EFFECT OF THE VOLUMETRIC FRACTION AND PARTICLE SIZE ON THE ABRASIVE MECHANISM IN CERAMIC GLAZES

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SUMMARY

Abrasion tests using the PEI - visual evaluation, rugosity and light's reflection techniques, were carried with the purpose to investigate the size and volumetric fraction effects of a reinforcing phase, on the ceramic glazes abrasive wear mechanism, based on the microstructural design. The microstructural design, elaborated from quantitative criteria shows to be suitable to predict the microstructure before firing process. The study of the microstructural aspects shows that when both, size and mean free path, of the reinforcing phase decrease and its volumetric fraction increases, the abrasive wear resistance increases. It was also observed, that a porosity reduction occurred when the size and volumetric fraction of the reinforcing phase decreased. The abrasive surface observation shows that the wear mechanism is characterized by multiple fractures of the conchoidal type, originated into the vitreous matrix, which can be evaluated from the indentation model for brittle materials.

1. INTRODUCTION

In the last decades, the research and development concerning the manufacturing technology of ceramic glazes have contributed very much to the quality improvement of the ceramic products, which have influenced significantlly to increase the product lifes. Recent publications [1,2,3,4] show that the investigations are directioned in most of the cases, to the study of abrasion resistance of the final properties of a ceramic glaze, whose purpose is to actuate like a coating of ceramic products destined to cover the surface on several of Society's sectors , the abrasion resistance is the most important, since it is decisive to product selection for a specific application. The abrasion resistance of ceramic glazes for ceramic floor tiles is a complex property, since its control is not directly related only to the material removing rate, but, specially, to the aesthetic aspect result from use.

The variation of the material removing rate is associated to the individual properties of the hardener particles and matrix, microstructural geometric parameters and the residual porosity; otherwise, the aesthetic aspect also requires a suitable combination of shine and colours. Based in these aspects, and

regarding that ceramic glazes usually have a microstructure like a composite material (vitreous matrix and dispersed hard crystalline particles), this work has as objetives to study the influence of the porosity and microstructural geometric parameters on the abrasive wear behavior of ceramic glazes formed by a vitreous matrix (brilliant transparent frit) reinforced by zircon crystalline particles with controlled size, distribution and volumetric fraction, with the purpose of establishing a methodology which allows the microstructure designs with high performance and a better understanding of the possible controller and limitator factors of the abrasion resistance. Knowing the microstructural factors which controlls the abrasion resistance, it is possible to design and obtain a suitable microsctructure to the use with optimized performance.

2. MICROSTRUCTURE DESIGN - THEORETICAL FUNDAMENTALS

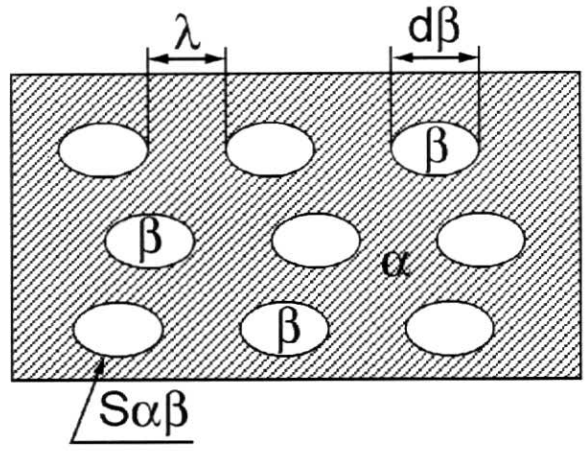
2.1 INTRODUCTION

Traditionally, the ceramic glaze layers deposited on the ceramic body are multiphase systems. Their microstructure consists of a high volumetric fraction of precipitates (crystalline phases) or dispersed phases, which have a hardness equal or higher than that of the abrasive particles. These reinforcing phases are obtained during the cooling process or are directly introduced into the vitreous matrix (frit) to form the desired composite. The reinforcing phases offer a good protection against abrasion, while the matrix is reponsible for overall thoughness and ceramic glaze bonding with the ceramic body. This technical result comes from a experimental confirmation (abrasive wear tests), but without controll of the microstructural variables, usually depending of the chemical composition, firing cycle and milling time of the elements which participate of the ceramic glaze.

