USE OF GLASS SHEETS IN CERAMIC TILE MANUFACTURE

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ABSTRACT

This study addresses the obtainment of ceramic tiles made up of a sheet of glass fused to a ceramic substrate. The procedure involves depositing the glass sheet, of appropriate dimensions, on the previously fired decorated body. Heat treatment then follows at low temperature, which softens the glass slightly, fusing it with the ceramic substrate. This process enables obtaining products with a mirror gloss, which exhibit the following advantages over similar products currently available in the market: zero surface porosity, easier production management, and new decorating possibilities.

1. INTRODUCTION

Some of the main characteristics differentiating ceramic tiles from other types of coverings are their asepsis and cleanability[1], features usually obtained by application of a glassy coating on the ceramic body. To improve the aesthetic appeal of these tiles, the glaze layer is sometimes polished, yielding a surface with a mirror gloss.

However, this procedure is complex and expensive, among other reasons, because of the small curvature that the tiles need to display, the need to apply a thick layer of glaze, the appearance of curvatures after polishing, the processing cost itself, etc.

An alternative to this procedure is the use of glass sheets. The process consists of depositing the glass sheet, of appropriate dimensions, on a previously fired, decorated ceramic substrate. A low-temperature heat treatment then follows which softens the glass slightly and fuses it with the ceramic substrate. The main advantage of this system is its greater simplicity, as it suppresses the polishing step, while simultaneously providing a perfectly flat glossy surface, free of porosity.

A study has been undertaken of the technical feasibility of obtaining ceramic tiles by the foregoing procedure for interior wall cladding, ventilated curtain walls and flooring. Since the surface properties of the product will correspond to those of the glass sheet used, we first characterised different commercial sheets of glass. The use of these materials requires having substrates with appropriate thermal expansion, which required developing specific body compositions for each type of glass. As an alternative to the use of commercial sheets of glass, new glass compositions with good mechanical properties and coefficients of expansion more similar to those of current ceramic bodies have been developed.

2. CHARACTERISATION OF GLASS SHEETS AND CERAMIC PRODUCTS

In this phase four samples of different types of commercial sheets of glass were characterised: glass for construction (FLT1 and FLT2), laboratory glass (P1) and glass with high resistance to thermal shock (N). Commercial ceramic products with a glossy surface were also tested to perform a comparative study: these consisted of a transparent glaze (VT) and an opaque glaze (VO); polished grit (GR) and polished pressed glass (VP).

Since the glasses were to provide the ceramic pieces with their surface properties, the characterisation centred on determining their mechanical properties and behaviour on exposure to abrasive wear. The thermal expansion of these materials was also determined in order to establish their compatibility with present ceramic bodies.

2.1. EXPERIMENTAL

In order to characterise the foregoing glass sheets and ceramic products, the following determinations were performed:

- Microhardness
- Toughness

- Wear resistance
- Thermal expansion curve: coefficients of thermal expansion.

Microhardness was determined from an indentation test with a tip of Berkovich geometry (triangular pyramid), in a Nanotest apparatus. Throughout the indentation test, this apparatus records the depths reached by the indenter as a function of the applied load.

The method used for determining toughness (K_{IC}) is based on the measurement of the radial cracks generated from the corners of the rhomboid track produced by a Vickers indenter as a result of the application of a load (P) on the sample surface[2]. The values of crack length (c), modulus of elasticity (E) and microhardness (H) allow calculating toughness from the following equation:

$$K_{IC} = 0.016 \cdot \left(\frac{E}{H}\right)^{0.5} \cdot P \cdot c^{-1.5}$$

Wear took place with an abrasion tester of the PEI type (described in the standards for ceramic tiles), which has been modified to reduce the area of the abraded circle from 82 mm to 25 mm. Abrasion stages of 5000 revolutions (approximately equivalent to 200 revolutions in the standard test) were applied.

