EFFECT OF THE PRESENCE OF CRYSTALS ON GLAZE WEAR RESISTANCE

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ABSTRACT

With a view to raising ceramic tile glaze wear resistance and better understanding the mechanisms that produce this increased resistance, this property was studied in glassy matrix composites containing crystals as reinforcing elements. The test specimens were made by adding the crystals (alumina, mullite, titanium oxide and zirconia) in various proportions (5, 10, 15, 20 and 25 vol%) in two matrices containing commercial frits as major components. Fired composite behaviour was determined with regard to microstructural characteristics, and the relation of these characteristics was established with the wear resistance measurements based on material volume loss, performed by the specifically designed test.

The influence of physical properties such as the difference in the coefficients of thermal expansion and Young's modulus between the crystals and glassy matrices were found to be attenuated by the development of continuous interfaces, which ensured good fit of the reinforcing phases. The rise in composite true porosity was found to be related to the great quantity of crystals added to the matrices. The results also show that the main characteristic responsible for the rise in specimen wear resistance was the hardness of the crystals added as reinforcing phases.

INTRODUCTION

Ceramic tile glazes are materials that are constantly subject to wear, this being one of the main factors in determining the durability of ceramic flooring.

Depending on the way abrasive wear occurs, it can be classified as two-element or three-element abrasion. In two-element abrasion, the abrasive particles move freely over the surface of the material, while in three-element abrasion, the abrasive particles act as an interface between the two surfaces.[1]

In the abrasive wear mechanisms that have been advanced to explain how material is removed from a surface, micro-chipping is the mechanism fitting wear in brittle materials most closely, and hence also that of glazes. In this model, the indentations and scratches produced by abrasive particles give rise to crack formation owing to high stress concentration. Micro-chipping takes place in glazes mainly by fracture caused by heavy abrasion. On applying a pyramidal type of indentation to a glaze surface, fracture appears through median vents and lateral vents. In an initial loading stage, a region of plastic strain develops around the indenter tip. When the load reaches a certain value, failure produced by the strain develops in the form of a small crack, known as a median vent. During load release, lateral vents develop from the median vent, running parallel to the surface. The loss of surface material arises as a result of lateral vent curvature in the direction of the surface, removing chips of material.[2]

Raising glaze wear resistance requires increasing glaze hardness. However, the introduction of chemical elements that heighten frit hardness also raise frit melting point, making industrial use unfeasible at the firing temperatures currently used by the ceramic tile industry. An alternative way of raising glaze hardness is using glass-ceramic composites, in which a crystalline phase, generally of greater hardness, is contained in a glassy phase. These composites can be produced in two ways: 1) by using frits that devitrify during firing, or 2) by incorporating crystalline powders together with the frits in the glaze formulations. The present study addresses the second glass-ceramic preparation method.

The interface between the matrix and the reinforcing phase is a discontinuity region that deserves special attention in obtaining glass-ceramic composites, as the fit of the reinforcing phase with the matrix needs to be sufficiently strong to prevent the crystals from separating during the abrasive wear process. The physical parameters for selecting the matrices and reinforcing crystals to be studied for improving this fit and concurrently heightening wear resistance include:

- Young's modulus: the ratio between Young's modulus of the crystal and matrix shall be larger than 1 ($E_c/E_m>1$).
- Coefficient of thermal expansion: it is desirable for the coefficient of thermal expansion of the matrix to be larger than that of the crystals ($\alpha_m>\alpha_c$). The difference in the value of this property will determine the extent of mechanical fit of the reinforcing phase.
- Hardness: the crystals shall exhibit greater hardness than the matrices.

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[1] Axén, N.; Jacobson, S.; *A model for the abrasive wear resistence of multiphase materials;* Wear, pp. 187-199, 174 (1994).

[2] Oliveira, A.P.M.; Rosa, F.G.; Alarcón, O.E.; *Efecto de la fracción volumétrica y la granulometría sobre el mecanismo de abrasión en los esmaltes cerámicos;* Anais Qualicer, pp.169-181, Castellon, España (1994).

