INFLUENCE OF THE BASE GLAZE ON THE DEVITRIFICATION OF GRANULARS

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ABSTRACT

Given the lack of studies in the literature on the effect of the base glaze on the devitrification of granulars, a study was undertaken of the devitrification of a commercial frit with a high calcium content with regard to the base glaze used, granular size and firing temperature and time. According to TTT studies, wollastonite and cristobalite are the two main phases in the devitrification process of the granular and develop by a different nucleation process: heterogeneous nucleation from the interface for wollastonite, kinetically favoured by activation energies of the order of 70 KJ/mol, and homogeneous crystallisation for cristobalite, with activation energies of the order of 400 KJ/mol. Wollastonite activation depends on the type of base used and the duration of the first cooling stage, whereas cristobalite activation largely depends on granular size. By adjusting the base, granular size, peak temperature, holding time at this temperature, and duration of the first cooling stage, the proportion of devitrifying phases can be controlled, hereby modifying the gloss and mechanical strength characteristics of the resulting devitrifying granular.

1. INTRODUCTION

Granulars are widely used materials in the ceramic floor and wall tile sector as a complement to the base glazes that cover the clay body [1]. Granulars are applied dry to these glazes in such a way as to remain on the tile surface after firing, thus being the first features to undergo wear on use.

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[1] B. JACOBY, SIZED DRY GLAZES, *A Decorating Alternative*, Ceram. Bull. 70 (1991)91-93.

Granulars are frits that are dry milled by different systems, with a carefully selected particle size obtained by sieving. They are normally glassy materials, but given their special chemical composition, they exhibit a high tendency to crystallise on undergoing heat treatment, as in tile firing. Besides other functions, the appearance of these crystalline phases enables:

- Producing a protective effect against abrasion on raising the hardness and mechanical strength of the arising glass-ceramic composite made up of crystalline phases formed by devitrification and a residual glassy phase.
- Obtaining aesthetic effects as a result of the "gloss-matt" contrast between the base glaze and the granular or simply because of the characteristic shapes of the crystals that form.

With this dual objective, granulars are prepared which must meet the following and other conditions [1,2,3]: (a) the chemical composition shall be compatible with that of the base onto which it is applied and with the composition of the other accompanying glazes (screen prints, fumés, etc.); (b) the material shall be prepared with a controlled, selected particle-size in terms of particle morphology and mean size as well as in the size-distribution of in a given particle-size fraction, and (c) the particles shall exhibit a perfectly homogeneous mass to keep phase segregation or differences in behaviour from occurring during firing.

The processing variables of these materials differ from those of the wet glazes, as factors such as solubility in water of the components, or the coefficient of thermal expansion are not of fundamental importance. In contrast, other aspects such as meltability, melt viscosity or surface tension become key factors, as they are vital to achieving good compatibility with the other materials mentioned above.

2. OBJECTIVE

Numerous works can be found in the literature, in the field of gasses, glass-ceramics or glazes, in which crystallisation is studied in independent materials, either in bulk or in a thin layer. However, taking into consideration the points indicated in the introduction, granulars are always associated with a base glaze and therefore a study of granulars, regardless of their nature, needs to include the possible influence this glaze.

The present work was therefore undertaken to study the devitrification of a commercial frit with a high calcium content with regard, not just to classic parameters such as firing cycle and particle size, but also to the nature of the base onto which the granular is applied.

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[1] B. Jacoby, Sized Dry Glazes, *A Decorating Alternative*, Ceram. Bull. 70 (1991)91-93.

[2] B. Burzacchini, *Technical Developments in Ceramic Tile Glazes and Related Applications*, Ceram. Bull, 70 (1991) 394-403.

[3] F. Lamilla, E. Wagg, *Decoration Techniques for Single-Fire, Fast-Fire Tile Production*, Ceram. Eng. Sci. Proc., 16(1995) 80-81.

This required first characterising the materials involved in the study by hot-stage microscopy and TTT tests (transformation-time-temperature) to establish the compatibility between the granular and the different bases, and identify the arising crystalline phases in subsequent tests. Having determined these features, kinetic studies were conducted to determine the activation energies of the various crystalline phases identified, according to the base used, in order to establish which of these phases are most likely to be present after heat treatment with a firing cycle like the ones commonly used in industry.

3. CHARACTERISATION OF THE MATERIALS AND TTT DIAGRAM.

The granular and bases used were characterised by different techniques. The resulting data are discussed below.

3.1. CHEMICAL COMPOSITION AND CRYSTALLINE PHASES

Table I presents the chemical composition of the granular. A material rich in silica and calcium is involved, with an important presence of zirconium and RO lattice modifiers, so that in principle, it could be expected to exhibit a strong tendency to devitrify wollastonite.

Oxide	%
SiO_2	47 – 48
CaO	22 – 23
B_2O_3	3-4
ZrO_2	8-9
Al_2O_3	0-1
RO	12-13
R_2O	4-5

Table 1. *Chemical composition of the granular.*

The ceramic composition of the three bases used was as follows:

- Glossy base: containing over 90% of a zirconium silicate devitrifying frit. The rest was made up of the standard additives (suspending agents, binders, deflocculants, etc.)
- Semi-glossy base: mainly containing (>50%) a zirconium silicate devitrifying frit. The rest was made up of non-plastic materials such as alumina and quartz, and the standard additives.
- Matt base: mainly containing (>60%) of a frit with a high tendency to devitrify principally celsian and willemite. The second major component (>20%) was a sodium-potassium feldspar, the rest were standard additives.

The behaviour of the bases in a firing cycle like the one depicted in Figure 1 shows, on subjecting the samples to X-ray diffraction (XRD), the presence of the following crystalline phases:

- Glossy base: zirconium silicate devitrified with medium intensity peaks.
- Semi-glossy base: zirconium silicate devitrified in a similar proportion to the glossy base and more intense peaks were detected of the quartz added to the mill charge, which did not solubilise.
- Matt base: mainly celsian ($BaAl_2Si_2O_8$) devitrification was detected and a minor proportion of willemite (Zn_2SiO_4).