2.2. RESULTS AND DISCUSSION

Figure 1 shows the results of the wear resistance test, plotted as percentage gloss loss versus the number of revolutions. The data have been represented in this way due to the difference in initial gloss displayed by the different tested materials (Table 1). It can be observed that the material which performs best versus abrasive wear is the opaque glaze (VO), followed by the transparent glaze (VT). Then comes a group of three samples: glass sheet P1, grit (GR) and pressed glass (VP). Sheet N exhibits slightly lower wear resistance than this group, and slightly higher wear resistance than glass sheets FLT1 and FLT2.

These differences in behaviour can be attributed to the different microstructure and composition of the samples. Thus, the good performance of glaze VO is due to the absence of surface porosity and the devitrification of small $ZrSiO_4$ crystals (0.5 μm), which reinforce the glassy structure[3].

In regard to the other samples, the differences observed are small, and are due to the surface microstructure as well as to the structure and composition of the glass itself. Samples VT, GR and VP exhibit a similar chemical composition, so that the differences must be related to the state of their surface. Thus, while sample VT displays a smooth surface, free of porosity and breaks, samples GR and VP have a more damaged surface, with some open pores, grooves and cracks, as a result of the polishing process[4]. On the other hand, in the glass sheet samples, the differences observed must be related to sample chemical composition, since all their surfaces are similar. Thus, the SiO_2 content of the samples and sample wear resistance diminish according to the sequence P1>N>FLT, which matches the loss of mechanical properties undergone by silica glasses, as oxide modifiers are introduced[5].

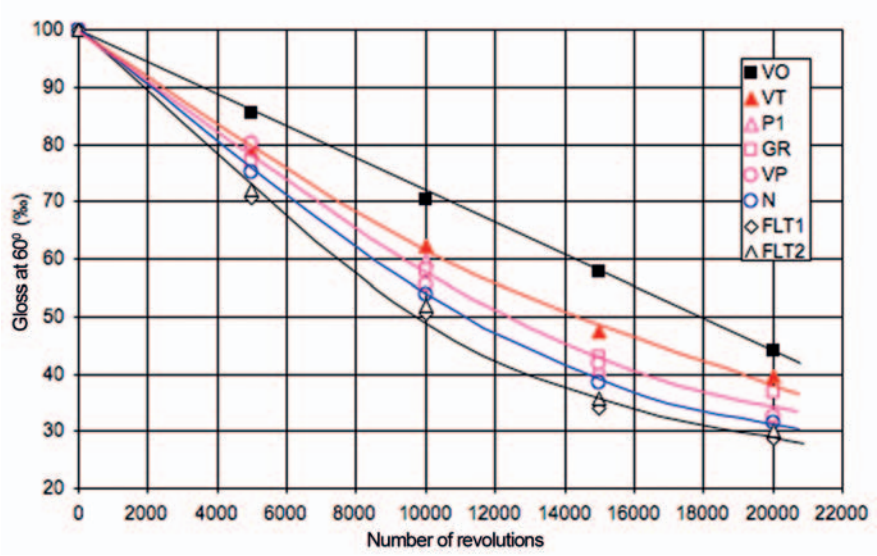

Figure 1. Evolution of gloss in the samples during the abrasive wear test.

The slope of the curves in the initial section (δ) was calculated from Figure 1 in order to have a parameter that would evaluate gloss loss during abrasive wear. This parameter, together with the values of initial gloss (β_0), microhardness (HB), toughness (K_{IC}) and the coefficients of expansion (α) are set out in Table 1. The table shows:

- The values of initial gloss of the materials that did not undergo a polishing process (VO, VT, P1, N, FLT1 and FLT2) are higher than those of the mechanically polished materials (GR and VP).
- There are no important differences in the microhardness data of the samples.
- Toughness (K_{IC}) of the samples varies significantly. Thus, sample VO displays the highest toughness because it is a glass-ceramic material, in which the presence of microcrystals of zircon diminishes the tendency for cracks to propagate[6].
- Glass sheets N and P1 displayed mechanical properties similar to those of certain ceramic materials used at present, such as transparent glazes and polished grits, while presenting, as advantages, their greater gloss and absence of porosity, which will provide good performance in regard to staining.
- Glass sheets FLT1 and FLT2 have very similar properties and perform very similarly to each other, although the toughness and wear resistance values indicate that their properties are not as good as those of samples N and P1. This suggests that they could be used in areas where high mechanical performance is not required, such as interior wall cladding and facades.
- The thermal expansion of the glass sheets differs appreciably from that of the ceramic bodies used at present in tile manufacture. For this reason, in order to be able to use these glass sheets, the ceramic bodies need modifying and adapting.
- Sample gloss loss (δ) is related to sample toughness (Figure 2); as toughness increases, the wear resistance of the pieces rises, as reported in the literature[6].

Summing up, the tested commercial glass sheets display appropriate properties for use in interior wall cladding and facades, where high abrasion resistance is not required. In the case of use for floor tile, the P1 sheet would be the most suitable, in view of its better properties. Some of the technical advantages compared with current ceramic tiles are the greater gloss, absence of porosity, and greater simplicity of the manufacturing process.

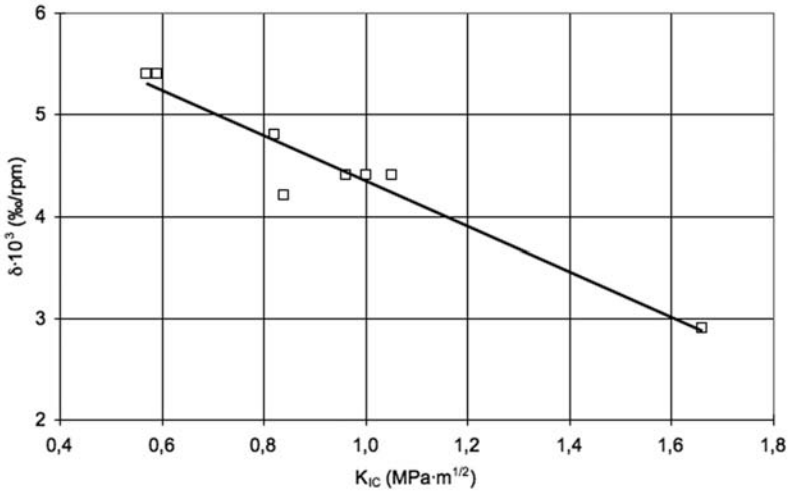

Figure 2. Relation between wear rate and toughness

	β_0 (‰)	$\delta \cdot 10^3$ (‰/rpm)	HB (GPa)	K_{IC} (Mpa·m$^{1/2}$)	$\alpha_{25\text{-}300} \cdot 10^7$ (°C^{-1})
VO	97	2.9	9.0	1.66	65
VT	100	4.2	8.6	0.84	70
P1	128	4.4	9.2	1.00	32
GR	89	4.4	6.3	1.05	68
VP	93	4.4	9.4	0.96	70
N	125	4.8	10.8	0.82	-3
FLT1	117	5.4	8.9	0.57	93
FLT2	120	5.4	9.0	0.59	91

Table 1. Characteristics of the studied glass sheets and ceramic products.

3. DEVELOPMENT OF BODY COMPOSITIONS COMPATIBLE WITH THE GLASS SHEETS

The manufacture of ceramic tiles by fusing a sheet of glass to a substrate requires a certain compatibility between the coefficients of expansion of both layers, otherwise problems of curvatures, breakage, cracks, etc. can occur during the cooling stage. In this section two types of body compositions have been developed: one with compatible coefficients of expansion with those of the glass sheets with high thermal expansion (FLT1 and FLT2), whose properties make them appropriate for use in interior wall

cladding and facades; and another, compatible with the glass sheet with low thermal expansion (P1), more appropriate for flooring owing to the greater toughness.