EXPERIMENTAL PROCEDURE

MATERIALS

Two commercial frits (A and B) were used. Table 1 presents their chemical composition. These frits exhibited no significant devitrification during heat treatment, as shown by differential thermal analysis (DTA) at a heating rate of 10°C/min up to 1200°C. The oxide composition shows that the frits mainly differed in ZnO content. Table 2 details the physical properties of the frits.

	Oxide %														
Frit	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**Na_2O**	**K_2O**	**MnO**	**TiO_2**	**MgO**	**P_2O_5**	**BaO**	**ZnO**	**ZrO_2**	**B_2O_3**	**PbO**
A	60.16	7.51	0.05	13.08	<0.01	4.08	0.01	0.03	0.84	0.04	0.84	11.41	0.85	1.09	----
B	64.73	8.42	0.12	11.06	0.86	3.00	0.01	0.04	0.70	0.04	0.91	5.49	0.84	3.77	----

Table 1. *Chemical analysis of the frits used.*

Frit	**Hardness (Mohs)**	**Density (g/cm^3)**	**$E^{(1)}$ (GPa)**	**$\alpha^{(1)}$ (10^{-7} °C^{-1})**
A	6 – 6.5	2.66	30	64.60
B	6 – 6.5	2.57	27	58.40

(1) theoretical values calculated by a specific software used for frit formulation.

Table 2. *Physical properties of the frits used in formulating the glassy matrices.*

The criterion adopted for selecting the crystalline phases was based on the difference in properties (hardness, Young's modulus and coefficient of thermal expansion) between the matrices (Table 2) and the crystals (Table 3), using five types of crystals for the present study.

Reinforcing crystal	**Hardness(1) (Mohs)**	**Density(2) (g/cm^3)**	**$E_c^{(1)}$ (GPa)**	**$\alpha_c^{(1)}$ (10^{-7} °C^{-1})**
Alumina (Al_2O_3)	9	3.961	380	88
Magnesia (MgO)	5.5	3.481	207	140 (20°C) 90 (0°C)
Zirconia (ZrO_2)	6.5	5.780	207	100
Titanium oxide (TiO_2)	6 - 6.5	4.196	283	94
Mullita ($3Al_2O_3.2SiO_2$)	6 – 7	3.201	145	58

(1) Theoretical values.
(2) Measurement performed by helium gas pycnometer.

Table 3. *Physical properties of the crystals used as reinforcing phases.*

Of the crystals listed in Table 3, alumina, zirconia and mullite were raw materials produced by electrofusion, supplied by *Elfusa Geral de Eletrofusão Ltda.* Titanium oxide (2059) was made by *Kronos*. All the crystals were used with particle sizes between 44 and 74 μm.

TEST SPECIMENS

Initially, wet milled material (Table 4) ground in a high-speed planetary mill with high alumina balls was used to prepare the test specimens. Milling lasted until a 2-3% solids reject was obtained on an ASTM No. 100 mesh. After drying and breaking up the materials, the crystals were added in quantities of 5, 10, 15, 20 and 25 vol%. The different glaze compositions, with and without crystals, were wetted and homogenised with 6 wt% water, subsequently pressing uniaxially at 150kgf/cm^2, forming rectangular test specimens measuring 5.0 x 5.0 cm with a mass of 20g.

After drying, the pressed specimens were fired using a 45-min cycle and peak firing temperature of 1150°C with a 5-min hold at this temperature.

Material	wt%
Frit (A and B)	59.34
Water	35.37
Kaolin	5.18
Carboxymethylcellulose (CMC)	0.071
Sodium tripolyphosphate (STPP)	0.039

Table 4. *Milling charges.*

TEST SPECIMEN CHARACTERISATION

Specimen microstructure after firing was observed by scanning electron microscopy (SEM).