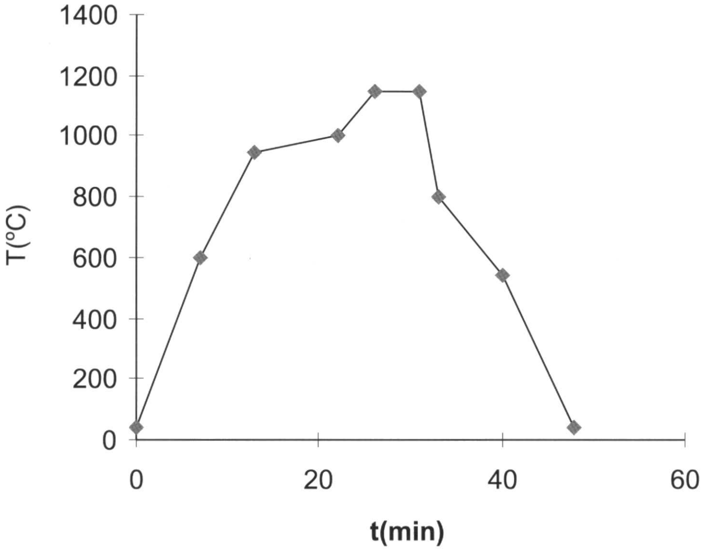

Figure 1. *Standard firing cycle.*

3.2. VARIATION OF GRANULAR AND BASE MELT VISCOSITY WITH TEMPERATURE HOT-STAGE MICROSCOPY

With a view to determining the behaviour of the granular and the bases with temperature, these materials were studied by hot-stage microscopy. Pressed test specimens of the various samples underwent progressive heating from ambient temperature up to 1350°C, measuring specimen height shrinkage and contact angle every 5°C, as well as the variations in size and shape, establishing characteristics such as sintering, softening, sphering and semi-sphering temperature.

The results obtained with the four materials are presented in Figure 2, in which the glossy base is observed to be the most meltable of the three used, reaching the semi-sphering point at 1150°C. The semi-glossy base exhibits a parallel curve to that the glossy base, with a shifted towards higher temperatures, so that semi-sphering takes place at 1250°C. With regard to the matt base, although it presents the highest sintering temperature, its melt viscosity drops much faster, at 1140 °C crossing the semi-glossy base curve and reaching the semi-sphering point a little above 1200°C. With regard to the granular, it is to be noted that although its softening temperature is much lower than that of the studied bases, at 1150°C its melt viscosity matched that of the glossy glaze, in principle indicating that it has the greatest compatibility with this base.

Thus, melt viscosity indicates a general granular characteristic, namely that it must always be less surface-active than the base. The granular thus acts as a wetting solvent on the base, producing an interaction interface or granular-base reaction, however allowing the granular to maintain its identity. If the base was less surface-active than the granular, it would wet it and dissolve it easily.

3.3. TTT DIAGRAM (TRANSFORMATION-TIME-TEMPERATURE) OF THE GRANULAR USED

With a view to studying devitrification by TTT analysis in the granular, compacts were formed after wetting by uniaxial pressing at a pressure of 100 kg/cm^2 of the different particle size fractions: (p) 100-200 μm, (m) 400-500 μm and (g) 700-800 μm. The granular was then melted, and obtained bulk as cast glass. Forming in compacts allows keeping the identity of the particles in the system, so that at the same forming pressure, crystallisation in the compact will be a function of particle size: cast glass means the extrapolation to the granular of an infinite particle size. This method allows TTT analysis in terms of granular particle size. The fired specimens were cut at right angles to the shaping direction, then polished and the external face and the internal cut face were analysed by XRD.

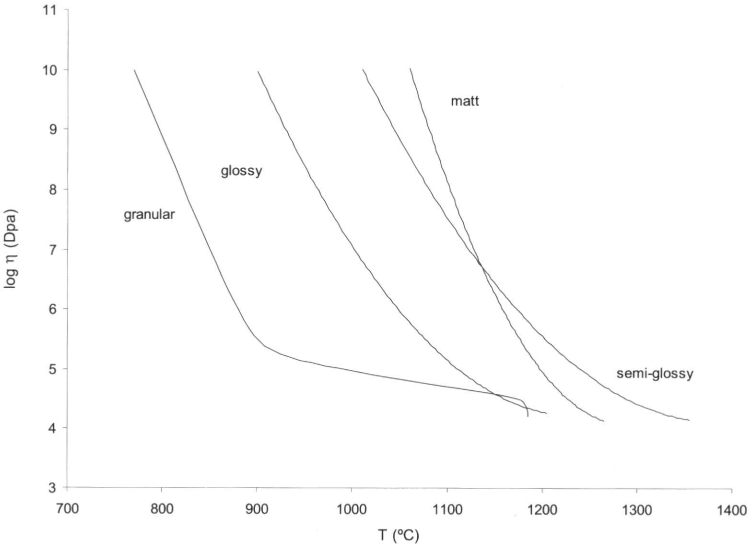

Figure 2. *Variation of melt viscosity of the granular and the three bases used (hot-stage microscopy).*

As two important devitrification bands appear in the DTA-TG study of the granulars, discussed in detail in Section 5, - the first between 800-1000ºC and the second between 1000-1150ºC depending on granular particle size - the TTT study was conducted at temperatures of 800ºC, 950ºC and 1050ºC, respectively before the first devitrification band, within the first devitrification band and within the second devitrification band.

The compacts and cast glass were fired in an electric laboratory kiln at a heating rate of 10ºC/min and residence time of 1h/3h/12h at the corresponding temperature. Figure 3 presents the simplified TTT diagram just for the granular with the smallest particle fraction used (100-200 μm) and for the cast glass. The intermediate particle sizes exhibited intermediate behaviour, which is not shown in order not to go into excessive detail. The following points may be highlighted on analysing all the data obtained:

(i) Crystallisations were not found at 800°C in any of the materials used, independently of treatment time.

(ii) Increase of the cristobalite volume concentration with temperature (T) and also with holding time (t), so that this was always the most abundant phases at 12 hours. This process, which we shall call the "cristobalisation of the material" can be observed as an example in the diffractograms that appear in Figure 4, which correspond to the granular (700-800 (m) treated at 950 °C for different times.

(iii) In general, there are always three crystalline phases: Wollastonite, Calcium Oxozirconate and Cristobalite. Moreover, peaks appear at $^{\circ}2\theta=14{,}0/23{,}2/25{,}5/31{,}8$, which are associated with a silico-zirconate or a blend of various compounds of this composition, termed X in Figure 4.

(iv) The preponderance of one phase or another varies depending on the material. Thus, in the granulars, the major phase at the start of treatment is wollastonite, while in the glass this is oxozirconate. The T-t evolution in the former causes the glass to reach the degree of "cristobalisation" faster.

(v) The evolution on the outside of the glass was no different from the inside. On the outside of the glass, only the non-assigned X silico-zirconates exhibited a greater peak intensity at the end of the treatment.