The emphasis based on the microstructual design used in this work tries to establish a quantitative relation between microstructural parameters and properties, specially abrasion resistance. Knowing the microstructural factors which control the abrasion resistance it is possible to design and to obtain a suitable microstructure to use with maximum performance.

2.2 MICROSTRUCTURAL QUANTITATIVE MODEL

Figure 1 shows the important parameters for quantitative microstrutural analysis which have been established to describe two-phase materials [5,6,7].



$$\lambda = \frac{2d\beta(1-fv\beta)}{3fv\beta} \qquad (1)$$

$$S\alpha\beta = \frac{6fv\beta}{d\beta} \qquad (2)$$

Figura 1. *Microstrutural parameters in a two-phase material [7].*

Where:

$fv\beta$ = volumetric fraction of β phase [-];
$d\beta$ = size of β phase [μm];
λ = mean free path between β phase [μm];
$S\alpha\beta$ = total interfacel area [$\mu m^2/\mu m^3$]

Under defined conditions, a given phase shows a specific wear mode and wear rate, which is controlled by its individual properties. Consequently, when various phases are combined, forming a multiphase material, it is expected that the overall behavior will be a function of the corresponding contributions of each phase. Based on this approach, the wear resistance has been mathematically described by Khruschov in [7] as a linear function of the volumetric fraction of the occurring phases . Garrison in [7], demonstrated that Khruschov's model predicts the wear behavior of multiphase materials only when each phase shows a wear rate proportional to the applied load. That is the case of ductile materials. However, when hard phase and ceramic materials are involved, the wear rate is not linear. Another important point is the particle-matrix interfacial bond strength.

The model proposed is this work (fig. 1) is based in no-phase interaction for uniform spherical particles. In order to better understand the mechanism involved in the total tribological system, the interacting effects among the geometrical factors will be analysed. The total abrasive action on the multiphase system is considered to be a macroscopic sum of each microscopic effect produced by an individual abrasive particle. Each of these wear microevents generates a groove in the material. It is expected that the reinforcing role of a dispersed phase may change when its size and mean free path is higher or lower that the abrasive particle size. This concept reflects the intensity of the abrasion phenomenon and takes into account abrasive properties, such as hardness, chape and size, and it includes the load which the abrasive particle is subjected to on the surface.

The relationship between composite microstructure and abrasive microevent is shown in Fig.2 in schematic form. The figure is based on the hypothetical analysis of a two-phase composite subjected to abrasion.

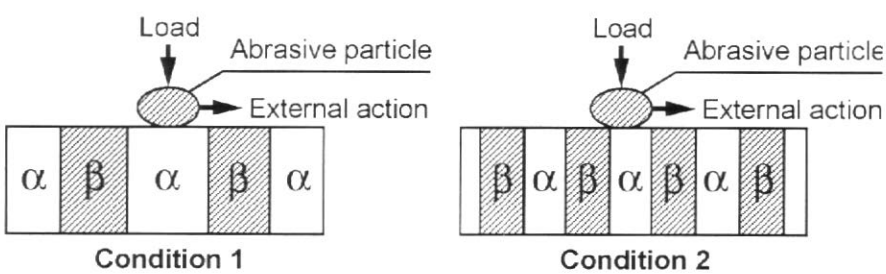


Figura 2. *Relation between the microstructural parameters, regarding an abrasive microevent. Condition 1 : mean free path higher than the abrasive particle size ; Condition 2 : mean free path lower than the abrasive particle size [7].*

The condition 1 (in Fig. 2) represents a small abrasive particle comparing to the size of the microstructural phases. The abrasive particle wears α and β alternately in an independent manner. Interfacial effects are not expected to be involved to any great extent. The specific wear mode of each phase independently would essentially contribute to the total wear rate. In condition 2 (also shown in Fig. 2), the microstructural parameters are lower or equal than the abrasive particle size. Abrasive action is produced simultaneously on α and β and also on the interface. In this case, the interface may play a more important role in the overall wear behavior.