The values were determined of true porosity (PT) and sealed porosity (PF) of the specimens, using Equations 1, 2 and 3.

$$PT = \left[1 - \left(\frac{DA}{\rho_R}\right)\right] . 100 \qquad (1)$$

$$PA = (AA).(DA) \qquad (2)$$

$$PF = (PT) - (PA) \qquad (3)$$

where PA is apparent porosity, DA and AA are bulk density and water absorption respectively, determined by the method based on the Archimedean principle, and ρ_R is composite true density, calculated from each of the added crystalline phases (determined by helium gas pyconmetry) and applying the mixture linear rule according to the known fraction of each phase in the composite.

Equation 4 was used to derive the Vickers microhardness values (H_v) of the crystals and the matrices, where I is the measurement of the resulting diagonal of the indentation and P the applied load (100g for 10s).

$$H_V = \frac{1{,}854\,P}{l^2} \qquad (4)$$

To quantify the wear, specimens were cut with a cylindrical shape and diameter of 2.45 cm. Their surfaces were subsequently smoothed and polished. The tests were performed on a MINIMET 1000 automatic polisher adapted to hold the specimens. The arising random movements keep wear from occurring in preferential directions. Silicon carbide abrasive ASTM No. 120 was used, adding 5ml water to the test medium, thus producing a three-element abrasion test. The other fixed parameters were the rotation rate (50 r.p.m.) and applied load (5N). The resulting wear was quantified through the total percentage of material volume loss ($\%P_V$), this being determined by the ratio between the difference in mass of each specimen, before and after abrading, and corresponding specimen bulk density (DA).

RESULTS Y DISCUSSIONS

Observation of composite microstructure revealed that despite the severe specimen preparation conditions, which included polishing with silicon carbide particles of around 80 μm, no significant crystal separation was found. The presence of morphologically rounded, sealed pores was also observed, as shown in Figure 1. This porosity was probably due to bubble coagulation during glassy matrix sintering, while bubble elimination in the presence of a viscous liquid appears hindered by a growing crystal presence.

Figure 2 presents an assessment of specimen true porosity. The rising crystal addition to matrix A tended to raise true porosity, in which at values of 20 and 25% crystals, composite true porosity rose far above the porosities found for the actual matrix. High crystal additions to matrix B also tended to raise specimen true porosity.

In this study, the absolute values of porosity only indicate a comparison between different composites and they probably differ from the absolute values that would be obtained with the same materials if these were applied as glazes to ceramic tiles. This is because glaze coatings are much thinner (about 10 times), so that in the tested specimens the path for bubble removal is less free in fast-fire cycles. However, it can be said that the same tendency in behaviour was expected in both cases. Table 5 details the sealed porosity values found for the matrices and composites in this study. The presence of closed pores, observed in Figure 1, plays a very important role in ceramic tile glazes, as they are related to the dirt that can accumulate after abrasion and which can limit glaze abrasion resistance. Sealed pores, as well as true porosity, tend to increase with growing crystal additions to the matrices, i.e., during matrix sintering, the bubbles need to be removed through the specimen surface, while bubble movement in this direction is hindered by the presence of crystals. The observation of closed pores joined (or anchored) to the crystals is probably related to the decrease in surface energy produced by this arrangement.