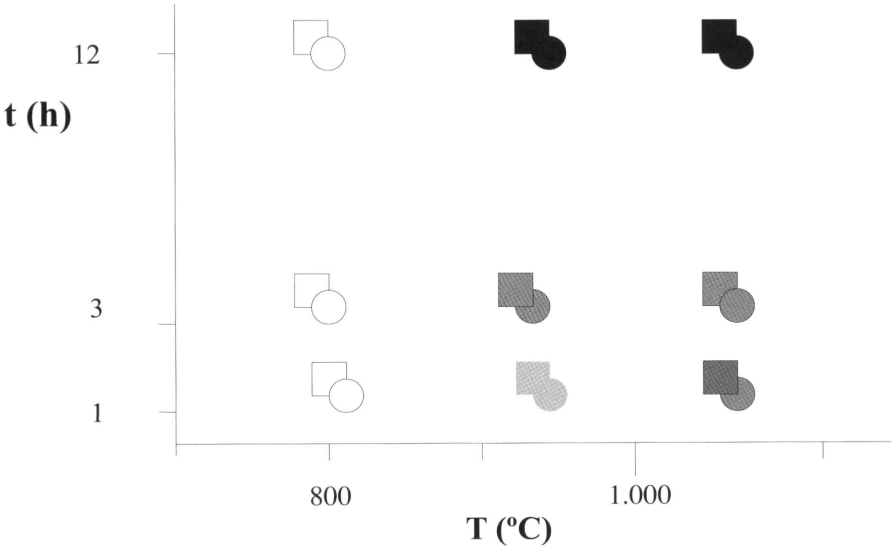

Figure 3. *TTT diagram of granular 100-200 µm and of the cast glass.*

Legend: Appearance of the test specimen and relative major crystalline phase detected by XRD (wollastonite ,oxozirconate and cristobalite)

GRANULAR 100-200 µm.	*CAST GLASS*
○, translucent, amorphous	□ transparent, amorphous
◍ translucent, wollastonite	▨ transparent, oxozirconate-wollastonite
◉ opaque, wollastonite-cristobalite	▩ opaque, cristobalite-wollastonite
● opaque, cristobalite	■ opaque, cristobalite

4. QUALITATIVE ANALYSIS OF THE DEVITRIFICATION PROCESS OF THE GRANULAR.

The devitrification of a glass is its tendency to crystallise. In the devitrification mechanism, according to the Tamman nucleation-crystalline growth theory [4,5,6], homogeneous nucleation requires a critical nucleus size above which nucleation is effective. This effectivity depends on crystallisation energy and surface tension of the nucleus-melt interface.

When nucleation is heterogeneous (as is possible in this case, in which there are crystalline particles at the interface with the base), maximum variation of free energy will also depend on a proportionality factor that will be a function of the existing affinity between the heterogeneous phase and the melt.

Although XRD studies allowed determining the evolution of granular devitrification, it is important besides this to know not just which phases crystallise, but also the kinetic mechanism controlling crystallisation.

With this view in mind, small quantities of granular were applied onto bodies glazed with the three bases. After suitably firing, cutting and polishing the specimens, the morphology of the granular-base interface was analysed by scanning microscopy with a back-scattered electron detector.

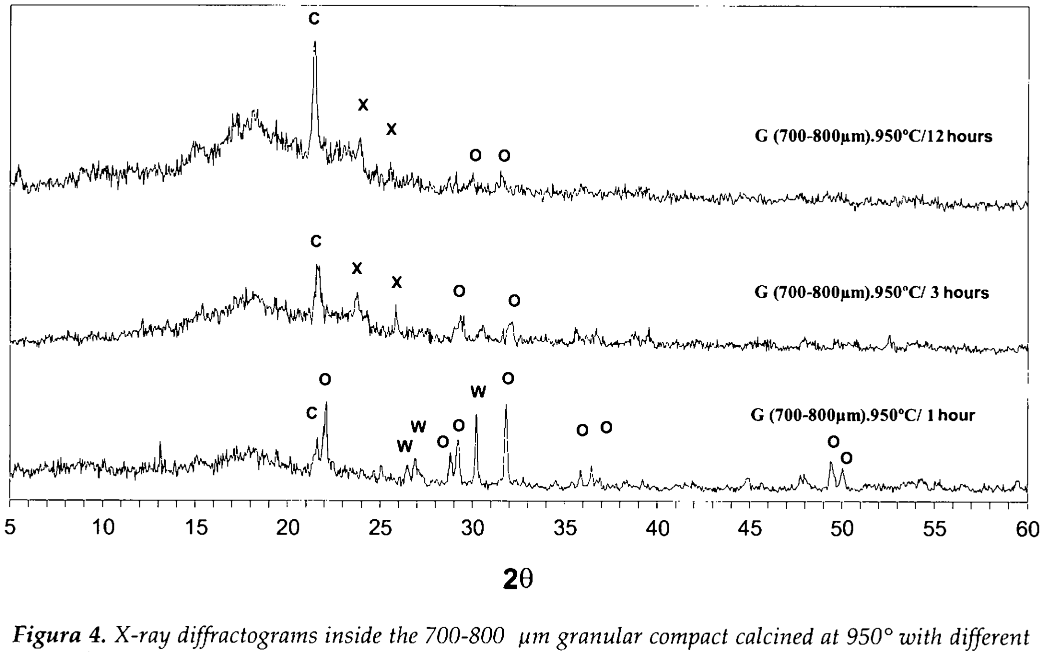

Figura 4. X-ray diffractograms inside the 700-800 µm granular compact calcined at 950° with different holding times: C (Cristobalite), O (Oxozirconate), W (Wollastonite), X (silico-zirconates).

Different granular particle sizes were used (from 100 µm to 2000 µm), as well as cast glass. The cycle used for sample firing is depicted in Figure 1, varying maximum

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[4] G. TAMMAN G, W. HESSE, *Die Abhäugigkeit der viksität vonder temperatur bei unterkühlten flüssigkeiten.* Z. anorg. allog. chem., 156(1926)245-256.

[5] P.W. MCMILLAN, *Glass-Ceramics,* Academic Press, 2a. ed., New York 1979.

[6] KENONG XIA, TERENCE G. LANGDON, *The thoughenining and strenthening of ceramic materials though discontinous reinforcement,* J. of Mat. Sci. 29(1994)5219-5231.

temperature from 1085°C to 1200°C. The result of these microscopic observations indicates that in the granulars with a small particle size it was difficult to observe any different crystallisation from that of cristobalite or oxozirconate. At high temperatures (1200°C) these phases were hardly observable as the specimens appeared over-fired, while at 1085°C the granulars crumbled in the cutting process and could not be observed (mainly with the semi-glossy and matt bases, on not having been adequately bonded to these glazes). It was thus found that to monitor the devitrification process, sufficiently large-size granulars needed to be used (500 µm or larger) and temperatures in the granular-base bonding range which, following the standard cycle used, range from 1100 to 1150 °C.