This quantitative model, which establishes a hyphotetical relation of interaction between abrasive particle and microstructure as a causer of the material's wear, is the theoretical base established for the study of the effect on the size and distribution of particles in the abrasion wear resistance and mechanism.

3. EXPERIMENTAL PROCEDURES

The raw materials used were a non-alkaline brilliant transparent frit (vitreous matrix) and zircon (hardener element) . The designed conditions for study are shown in Table 1, where two mean particle sizes ($d\beta$ = 34.0 and 48.5 μm) and three mean free paths (λ = 60 , 120 and 180 μm) were established. Using the equations (1) and (2) the volumetric fractions and the interfacial areas $S\alpha\beta$ were calculated.

Table 1. *Design compositions*

Composition	λ [μm]	$d\beta$ [μm]	$fv\beta$ [-]	weigth %	$S\alpha\beta$ [mm^2/mm^3]
1	-	-	0.00	0.00	0.00
2	60	34,0	0.274	39.17	48.35
3	120		0.159	24.39	28.05
4	180		0.112	17.71	19.76
5	60	48,5	0.350	47.88	43.40
6	120		0.212	31.46	26.23
7	180		0.152	23.42	18.80

The milling process, mixing and deposition were conducted by the usual laboratory method. To avoid the body interferences in the porosity evoluation, the ceramic glaze deposition was made on an inertized ceramic body. The samples were fired in a fast cycle laboratory furnace at the temperature of 1170 °C, which was determined by the viscosity method described by Vogel-Fulcher-Tamman [8,10,11,13] following a single fast-firing cycle. The abrasion wear resistance was evaluated by the PEI - method (EN - 154) and ISO/TC 189 project for a staining test, and a quantitative determination of the material loss, during the abrasive test was determinated from a laser rugosimeter. Also, a measurement technique based in reflected light model POZ-01 was developed, with the finality of quantify the effects from visual analysis of the abrasive wear, which allowed to determinate the reflected light, in Volts, from the non-abrased and abrased surfaces, in two different levels of revolutions. The device is formed by an illumination system (white light) and lenses which produce parallel rays , which reach the sample obliquely , illuminating all the abrased area , the reflected light rays reach a LDR resistor type which is conected in series association to a conventional resistor, being the assemblage excited by a continuous tension of 10 V (stabilized source). The tension on the LDR resistor is measured by a digital voltmeter of 3 1/2 digits (reading erros of 0.2%).

The quantitative determination of the microstrutural parameters including the residual porosity and the wear mechanism study were conducted in an optical and scanning electron microscopes.

4. RESULTS AND DISCUSSION

4.1 FRIT´S PHYSICAL CHARACTERIZATION

The initial step results of the frit's physical characterization which made possible the fire gap determination and consequently, the fire temperature selection, are shown in Fig. 3 and Table 2.

Table 2. *Frit's characteristic viscosity points*

Material	Tg [°C] $\eta = 10^{13}$P	Tw [°C] $\eta = 10^{10.25}$P	Tm [°C] $\eta = 10^{4.55}$P	Temperature fire gap [°C]
Frit	659	793	1156	1156-1370

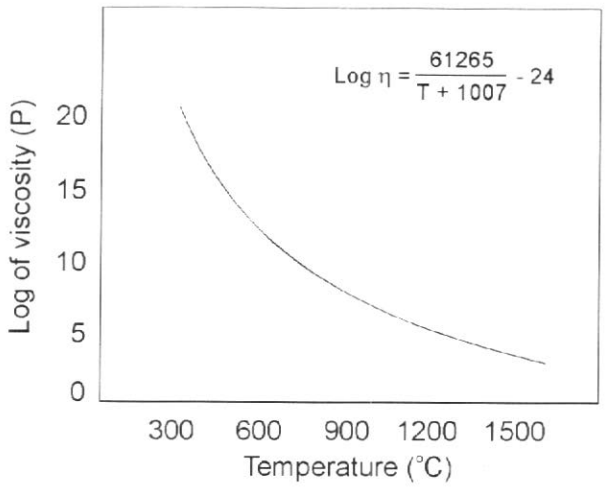


Figura 3. *Log η vs. temperature of the frit.*

From these data the fire temperature of 1170 °C was chosen, being all the samples subjected to the same thermal cycle of fast single fire.