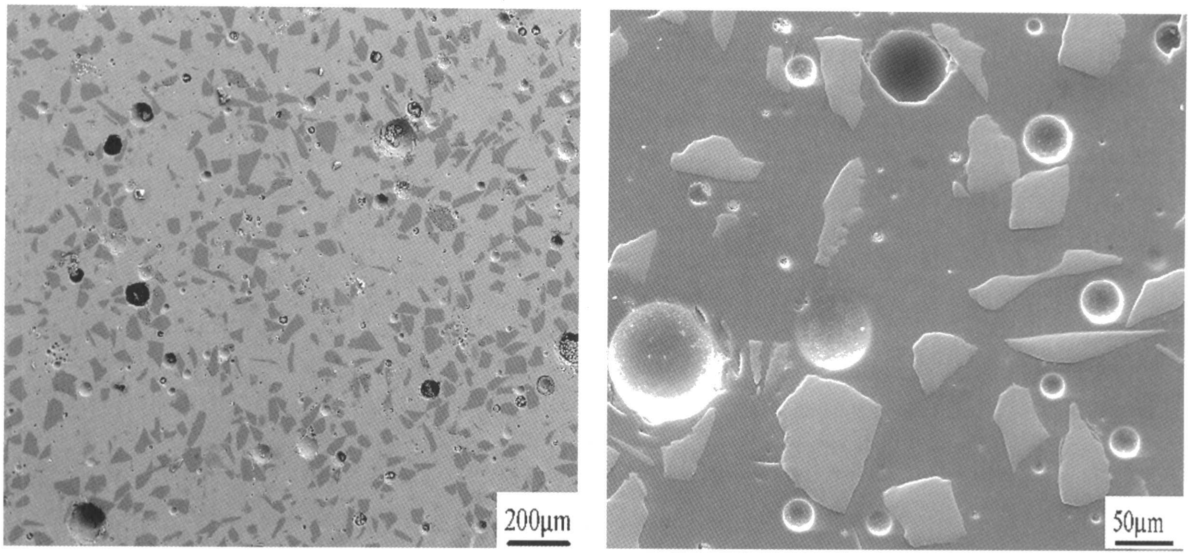

Figure 1. Composites containing: (a) 20 vol% mullite and (b) 25 vol% zirconia.

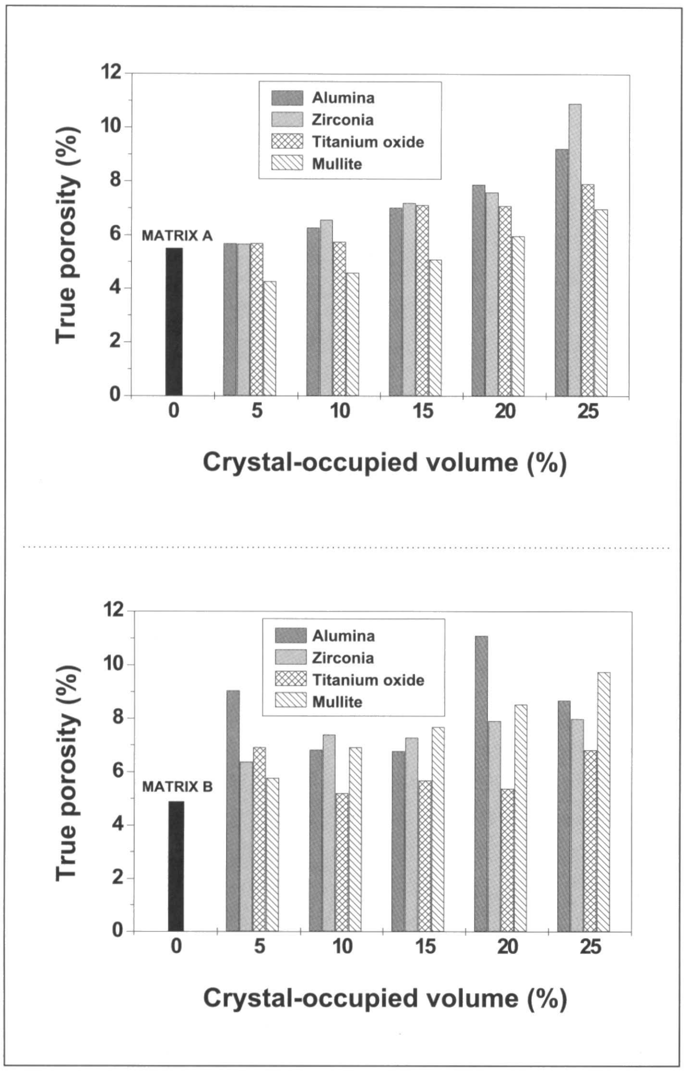

Figure 2. True porosity for composites with different crystal addition contents in matrices A and B.

