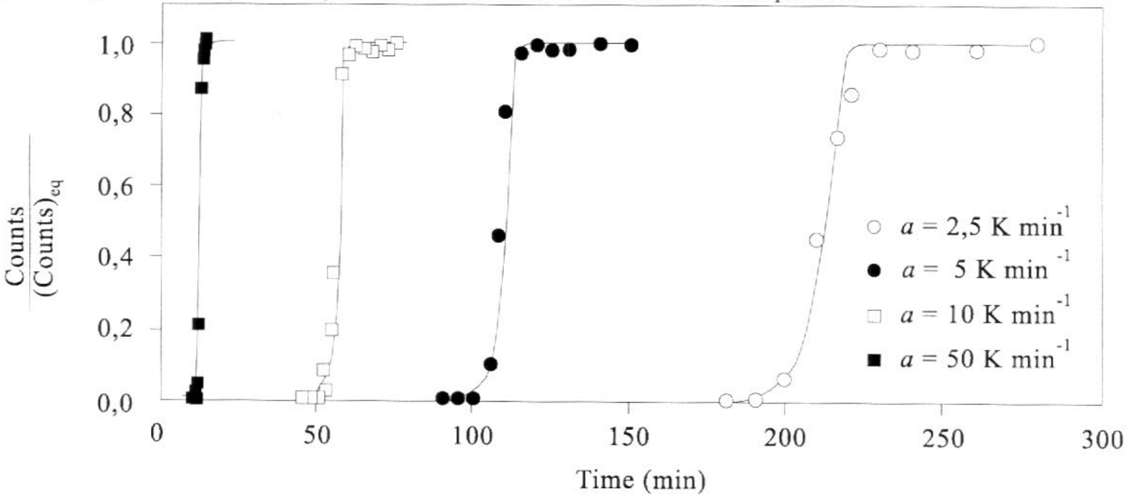


Figure 27. *Fit of the proposed model to the nonisothermal experiments.*

v) Usefulness of an equation like Equation (6) for predicting the degree of crystallization advance in firing a glaze layer (in single- and twice-firing)

As Equation (6) is applicable both to the series of experiments at constant temperature and to the series of experiments at constant-rate heating, it should serve for calculating the degree of crystallization that will arise on firing a consolidated layer of particles from the studied frit, which have the same particle-size distribution as the one used in the preliminary experimentation, where the corresponding temperature-time diagram is known of the relevant firing cycle and the experimentally derived, known values of A, E and $\alpha_c^e(T)$ are used, or the values of T_0 and ΔT of Equation (6), if these had previously been determined.

The method involves breaking down the industrial firing schedule into constant-rate-of-heating and constant temperature segments, and integrating Equation (6) through each segment, calculating the value of the number of counts (or any other representative magnitude of the amount of arising crystalline phase), at the end of the peak temperature interval of this firing cycle, that is, when the cooling step starts.

Applying this method to the frit and particle size of the example under consideration, and using the following values for parameters A and E/R [30]: $A = 2.0 \times 10^{13}$; $E/R= 41350$ (K), and rewriting Equation (6) in the form:

$$\frac{d\alpha_c}{dt} = (\alpha_c)^{2/3}\cdot(\alpha_c^e-\alpha_c)\cdot A\cdot\exp\left[\frac{E/R}{(T_0+\Delta T+a\cdot(t-t_0))}\right] \qquad (7)$$

in order to integrate the equation in each segment, T_0 and t_0 are substituted by temperature (K) and the time elapsed (min) from firing start to the beginning of the segment involved; *a* is substituted by the heating rate corresponding to this segment (zero if it is isothermal), and ΔT should be substituted, if its value is known, which must be experimentally determined. In the most unfavourable circumstances, it is possible to set $\Delta T=0$, in order to see whether it is possible to achieve the sought degree of crystallization.

Fig. 28 shows a typical industrial firing cycle used for manufacturing porous, single-fired glazed wall tile (continuous line), to which the method described was applied. This figure also depicts (bold dashed line) the curve $\alpha_c=f(t)$, found on integrating Equation (7) up to 900°C, assuming that $\alpha_c^e=2250$, which is the value of this variable at 900°C. The remainder of the curve has been built on the basis of the experimental values of α_c^e calculated at 950; 1000; 1050; 1100 and 1150°C respectively. It can be observed that at the start of segment IV of the firing cycle, much earlier than the commencement of the flat, peak-temperature stretch, the maximum "number of counts of the maximum intensity peak" of diopside has already been reached, namely $\alpha_c^e=2250$, which corresponds to a temperature of 900°C, and which has been used as a constant value in Equation (7) until t=12.5 min (time required for the kiln to reach this temperature).

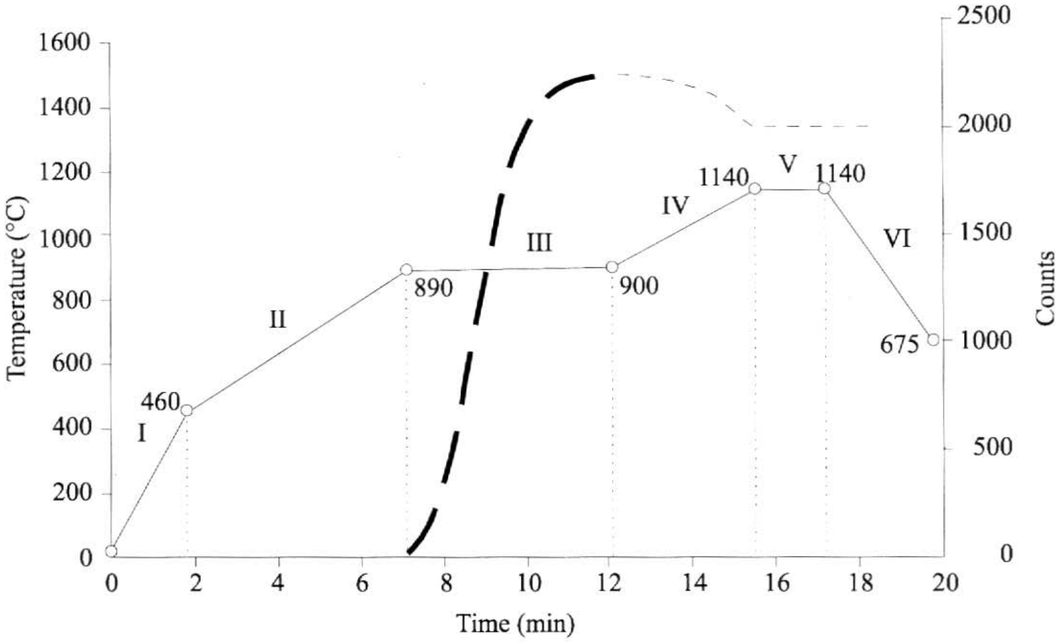


Figure 28. *rediction of the variation of frit diopside content with the industrial firing cycle it undergoes.*

The result shows that in the case of the studied frit, the maximum attainable degree of crystallization was fully reached in the tested firing cycle, even though this cycle was chosen from among the shortest schedules that are usually employed in the tile industry, in order to test the most unfavourable case. The problem, in this example, was that the crystals that formed partially dissolved in the interval 950-1140°C, thus slightly lowering their proportion in the final glaze.

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