In both cases, the behaviour of the resulting compositions in the different manufacturing process stages needs to allow processing in current facilities, without modifying excessively the usual operating variables, in addition to providing low apparent porosity with a view to assuring frost resistance, in particular for outdoor applications.

3.1. DEVELOPMENT OF A PORCELAIN TILE BODY COMPOSITION WITH HIGH THERMAL EXPANSION

Given the high thermal expansion of glasses FLT1 and FLT2 (coefficient of expansion value of $91 \cdot 10^{-7}$ °C^{-1}), the new body needed to have an expansion coefficient value of around $88 \cdot 10^{-7}$ °C^{-1}, for both to be thermally compatible.

The best result was obtained by modifying a standard composition used for manufacturing conventional porcelain tile, introducing a frit with a high coefficient of thermal expansion (Frit A), in a percentage of 10%. Table 2 details the characteristics of the green and fired new composition (CSA), compared with those of the usual glazed porcelain tile composition (STD). It can be observed that composition CSA provides the dry pieces with a slightly lower compactness compared with that of the usual composition, although it has very high dry mechanical strength. In addition, the composition can be processed at the usual temperatures and firing cycles with a sufficiently wide firing range. The high coefficient of expansion enables the cooling stage to take place without any curvature or crazing problems originating as a result of a mismatch between the thermal expansion of both layers (body and glass). Finally, the fired pieces display low water absorption and a high degree of whiteness.

CHARACTERISTIC	STD	CSA	CSB
Dry bulk density (g/cm^3)	1.90-1.95	1.88	1.88
Dry mechanical strength (kg/cm^2)	35-45	95	30
Peak firing temperature (°C)	1180-1200	1180	1190
Linear shrinkage (%)	7.0-8.0	6.8	8.5
Water absorption (%)	<0.5	<0.5	<0.5
Fired bulk density (g/cm^3)	2.30-2.38	2.23	2.45
Coefficient of expansion (°C^{-1})	$70\text{-}75 \cdot 10^{-7}$	$87 \cdot 10^{-7}$	$45 \cdot 10^{-7}$
L* coordinate	75-80	80	85

Table 2. Characteristics of the body compositions.

3.2. DEVELOPMENT OF A PORCELAIN TILE BODY COMPOSITION WITH LOW THERMAL EXPANSION

In this case, the low thermal expansion of glass P1 (coefficient of expansion value of $32 \cdot 10^{-7}$ °C^{-1}) required developing a body composition with a coefficient of expansion value close to $40 \cdot 10^{-7}$ °C^{-1}, for both to be thermally compatible.

Therefore, a composition was developed, based on those normally used for the manufacture of porcelain tile, which incorporated a frit with a low coefficient of

expansion (frit B), in an addition of around 15%. Table 2 sets out the characteristics of this composition (CSB).

4. DEVELOPMENT OF COMPOSITIONS FOR OBTAINING GLASS SHEETS

Some of the disadvantages found in the use of commercial glass sheets for fabricating ceramic tiles are their moderate mechanical performance, which could prevent their use as flooring, and the need to develop body compositions that have a compatible thermal expansion with the glass sheets.

For this reason, in this section the feasibility was studied of developing glass compositions with better technical performance than that of commercial glasses. The required glass characteristics were: low abrasive wear resistance, high transparency – involving a scarce tendency to devitrify and phase-separate – more similar thermal expansion to that of present ceramic bodies, and moderate cost.

4.1. EXPERIMENTAL

In order to develop these glasses, albite was used as a base raw material, since it produces glasses with high percentages of SiO_2 and Al_2O_3, which should, in principle, provide the glass with good mechanical properties[5][8]. However, albite is a raw material that cannot be processed in standard glass manufacturing conditions. Different fluxing oxides were added, therefore, to reduce melt viscosity. High-temperature fluxing oxides were selected from the fluxing oxides that are typically used in the manufacture of frits, as the most appropriate (alkaline-earth oxides and zinc oxide). This was because, compared with low-temperature fluxing oxides (boron and alkaline oxides), these provide the glassy phase with the best mechanical properties.