The loss of material in the composites with matrices A and B, with high crystal additions, after a 10-min wear test is presented in Figure 3. In both matrices, a volume fraction of 5% corundum was enough to appreciably reduce the volume of removed material, and higher fractions contributed little to improve wear. In the composites with zirconia, volume loss started to stabilise at a 10% crystal addition to matrix A, and exhibited a more gradual reduction in volume loss when matrix B was involved. The use of titanium oxide as a reinforcing element exhibited a minor contribution (in the case of matrix B), even having a detrimental effect on wear resistance (in the case of matrix A), compared to the other crystals when large quantities of titanium oxide were added. On the other hand, the specimens with high added mullite crystal contents yielded a gradual decrease in volume loss of the studied composites. However, a 5% mullite addition was already enough to produce a reduction in volume loss of over 50% compared to matrices A and B without any crystal additions.

Matrix	Crystal volume (%)	Reinforcing crystal				
		----	Alumina	Zirconia	Titanium oxide	Mullite
A	0	4.244	----	----	----	----
	5	----	4.20	4.16	4.35	4.17
	10	----	4.64	4.73	4.57	4.47
	15	----	5.09	5.62	4.99	4.93
	20	----	5.98	5.68	5.35	5.78
	25	----	6.42	8.79	6.32	6.64
B	0	3.284	----	----	----	----
	5	----	7.56	495	5.33	4.41
	10	----	5.65	497	3.20	5.02
	15	----	5.04	544	3.40	5.89
	20	----	8.73	579	3.78	6.90
	25	----	6.63	562	5.02	7.71

Table 5. *Percentage data of sealed porosity.*

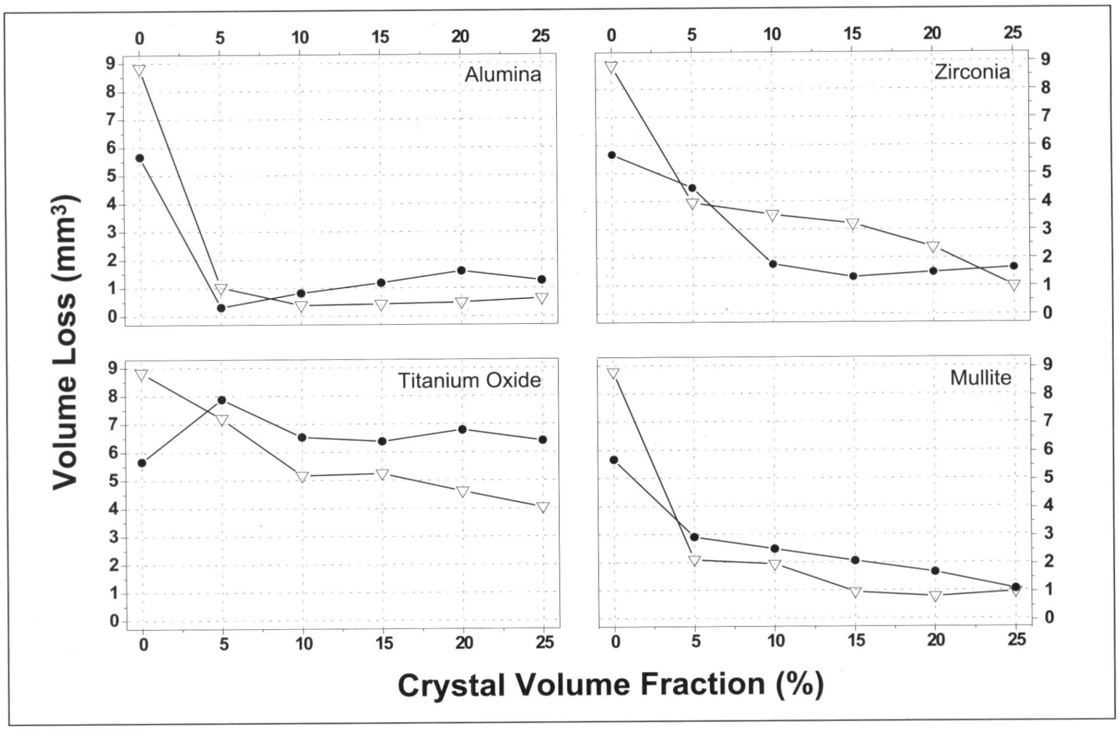

Figure 3 . *Volume loss found for matrix A (—●—)and B (—▽—) composites, after a 10min wear test.*

The addition of crystals, in the particle size range set for the study, in quantities of 10% of the total specimen volume, appeared to be ideal for enhancing wear resistance and at the same time keeping a sufficiently low porosity to avoid compromising the microstructure, i.e., making these composites feasible for use as glazes.