Analysis of all the samples obtained reveals that oxozirconate crystallises first at the granular-base interface. Wollastonite then crystallises on the oxozirconate and on the particulate base, growing as irisations from the boundary until the granular body is occupied. Finally, wollastonite is digested and cristobalite crystallises homogeneously throughout the granular mass, appearing to be thermodynamically the most stable phase.

In general lines, the observed devitrification process is common to the three studied bases, allowing the following evolution to be established:

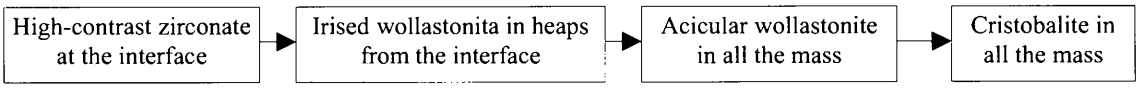

Figure 5 presents a selection of representative micrographs of this devitrification process.

- Fig. 5.a (2000 µm granular fired in a standard cycle with a 5-min hold at 1150°C on a semi-glossy base), presents the first devitrification stage in the granular root with the development of strongly contrasting aciculars in the back-scattered electron detector, which according to the TTT findings, can only be associated with the relatively heaviest of the three observed phases: oxozirconate. This association was confirmed by point EDAX analysis, which indicated high zirconium contents in the aciculars, besides silicon and calcium. Low-contrast acicular devitrifications were also observed, growing in a circular corona from the interface, which can be associated with wollastonite.
- Fig 5.b (2000 µm granular fired in a standard cycle with a 10-min hold at 1150°C on a semi-glossy base), presents the intermediate devitrification stage in which the circular corona has developed from the boundary. According to point EDAX analysis, this devitrification is associated with wollastonite.
- Fig 5.c (800 µm granular fired in a standard cycle with a 15-min hold at 1150°C on a matt base), presents the final process stage. The wollastonite aciculars have disappeared, being left as grey heaps near the interface and only a profuse contrast crystallisation is perceptible, not very distinguishable from the glassy matrix, associated by EDAX with cristobalite.

As mentioned before, in general lines the devitrification process is the same for the three bases. However they have an important influence on the process rate, as they interact differently with the granular depending on nature of the base. Thus it can be observed in Figure 5, which presents the micrographs of granular 700-800 μm on the glossy base (Fig. 5.d), on the semi-glossy base (Fig. 5.e) and on the matt base (Fig 5.f), at the same magnification and firing cycle (1150°C peak temperature), that the granular has spread over the glossy base so as to only allow seeing part of the particle, whereas on the semi-glossy and matt bases, the granular is maintained as a drop with an identity of its own as a result of its surface tension. Moreover, while wollastonite (grey areas) is only residual on the glossy base with already advanced cristobalite, on the semi-glossy and matt base a type of wollastonite spherulisation appears throughout the material.

5. STUDY OF DEVITRIFICATION KINETICS

To allow comparing the devitrification kinetics of the two phases that appear to play a fundamental role in the studied granular (wollastonite and cristobalite) [7,8], it is necessary to us different techniques, as the former develops by a heterogeneous nucleation process from the interface, which favours it kinetically, and the latter by a homogeneous nucleation process. The Johnson-Mehl-Avrami model [9,10] was followed for cristobalite devitrification and the Schmalzried diffusion model [11] for wollastonite.

5.1. KINETICS OF CRISTOBALITE DEVITRIFICATION

The kinetics of crystallisation by glaze devitrification often follows the Johnson-Mehl-Avrami based on the equation 5 [9].

$$x = 1 - \exp(-kt^n) \qquad \text{(eq. 5)}$$

where x is the transformed volume fraction, k is the rate constant, n is reaction order and t is time. Exponent n is a unit for a first-order crystallisation process, exothermic transformation process. The rate constant k is that of a thermally activated process and follows Eq. 6 of the Arrhenius type.

$$k = \nu \exp\left[\frac{-E}{RT}\right] \qquad \text{(eq. 6)}$$

where ν is the frequency factor, E is transformation activation energy, R is the perfect gas constant and T is absolute temperature.

In the Kissinger analysis [10] for non-isothermal treatments with temperature variation with time, the reaction rate is given by Eq. 7.

$$\frac{dx}{dt} = \left(\frac{\partial x}{\partial t}\right)_T + \left(\frac{\partial x}{\partial T}\right)_t \frac{dT}{dt} \qquad \text{(eq. 7)}$$

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[7] *La Wollastonita,* Bol. Soc. Esp. Cer y Vidr., 35 (1996).

[8] S. Robinson, *Significance of Wollastonite in Ceramic Whitewares,* Ceram. Eng. Sci. Proc., 18(1997)359-366.

[9] J. McKittrick, B. Hoghooghi, O.A. Lopez, *Vitrificaction and Crystallization of barium aluminosilicate glass ceramics from zeolite precursors,* J. of Non Crystall. Solids, 197(1996)170-178.