Four compositions, referenced PFMg, PFCa, PFSr and PFZn, were tested; these had the following composition (% in moles): 66.0 SiO_2, 10.4 Al_2O_3, 14.1 RO, 9.5 Na_2O, where the RO oxide = MgO, CaO, SrO or ZnO, MgO, CaO, SrO or ZnO, respectively. Two industrial frit compositions, FT and FO, were also tested. These had been used to obtain the transparent and opaque glazes characterised in section 2.

The compositions to be tested were fused in an electric laboratory kiln. The melt was poured into a steel die, yielding a 4x6 cm glass test specimen, approximately 0.5 cm thick. Given the difficulty of performing abrasion tests on these test specimens (the surfaces were not completely flat), their microhardness and toughness were determined; this last parameter is related to abrasion resistance, as was observed in Figure 2.

In addition, in order to determine the tendency of these glasses to phase-separate and devitrify when they are subjected to thermal treatment, they were heat treated for 60 minutes at a temperature close to that of glass softening, and they were then examined to establish if there was any opalescence.

4.2. RESULTS AND DISCUSSION

The appearance of the glass test specimens obtained is shown in Figure 3 (top). It can be observed that, except for composition FT, the rest gave rise to transparent

glasses, although in some samples, such as FO and PFZn, a greenish colour developed, probably due to the oxidation state of the iron present. Composition FT provided less transparency and a bluish shade, owing to phase separation.

Table 3 sets out the results of the microhardness and toughness determinations of the different tested glasses. It shows that the microhardness values are very similar among the different samples; only glass FO stands out for its slightly higher value, as does glass PFZn for its slightly lower microhardness. With regard to toughness, the results are also quite similar, except for sample FT, which displays a lower value.

SAMPLE	HB (GPa)	K_{IC} (MPa*$m^{1/2}$)
FO	10.2	1.01
FT	9.3	0.86
PFMg	9.1	0.97
PFCa	9.0	1.11
PFSr	9.0	1.1
PFZn	8	1.05

Table 3. Microhardness and toughness of the samples.

In regard to the results obtained in section 2, the following may be noted:

- There are no differences between samples VT and FT.
- An important reduction is observed in the toughness of the glass obtained from frit FO with respect to glaze VO. This is because zircon has not devitrified in the glass test specimen.
- The glasses obtained from albite display higher toughness than glass sheets FLT and N, and similar toughness to that of glass P1.

We then studied the tendency of the glasses obtained to phase-separate and to devitrify, during both the slow cooling stage in glass sheet manufacture and in the fusion of the glass sheet with the ceramic body. For this, glass test specimens were subjected to different thermal cycles, which sought to simulate the processes indicated previously. By way of example, Figure 3 (bottom) shows the appearance of some of these test specimens after heat treatment.

The results indicate that the transparent and opaque frits (FT and FO), as well as the PFZn composition, give rise to opalescent glasses, whereas the rest of the compositions, PFCa, PFMg and PFSr, yield transparent specimens after the heat treatment (Figure 3 bottom). SEM observation of the test specimens established that the opalescence in specimens FT and FO was due to large-sized phase separation, whereas in specimen PFZn it was due to willemite crystallisation.

Based on these results the PFCa composition was selected for subsequent full characterisation, because it yielded a transparent glaze after heat treatment and had a high toughness value, while the raw materials cost was the lowest of the tested compositions. Table 4 details the results: they show the composition has high gloss, high toughness – which should provide good wear resistance – and a thermal expansion that matches that of current ceramic bodies more closely.

These results open up the possibility of obtaining glass sheets with compositions different from the present ones, and which display better-balanced properties. The PFCa composition allows fabricating transparent glass sheets with mechanical properties similar to those of the P1 sample, and appreciably better ones than those corresponding to construction glasses (FLT), with very steady transparency, thus enabling heat treatments to be performed to fuse the glass sheet to the ceramic body with a better-matching coefficient of expansion.