4.2 MICROSTRUCTURAL CHARACTERIZATION

The microstructure and residual porosity aspect in some of the ceramic glaze layers studied including the frit and the zircon powder are shown in a micrograph of the fig. 4.

The micrographs (fig. 4) show the zircon crystalline phase whose colour is white and irregular morphology distributed randomly, the vitreous matrix (frit) whose colour is gray and pores. The morphology of the zircon particles is maintained, since the zircon is not dissolved in the fire temperature (1170 °C) and by comparing of the fig. 4 (d) with the other ones, the porous rounded shape which was observed in all the compositions indicates that the fire temperature was suitable. The microstructural parameters and residual porosity measured are shown in Table 3, including the designed microstructural parameters.

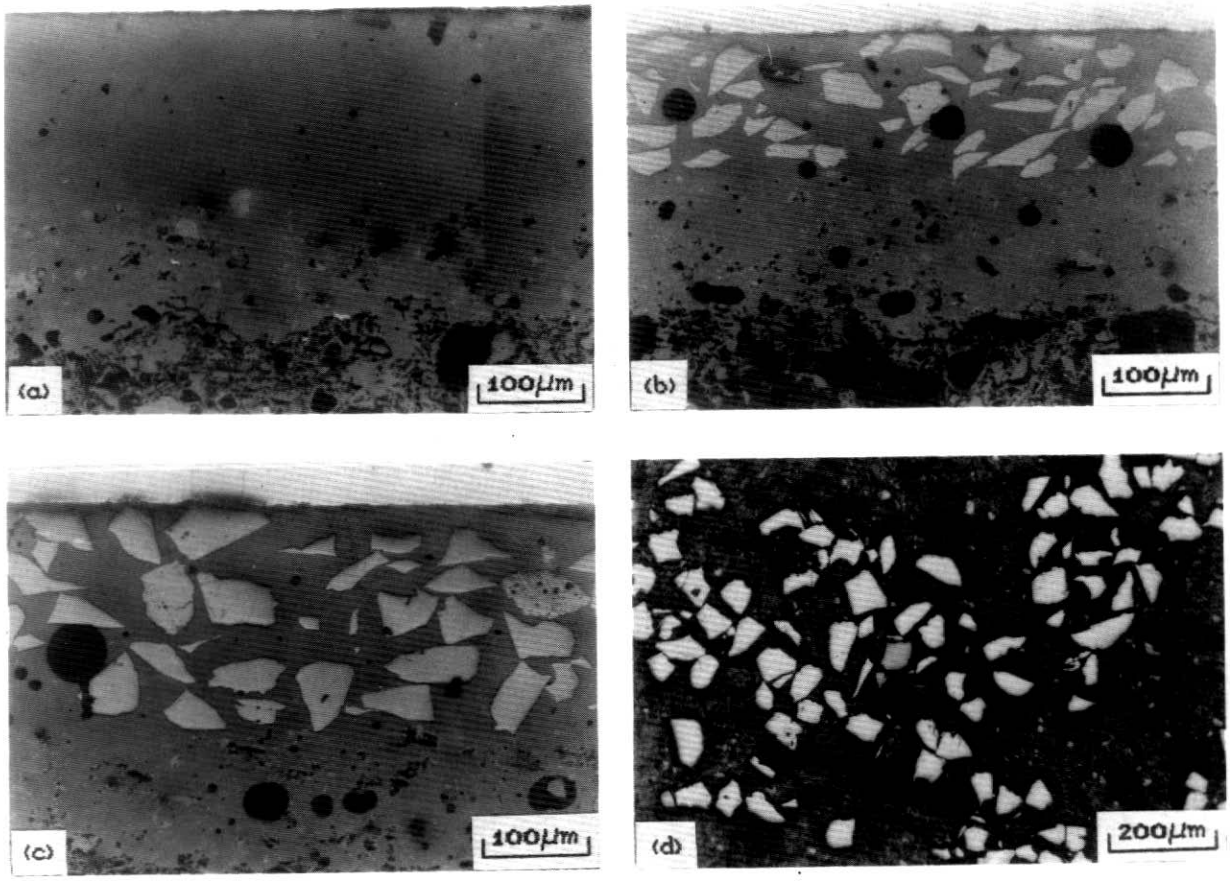


Figura 4. *Ceramic glazes and zircon powder optical micrographs, polish only - non-etched. (a) pure frit; (b) $fv\beta=0.273$, $d = 47.74$ μm, $\lambda = 22.35$ μm; (c) $fv\beta = 0.300$, $d = 83.00$ μm, $\lambda = 47.16$ μm; (d) zircon powder.*

The Table 3 shows that the pores/mm^2 number decreases when the zircon volumetric fraction increases, being this influence more accentuated for the composition groups with smaller mean zircon particle size. The pores/mm^2 number decrease is a consequence of the vitreous phase volumetric fraction decreasing , since, its decreasing is associated to the zircon volumetric fraction increasing ,and that, the porosity is originated in the vitreous phase.

The total porosity increasing , as a consequence of the zircon volumetric fraction increasing and the mean free path decreasing is a result of the anchoring, generating , consequently, the bubles growing during the firing process , like the case of compositions 2 and 5.