The observation that no reinforcing-phase separation occurred in the composites after the wear tests indicates that independently of the differences in the coefficients of thermal expansion and selected Young's moduli of the glassy matrices and crystals, good bonding was achieved in these composites. In the properties of the reinforcing phases, the one that decisively influenced decreased material volume loss was crystal hardness. Figure 4 shows the decreased tendency for material volume loss to arise in the bodies reinforced with particles of greater Vickers hardness, compared to the matrices without crystal additions.

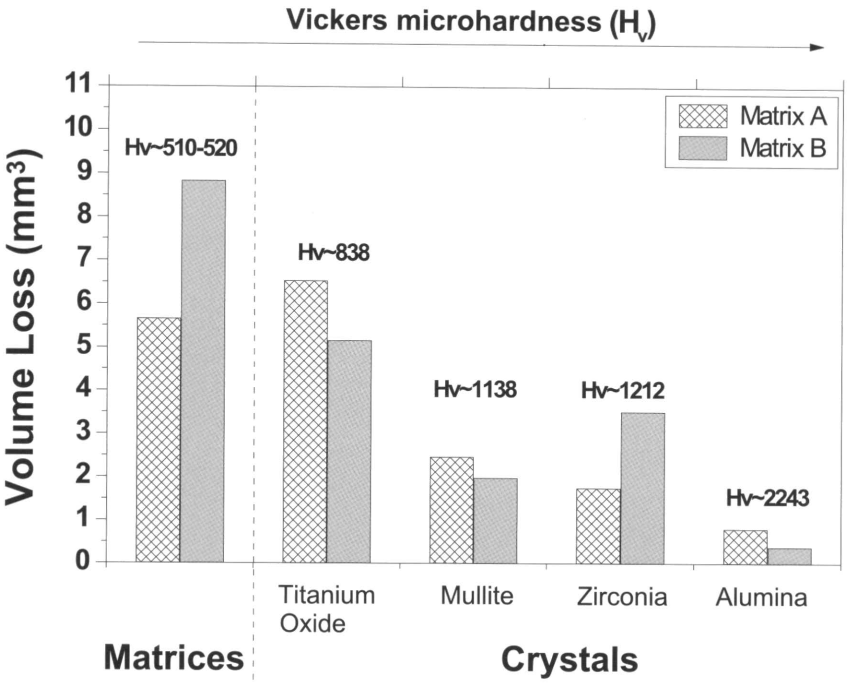

Figure 4. *Correlation between material volume loss (in specimens with 10% crystals, after a 10-min wear test) and Vickers microhardness of the matrices and crystals separately.*

CONCLUSIONS

The study has shown that the addition of a reinforcing crystalline phase to the glassy matrix produced a rise in abrasive wear resistance. The harder crystals used (in a particle-size range of 44-74μm), added in a 5-10 vol% to the composites, significantly reduced material total volume loss.

The porosity of the composites was strongly affected by the growing presence of crystals. Crystal volume fractions below 10% were found to be appropriate in specimens where the porosity values did not exceed those obtained in specimens without any crystal additions.

The studied differences in the coefficients of thermal expansion and Young's moduli between the matrices and the reinforcing phases did not significantly affect the material volume loss of the composites. This means that a large quantity of crystals can be used successfully for obtaining glazes reinforced with a second phase, without reinforcing-phase separation occurring as a result of the good interface properties in this type of composites.

The alumina, zirconia and mullite crystals yielded the best results with regard to wear. The high hardness of these crystals in respect of the glassy matrices to which they were added was found to be decisive to producing composites that exhibited low material volume loss on being subjected to abrasive wear.

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