FT FO PFMg PFCa PFSr PFZn

Figure 3. Top: Original glass piece. Bottom: Glass piece after heat treatment.

	β_0 (‰)	HB	K_{IC}	$\alpha_{25\text{-}300}\cdot10^7$ ($°C^{-1}$)
PFCa	95.9	9.0±0.4	1.11±0.14	82

Table 4. Characteristics of the glass test specimens obtained with composition PFCa

5. STUDY OF THE GLASS-TO-BODY FUSING PROCESS

A vitally important aspect of the new product is the quality of the interphase between both materials, which has a pronounced influence on key properties such as mechanical strength and impact resistance. A fusion process was therefore selected, since this would favour the formation of body–glaze interphase with good characteristics. In addition, to encourage the formation of this interphase, a ceramic frit of appropriate characteristics has been used, which was applied onto the body.

5.1. EXPERIMENTAL

With a view to determining the temperature at which heat treatment should take place to produce a good interphase, tests were conducted on pieces comprising the CSA body and glass FLT2. The tests consisted of determining the bond strength between the body and the glass as heat-treatment temperature was modified. For this, laboratory test specimens were prepared, as schematically illustrated in Figure 4, which were subjected to tensile strength tests in a universal testing machine. The bond area between both layers was kept constant at 11.5 cm^2. In addition, the (non-polished) cross-section of some of the test specimens was observed by scanning electron microscopy (SEM).

5.2. RESULTS

Figure 5 depicts the evolution of bond strength, expressed in N/mm^2, as a function of maximum fusing temperature.

It was observed that after heat treatment at 600°C the two layers had not fused, because this temperature was below that of frit fusion start. The fusing process began around 615°C, at which the bond strength was 0.07 N/mm^2. After this temperature an exponential increase in bond strength was observed up to 650°C. At temperatures above 675°C it was found, during the tensile strength test, that fracture of the glass occurred in a zone outside the contact area between both layers. This indicated that the bond strength between both layers was greater than the mechanical strength of the glass sheet. These results enabled establishing 675°C as the minimum temperature at which the heat treatment needed to be performed.

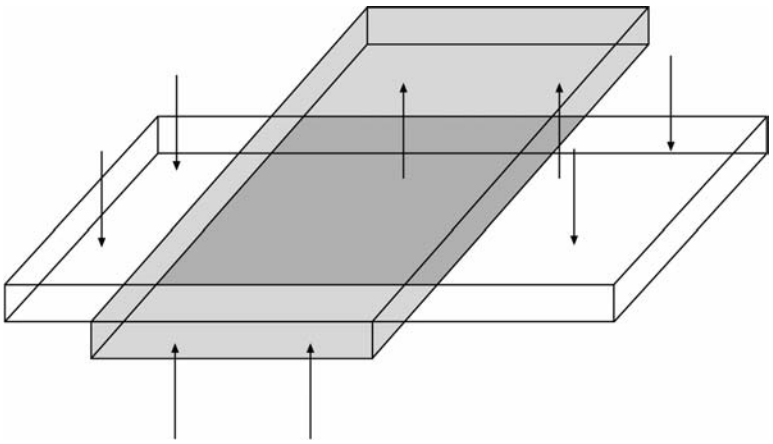

Figure 4. Schematic illustration of the test arrangement for determining tensile strength.