The comparison between measured and designed microstructural parameters shows , as expected, that deviations for λ parameter, are related to the size difference between measured and designed particles. Since this technique of granulometric separation of the employed additive was made by sieving. However, it was possible to get a mean free path variation which made it possible to investigate the desired effect. In fact, a measured and designed microstructural parameter optimization can be later obtained knowing the particle mean size distribution, after sieving, since, the mean size obtained for this selection technique shows a tendency to be higher than the estimated mean value, due to the irregular morphology of the particles, which are chracterizated by a high relation length/width . Consequently, the λ designed is larger than the λ measured.

Table 3. Measured and design microstructural parameters and porosity.

Composition	d [μm]	λ [μm]	fvβ [-]	Pores/mm^2 Number x 10	Total porosity [%]	pores % < 50 μm
1	-	-	-	21.20	0.61	100.00
2	(34.0) 47.74	(60) 22.35	(0.274) 0.273	9.20	5.31	100.00
3		(120) 39.57	(0.159) 0.134	12.40	2.13	100.00
4		(180) 60.33	(0.112) 0.112	13.40	1.08	100.00
5	(48.5) 83.00	(60) 47.16	(0.350) 0.300	7.80	12.12	64.11
6		(120) 87.23	(0.212) 0.234	13.75	2.03	100.00
7		(180) 105.32	(0.152) 0.155	17.80	2.80	75.00

( ) Design microestructural parameters.

4.3 ABRASION RESISTENCE CHARACTERIZATION

The results concerning to the behaviour under abrasive wear condition are shown at Fig. 5. Under a view point of PEI - classification the better results obtained were for compositions 1, 3,4 and 7, which show the classification PEI - V. However, these results are in contradiction with those obtained by abrasive wear physical evaluation, by the rugosimeter method. In this case, the compositions with better performances (lower material loss) are 2 and 5, which , correspond to the lower mean free path to the higher volumetric fractions, as was expected from the microstructural design concept. This observed contracdition is typical of the PEI - evaluation criteria, since this evaluation is based in visual criteria, were the contrast, shine and colour are factors who contribute to difficult the evaluation. In fact, the surfaces 1 and 2 show the higher relative reflections when subjected to the reflectometer.