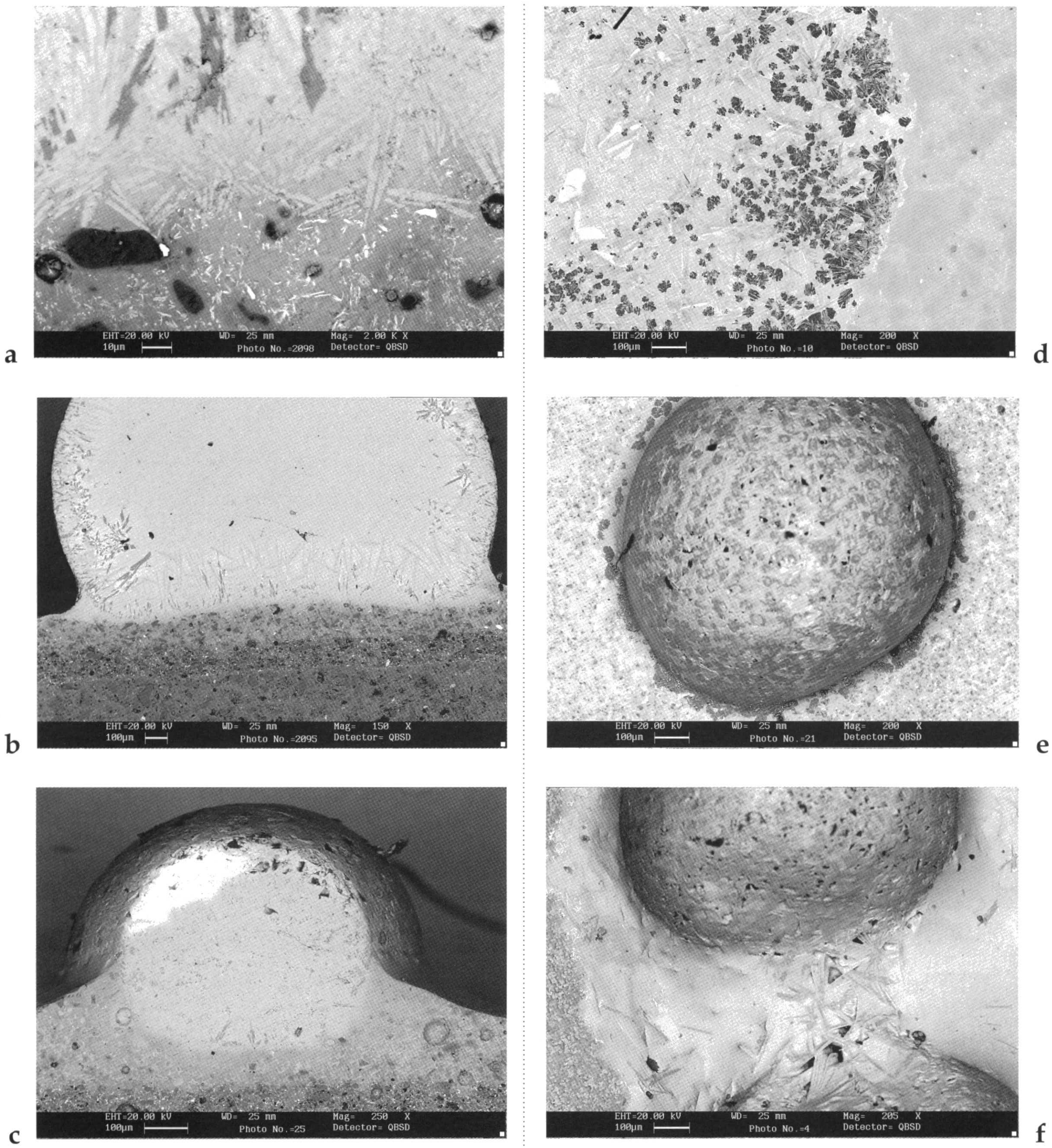
[10] H.E. Kissinger, Anal. Chem., 29(1957)1702.

[11] Herman Schmalzried, *Solid State Reactions,* Angew. Chem. Int. Ed. Engl. 2,5(1963)251-54.

Substituting Eqs. 6 and 5 in 7, the reaction rate becomes:

$$\frac{dx}{dt} = \nu\,(1-x)\exp\left(\frac{-E}{RT_c}\right) \qquad \text{(eq. 8)}$$

This rate peaks when $d^2x/dt^2=0$ which occurs at crystallisation temperature T_c, obeying:



(a,b,c) *Cross-sectional view of examples of representative SEM micrographs of the devitrification process of the 700-800µm granular particles treated at 1150°C for different times and on different bases.*

(d,e,f) *Top view of examples of representative SEM micrographs of behaviour in terms of a 700-800µm granular particle with the same heat treatment. (1150°C-5min.)*

Figure 5.

$$\frac{d^2x}{dt^2} = 0 = -\nu\left(\frac{dx}{dt}\right)\exp\left(\frac{-E}{RT_c}\right) + \nu(1-x)\left(\frac{E}{RT_c^2}\right)\exp\left(\frac{-E}{RT_c}\right)\left(\frac{dT}{dt}\right) \qquad \text{(eq. 9)}$$

$$\left(\frac{dx}{dt}\right) = (1-x)\left(\frac{E}{RT_c^2}\right)\left(\frac{dT}{dt}\right) \qquad \text{(eq. 10)}$$

Substituting Eq. 10 in kinetic Eq. 8 gives:

$$\frac{E}{RT_c^2}\frac{dT}{dt} = \nu\exp\left(\frac{-E}{RT_c}\right) \qquad \text{(eq. 11)}$$

This equation can be rewritten as:

$$\ln\left[\frac{T_c^2}{\Theta}\right] = \ln\left[\frac{E}{R\nu}\right] + \frac{E}{RT_c} \qquad \text{(eq. 12)}$$

Eq. 12 allows obtaining the energy activation values and the frequency factor from the DTA or scanning differential calorimetry (SDC) data. This can be done by plotting the square neper of crystallisation peak temperature divided by heating rate (θ) versus the inverse of crystallisation temperature: the plot should fit a straight line with a slope proportional to the activation energy.

The DTA-TG data were obtained for different granular particle sizes at different heating rates in a Perkin Elmer simultaneous calorimetric analysis instrument in air atmosphere, using platinum crucibles. The results of the different heating rates are set out in Table II.

Granulars	Θ (°C/min)	**Dehydration** (exo) T (°C)	**Devitrification** (exo) T(°C)
Small **100-200 μm**	2	240,430	640,660,**825, 960**
	5	300	520,610,650,720,820,**960,980**
	10	160	520,560,610,740,**1020,1130**
	20	-	500,580,620,730,**900,1060**
Medium **400-500 μm**	2	240,400	680,760, **820,1000**
	5	140	520,600,660,740,840,880,**1000,1020**
	10	100	580,665,740,880,**980,1080**
	20	-	520,620,720,840,**1045,1080**
Large **700-800 μm**	2	320,540	720,730,**820,1020**
	5	100	660,740,830,**980,1060**
	10	100	520,660,760,**860,1080**
	20	140	580,620,660,720,**980,1115**

Table 2. *DTA-TG data for the different granular fractions at different heating rates.*

Figure 6.a presents the devitrification kinetics for the last exothermic band observed in the studied granulars in accordance with Eq. 12. This band is associated with cristobalite devitrification in the process termed progressive cristobalisation. The data for the granulars satisfactorily match Johnson-Mehl-Avrami kinetics.

The activation energy for the different granular fractions derived from the slope of the plots in Fig. 6 and by Eq. 12, are presented in Figure 6.b, indicating that activation energy grows linearly with granular size from 400KJ/mol for fraction 100-200μm to 510KJ/mol for fraction 700-800μm.