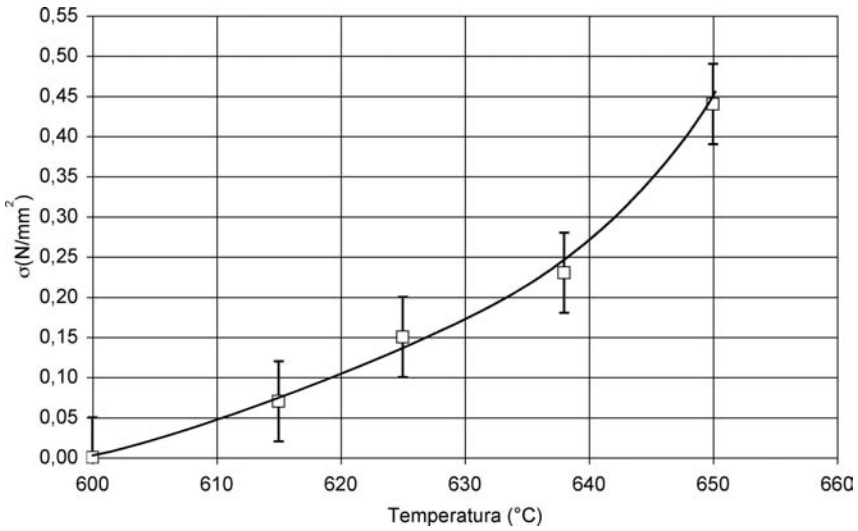

Figure 5. Evolution of tensile strength with temperature.

Figure 6 shows the appearance of the interphase between both layers after heat treatment at 675°C. The body can be clearly distinguished in the bottom area of the picture, together with the lighter-coloured frit layer in the middle, and the glass in the top area. The following can be observed in the micrograph:

- Porosity is present in the frit layer, mainly consisting of small pores (<10 μm).
- There is a slight diffusion of frit components (of a lighter colour) into the glass.
- There is a good interphase between the glass and the frit, as the fracture planes include both layers.

In order to observe whether an increase in temperature produced any improvement in the interphase, in particular between the frit and the body, the interphase of a piece treated at a higher temperature, 750°C (Figure 7) was observed by SEM. The micrograph shows that the number of pores has decreased, although they have increased in size, that the frit–glass interphase has become much thicker, and that the fracture planes exhibit continuity between the frit and the body. This effect is due to the increased diffusion of the different components of the glass, frit and body with higher temperature, thus giving rise to an interphase of intermediate composition that favours the bond between the body and the glass.

These results indicate that, although the temperature of 675ºC is already considered appropriate for obtaining good adhesion of the body to the glass, treatment at higher temperatures will considerably enhance the body–glass bond.

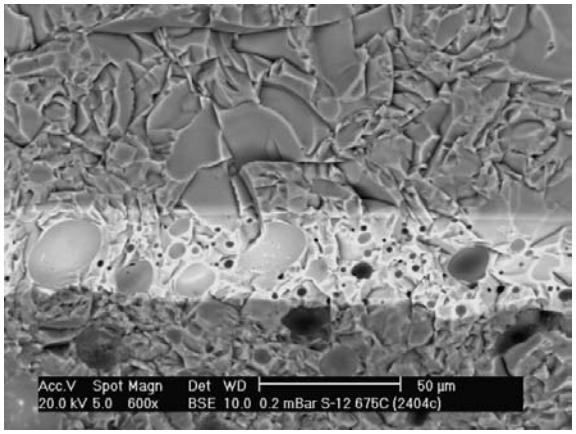

Figure 6. Appearance of the interphase. T=675 °C.

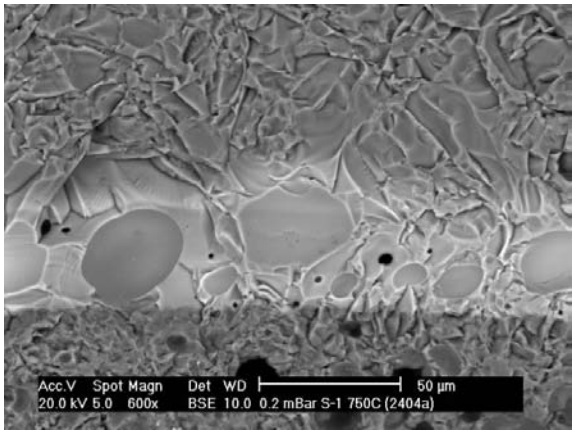

Figure 7. Appearance of the interphase. T=750 °C.