This observation contributes to the understanding of the contracditory results obtained by PEI - evaluation and rugosimeter. The tests employing the reflectometer proposed in this work, show to be a complementary tool to the PEI and rugosimeter methods.

Besides of the possibilities to obtain indirect measurements of the rugosity , in physical unities (Volts), the method can characterize the contrast between the non-abrased and abrased surfaces . Thus, lower values of reflected light indicate higher values of rugosity and lower values of brilliance, and higher values of relative reflection are related to high contrast.

Composition	Reflection [V]		Rugosity - Ra [μm]	
	N = 0	N = 1500	N = 0	N = 1500
1	7.15	6.66	0.24	1.13
2	6.95	6.33	2.38	2.80
3	7.17	6.67	0.60	1.80
4	7.08	6.66	0.24	1.49
5	6.23	5.73	6.24	11.8
6	6.98	6.52	1.14	2.04
7	7.18	6.72	0.56	1.49

N = Revolution number

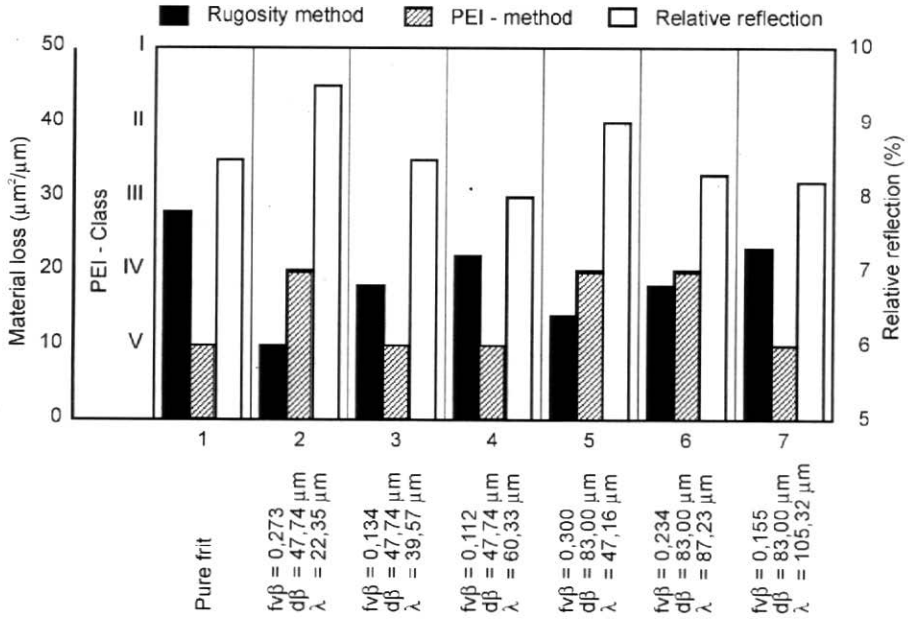


Figura 5. *Abrasion test results*

4.4 WEAR MECHANISN ANALISYS

The abrasive wear of brittle materials and specially of ceramic glazes is a complex phenomenon of difficult quantification, because it depends of a lot of factors , like hardness and surface rugosity, elasticity modulus, thoughness, and microstructural factors like crystalline phase and residual porosity [9,11,12]. Meanwhile, despite of many empirical investigations on the removal rate of materials in abrasive wear conditions, the understanding of wear mechanism is still not well known, because it is a fundamental requisite for the development of materials with optmized microstructural characteristics of abrasion resistance. In the particular case of ceramic glazes subjected to the abrasive wear by PEI - method , the material removal occurs due to the movement of particles harder than the vitreous material, under the action of mechanical forces parallel to the surface, producing the grooving and later the chipping and removal of material like it is shown in fig. 6.