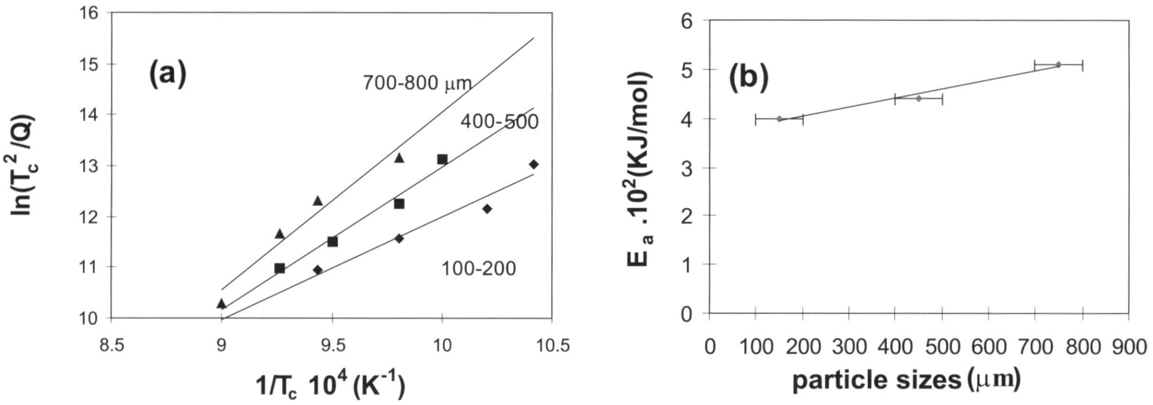


Figure 6. *(a) Cristobalite devitrification kinetics in three granular particle-size fractions, (b) variation of activation energy with granular particle sizes.*

5.2. WOLLASTONITE DEVITRIFICATION KINETICS

It was attempted to monitor wollastonite devitrification by the Schmalzried model [12] for diffusion-controlled crystalline growth, so that devitrification thickness x can be related to crystallisation time t by Eq. 13.

$$(\Delta x)^2 = Kvt \qquad \text{(eq. 13)}$$

where K is a rate constant and v is product specific volume.

In reality, the foregoing equation is affected by an ordinate at the origin owing to the devitrification produced in the cooling stages. The rate constant follows a variation of the Arrhenius type with temperature.

$$K = K_0 \exp\left[-\frac{E_0}{RT}\right] \qquad \text{(eq. 14)}$$

multiplying the terms by specific volume:

$$Kv = K_0 v \exp\left[-\frac{E_0}{RT}\right] \qquad \text{(eq. 15)}$$

and taking logarithms:

$$\ln(Kv) = \ln(K_0 v) - \frac{E_0}{RT} \qquad \text{(eq. 16)}$$

On plotting ln(Kv) versus 1/T the slope is Eo/R, which permits determining the activation energy associated with the process, assuming that in the heat-treatment temperature range used (1100-1150°C) the specific volume is constant.

To conduct the devitrification studies, a piece of 2-mm-high cast glass was used, to extend the wollastonite growth process from the interface and enable observing the full crystallisation development of this phase. The piece was fired according to the standard cycle depicted in Figure 1, varying peak temperature and residence times.

To determine the influence of the base glaze on the devitrification process, the study was performed at the granular-base interface and the granular-air interface.

5.2.1. Devitrification at the granular-base interface

Figure 7 shows the wollastonite devitrification process in the form of nucleated acicular irisations at the interface at different peak temperatures of the standard cycle. Progressive growth can be observed with temperature of the devitrified wollastonite layer thickness Δx, and its disappearance by cristobalisation at 1175°C. On raising the holding time at a given temperature, devitrification thickness increases similarly to that shown in Figure 7, which is not shown for the sake of simplicity.

The analysis performed at temperatures of 1050, 1075, 1100, 1125 and 1150°C with holds at each temperature of 5, 7, 10 and 15 minutes reveals good agreement with all the bases to the model proposed for wollastonite devitrification (Eq. 13 in Fig. 8.a and Eq. 16 in Fig. 8.b for the glossy base presented as an example).

The activation energies found are set out in Table III. The results indicate that the glossy base and the semi-glossy base facilitate wollastonite crystallisation to a greater extent than the matt base. The lower activation energy obtained with the semi-glossy base can be associated with the profusion of nucleating particles in this base, detected by XRD and SEM (added quartz and devitrified zircon). The glossy base exhibits fewer nucleating particles, but interacts efficiently with the granular owing to the similarity of the melt viscosity of both materials in the studied temperature range, as evidenced by the hot-stage microscopy study above. Finally, the matt base exhibits the least number of nucleating particles (devitrified celsian and willemite), so that the nucleation process is encouraged less.

5.2.2. Devitrification at the granular-air interface

Figure 9 presents the same devitrification process with temperature, but now for the granular surface in contact with air, revealing the same phenomenon as at the interface with the base, though with clearly smaller devitrification thicknesses.

The analysis performed at temperatures of 1050, 1075, 1100, 1125 and 1150°C with holds at each temperature of 5, 7, 10 and 15 minutes in this case also presents satisfactory agreement with the Schmalzried model for diffusion-controlled processes, as shown in Figure 10 for example in the glossy base, while the semi-glossy and matt glazes behave similarly.

The activation energies found, detailed in Table IV, are similar in each case, which was to be expected, as the process takes place without contact with the bases and is therefore independent of the bases. The value is much higher than the values associated with wollastonite crystallisation at the interface (Table III), which highlights the importance of the base glaze used. In the firing process therefore, wollastonite devitrification starts initially at the granular-base interface and subsequently at the granular-air interface, advancing in all directions towards the centre of the particle until the whole mass is crystallised. In accordance with point 5.2.1, this crystallisation start will also be favoured by bases containing crystals that act as nucleating agents.