6. CONCLUSIONS

The feasibility has been studied of using sheets of glass in the manufacture of ceramic tiles. The most significant results have been as follows:

- Commercial **sheets of glass** with appropriate properties for use in interior wall cladding and facades **have been characterised**. Their use for flooring is more limited, although there are some glasses with good properties.
- **Special body compositions** with properties similar to those of porcelain tile **have been developed**, whose thermal expansion matches that of each type of commercial glass, obtained by introducing frits into the body formulation.

- **To fuse the glass sheet with the ceramic body a ceramic glaze has been developed** which enables obtaining an interphase with good properties at the working temperature.
- **New compositions for the manufacture of glass sheets have been developed** which display better-balanced characteristics than commercial glasses with normal tile bodies.
- **This process has already been applied industrially** in the case of wall tile, and has yielded fully industrial pieces of 30 x 30, according to the following stages:
  - Spray drying of the body composition in a spray dryer.
  - Pressing.
  - Firing of the body at T=1180ºC.
  - Decoration of the ceramic body.
  - Application of the interphase glaze.
  - Application of the commercial glass sheet.
  - Firing of the glass at low temperature T=760ºC.
- **In the case of floor tile it is intended to improve the specular gloss properties of the pieces**, which are obtained at present by polishing the body (technical porcelain tile), or by polishing an important layer of glaze, generally grits. Since the polished surfaces always exhibit greater imperfections and porosity than vitrified ones, in this case glass sheets with high toughness (and low thermal expansion) have been applied on a laboratory scale onto a special body, appropriate for these types of glass sheets.
- **The decorative possibilities of the ceramic pieces obtained** by this technique are far superior in colour, definition and design to those obtained at present.
- **Given the enormous variety of different products that could be obtained** it is possible to enter new market segments in which ceramic tiles have not been considered appropriate until now.

REFERENCES

[1] ESCARDINO BENLLOCH, A. Y GONZÁLEZ CUDILLEIRO, M. (COORD.) *Azulejos y pavimentos cerámicos españoles*. [Castellón]: AICE, [1991].

[2] MORENO, A.; TOLEDO, J.; GAZULLA, M.F.; GARROTE, R. Toughness measurement in ceramic glazes. In: *Proceedings of the IV World Congress on Ceramic Tile Quality*. Castellón. Cámara Oficial de Comercio, Industria y Navegación. Vol. II, 731-732, 1996.

[3] MORENO, A.; MONTIEL, E.; TOLEDO, J.; ESCARDINO A. Relación entre las propiedades mecánicas de vidriados cerámicos y su comportamiento al someterlos a tensiones externas. *Cerámica Información*, 195, 2-9, 1994.

[4] WANG, C.; WEI, X.; YUAN, H. Polishing of ceramic tiles. *Mater. Manufact. Process*. 17(3), 401-413, 2002.

[5] FERNÁNDEZ NAVARRO, J.M. *El vidrio*. 3ª. Madrid: CSIC, 2003.

[6] GARCÍA-TEN, J.; MORENO, A.; QUEREDA, M.F.; SABURIT, A.; GARCÍA-SAINZ, J.; MANRIQUE, J.; USÓ, J. New high-performing ceramic tile compositions. In: *Proceedings of the VIII World Congress on Ceramic Tile Quality*. Castellón. Cámara Oficial de Comercio, Industria y Navegación. Vol.II, P.GI-415-432, 2004.

[7] ESCARDINO, A.; MORENO, A.; IBÁÑEZ, M.J.; BARBA, A. Relación entre las propiedades mecánicas de vidriados cerámicos y su resistencia al desgaste. *Bol. Soc. Esp. Ceram. Vidr.*, 39(2), 209-214, 2000

[8] SCHOLZE, H. *Glass: nature, structure, and properties*. New York: Springer-Verlag, 1991.