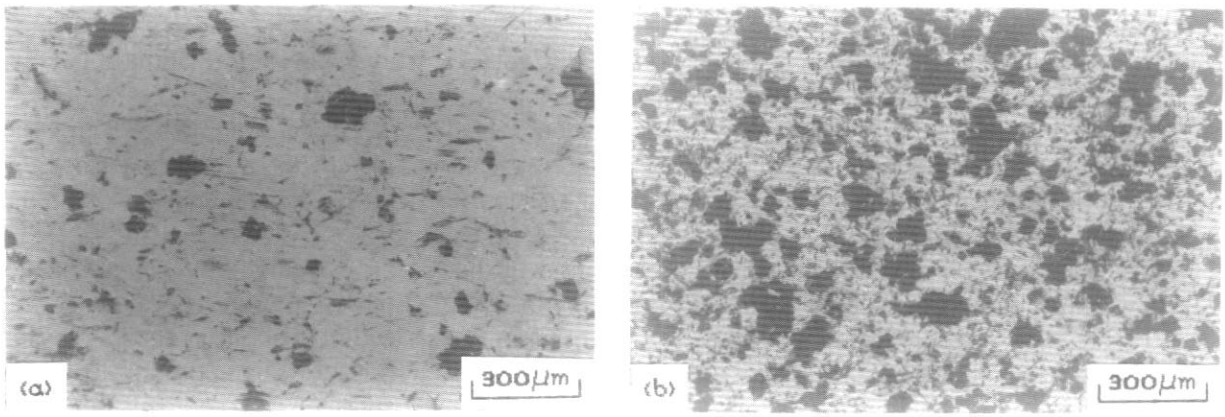


Figura 6. *Optical micrographs on a abrased surfaces, showing the abrasive wear evolution by PEI - method for the frit (a) 150; (b) 1500 revolutions.*

The surface aspect shows that the material removal occurs by the pulling out produced by localized small cracks in small material areas forming holes , with dimensions of approximately 10 to 250 μm of diametral extension.

Based in wide studies of the fracture mechanism during static indentation and localized impact , many authors [14,15,16] conviction has grown that the methods of fracture mechanism analysis by identation can be applied to help the understanding of fracture mechanism of vitreous materials. A fracture mechanism model with material removal which was recently indentified by several researchers [14,16] is the lateral fracture, which can be produced by the application of a load by an indentator (Vickers pyramidal diamond) at the material surface studied , and by the later analysis of the damages caused to this surface through optical and scanning electron microscopies. A schematic representation of the lateral fracture mechanism is presented at fig. 7.

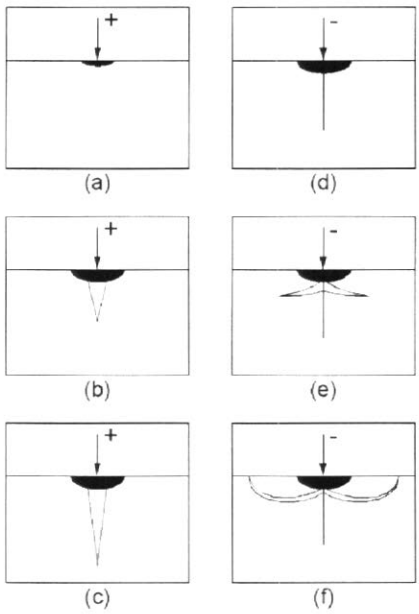


Figura 7. *Schematic of vent crack formation under point indentation. Median vent forms during loading (+) half-cycle, lateral vents during unloading (-) half-cycle. Fracture initiates form inelastic deformation zone (dark region) [15,16].*

The basic sequence of the events and subsequent crack propagation is the following [15,16]:

(a) initial loading : the sharp indenter induces a zone of irreversible deformation about the contact point. The size of this zone increases load;
(b) critical zone formation : at some critical indenter load a crack suddenly initiates below the contact point, where the stress concentration is greatest. This crack, commonly termed the median vent, lies on a plane of symmetry in the applied field. Its orientation depends on the indenter geometry.
(c) stable crack growth : increasing the load causes further, stable extension of the median vent;
(d) initial unloading : the median vent begins to close but not heal ;
(e) residual-stress cracking : relaxation of deformed material within the contact zone just prior to removal of the indenter superimposes intense residual tensile stress upon the applied field. Sideways-extending cracks, termed lateral vents, begin to appear;
(f) complete unload : lateral vents continue to extend, and may cause chipping.