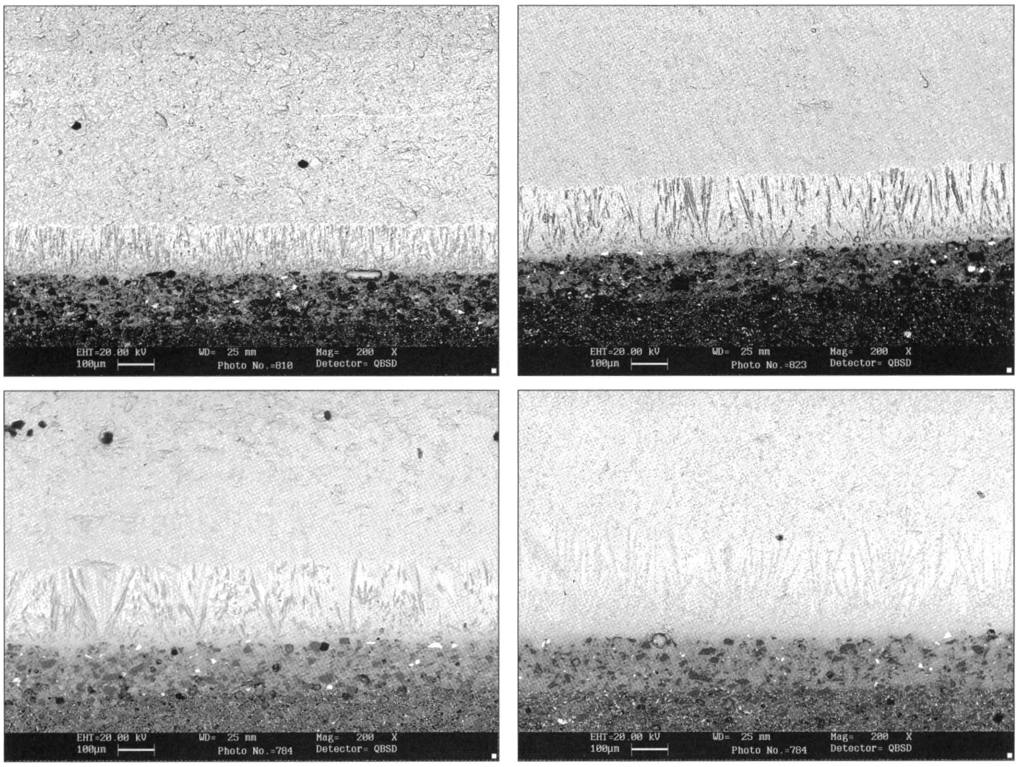


Figure 7. *Wollastonite devitrification at the interface with the semi-glossy base versus temperature: (a) 1050°C-5 min., (b) 1075°C-5 min., (c) 1100°C-5 min, (d) 1175°C-5 min.*

Base	**E$_a$(KJ/mol)**
Glossy	76.4
Semi-glossy	68.8
Matt	98.32

Table 3. *Wollastonite activation energies as a function of the base. Granular-base interface.*

Base	**E$_a$(air) (KJ/mol)**
Glossy	108
Semi-glossy	111
Matt	104

Table 4. *Wollastonite activation energies as a function of the base. Granular-air interface.*

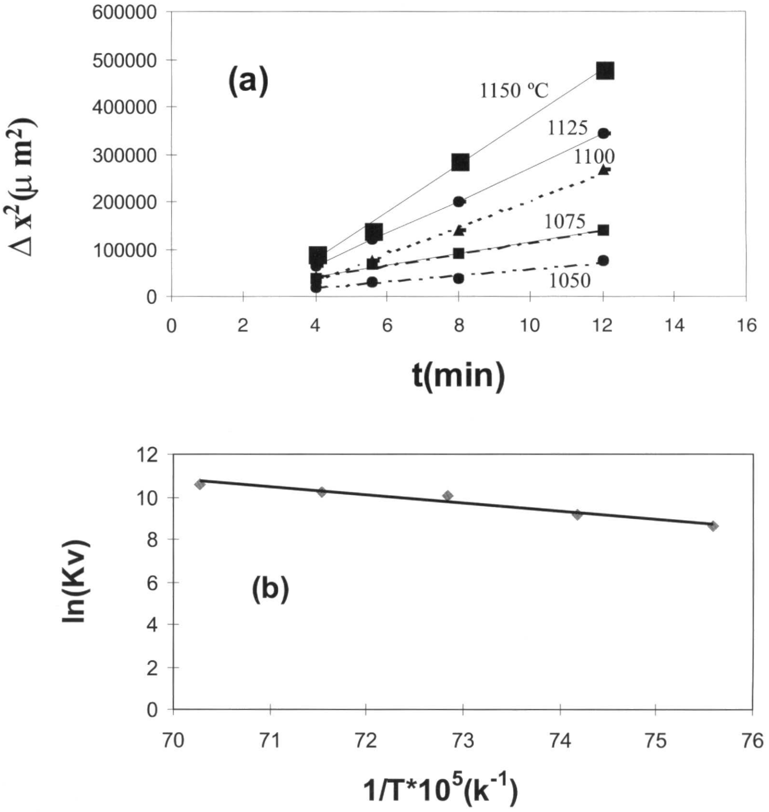


Figure 8. Wollastonite devitrification at the interface with the glossy base: (a) Eq. 13 fit for different temperatures, (b) Eq. 16 Arrhenius behaviour.

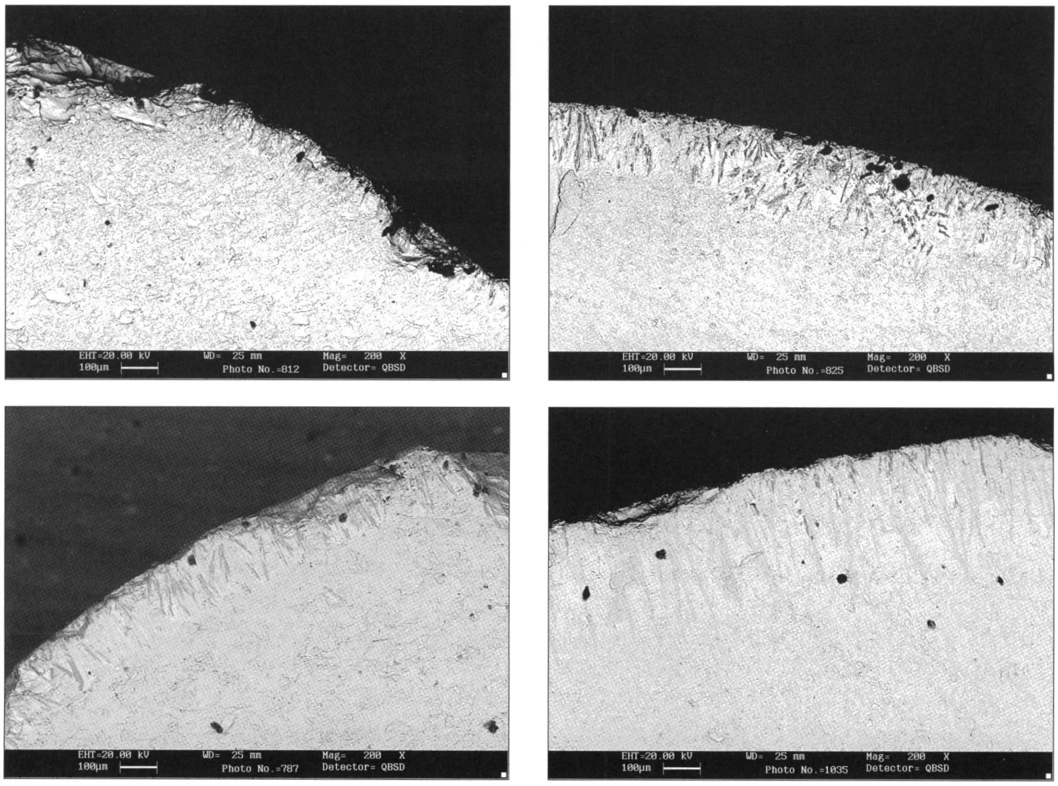


Figure 9. Wollastonite devitrification at the external surface (air), with the semi-glossy base versus temperature: (a) 1050°C-5 min, (b) 1075°C-5 min., (c) 1100°C-5min, (d) 1175°c-5 min.

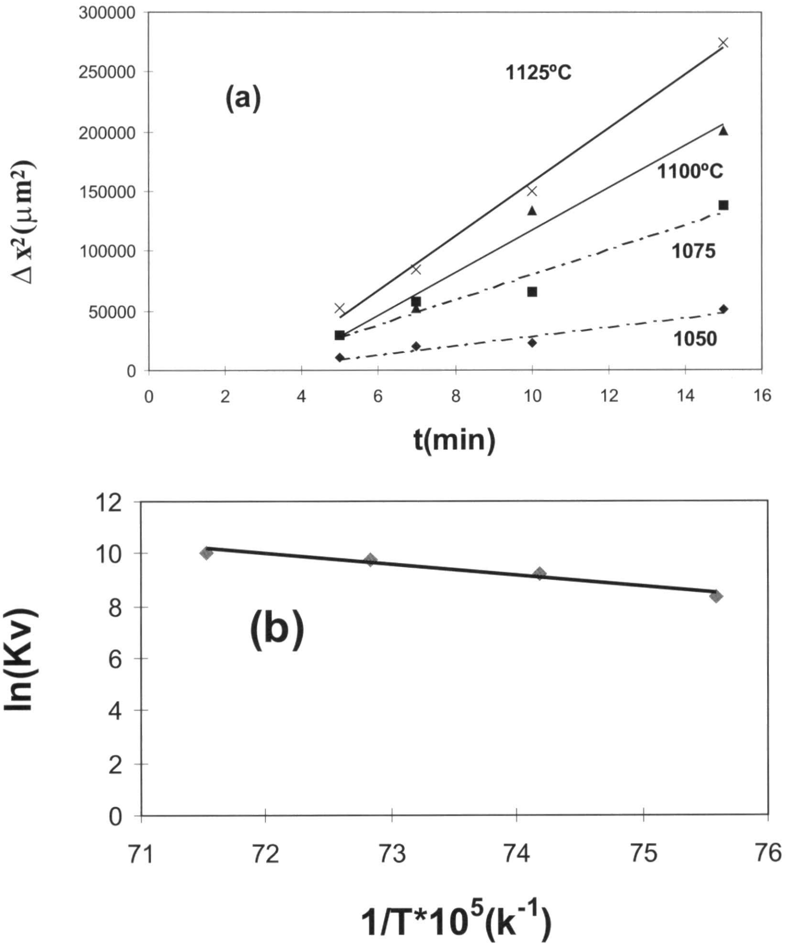


Figure 10. Wollastonite devitrification at the air interface (glossy base): (a) Eq. 13 fit for different temperatures, (b) Eq. 16 Arrhenius behaviour.

On the other hand it is important to note that the activation energy of wollastonite devitrification by heterogeneous nucleation presents a significantly lower value than that of homogeneous cristobalite crystallisation in the mass of the granular, evaluated by the Johnson-Mehl-Avrami from differential calorimetry data (Figure 6.b). This means that, although cristobalite is thermodynamically the most stable phase, the activation of its activation energy is considerably higher than that of wollastonite, whose crystallisation is kinetically favoured, this therefore being the most predominant phase with the industrial firing cycles used.

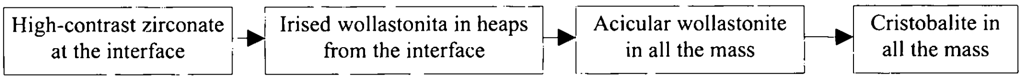
6. CONCLUSIONS

The following conclusions can be drawn, based on the foregoing discussion of the results.

1. Granular bonding to the base is closely related to the compatibility of base-granular surface tension: in general, granulars are less surface-active than bases, so that they act as wetting solvents, generating an interaction interface or granular-base reaction though permitting the granular to keep its

identity. If the base was less surface-active than the granular, the base would wet it and dissolve it easily.

2. For the studied granular, the general devitrification scheme was found to be as follows:



3. The TTT studies showed that cristobalite was the end phase detected in the largest proportion, so that the system can be considered to develop a progressive crisobalisation process. This process is faster when granular size is small, peak temperature of the cycle is higher, or residence time at peak temperature is longer.

4. Cristobalite crystallisation develops through a homogeneous nucleation mechanism that follows the Johnson-Mehl-Avrami model, with activation energies obtained by differential calorimetry studies, which increase linearly with granular size from 400 KJ/mol for size fraction 100-200μm up to 510 KJ/mol for 700-800μm.

5. Wollastonite crystallisation in the granular takes place by a heterogeneous nucleation process from the interfaces.

6. Wollastonite crystallisation from the interface with the base occurs at faster rates than from the surface of the granular in contact with air and is thermally activated by activation energies around 70 KJ/mol. However, this value depends on the base used: bases with a profuse presence of crystalline particles, capable of acting as an external nucleating agent, exhibit low energies while bases with few crystallisations exhibit higher energies. This activation energy is clearly lower than the one associated with cristobalite crystallisation, which explains the temporary kinetic stabilisation of wollastonite in the system.

7. In the granular-air interfase, wollastonite crystallisation occurs by a mechanism similar to that of the granular-glaze interface, but is independent of the base used. The associated activation energy is about 110 KJ/mol.

8. In the firing process, wollastonite crystallisation initiates at the granular-base interface and subsequently at the granular-air interface, advancing in all directions towards the centre of the granular particle. Crystallisation start is also favoured by bases containing crystals that act as nucleating agents.

9. By jointly optimising the base composition, granular size and firing cycle, crystallised granular particles will be produced throughout the mass, thus providing greater abrasion resistance.