The cross section observation of the observated samples by optical microscopy, as shown the fig. 8 , supplies a clear evidence of similarity between fracture model produced by an identer and that produced on the abrased ceramic glaze, which elucidates the mechanism of initial hole formation by lateral crack propagation.

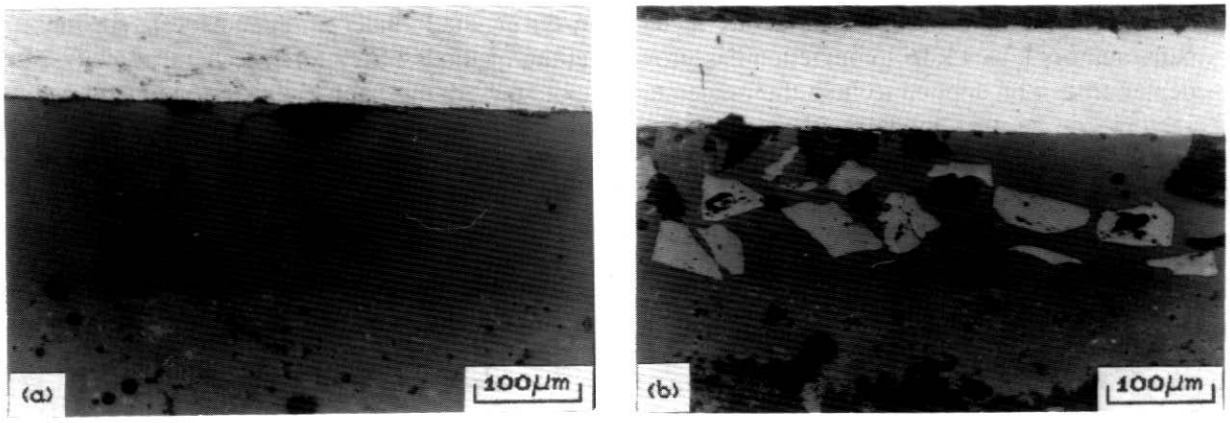


Figura 8. *Optical micrographs of the surface cross section abrased by PEI method (a) frit, (b) fvβ = 0.155, dβ = 83μm, λ = 105.32μm.*

The development of these cracks, therefore, will depend on the residual stresses created by abrasive particles (or by the indenter) when the particle looses contact with the surface. Its extension will depend, consequently, on the applied normal load caused by the abrasive particle on the ceramic glaze surface, the particle size and the material microstructure. In this particular case the most important microstructural parameter is the mean free path between the microstructural reinforcing particles. The microstructural evidences (wich can be seen at fig. 9) show in a sequence, the involved steps on the material removal process : grooving, lateral crack formation and hole formation. Figs. 9 (c) and (d) show the mean free path and reinforced particles size effects on the material removal mechanism. It can be seen a decrease of hole medium size with the decrease of reinforcing particle size and mean free path.

However, a reduction of the mean free path difficults the abrasion process in two manners. Statistically, the abrasive particles will have lower contact with the vitreous matrix, inhibiting the abrasive process development, i.e., difficulting the critical residual stress production , in order to produce the nucleation and propagation of lateral cracks.

On the other hand, the reinforcing particles being near each other, can easily actuate like "crack arrest", producing, consequently, lower size holes . The experimental evidences do not allow a clear understanding of the particle mean size effects on the abrasion resistance, since its effect can be confused with the mean free path.

However, as the lower size particles supply higher resistance than those of the higher size, these lower size particles must atenuate the abrasive wear process, since it is reasonable to suppose that the reinforcing particles participate of the abrasive wear mechanism , interacting with the main crack or nucleating secondary cracks.

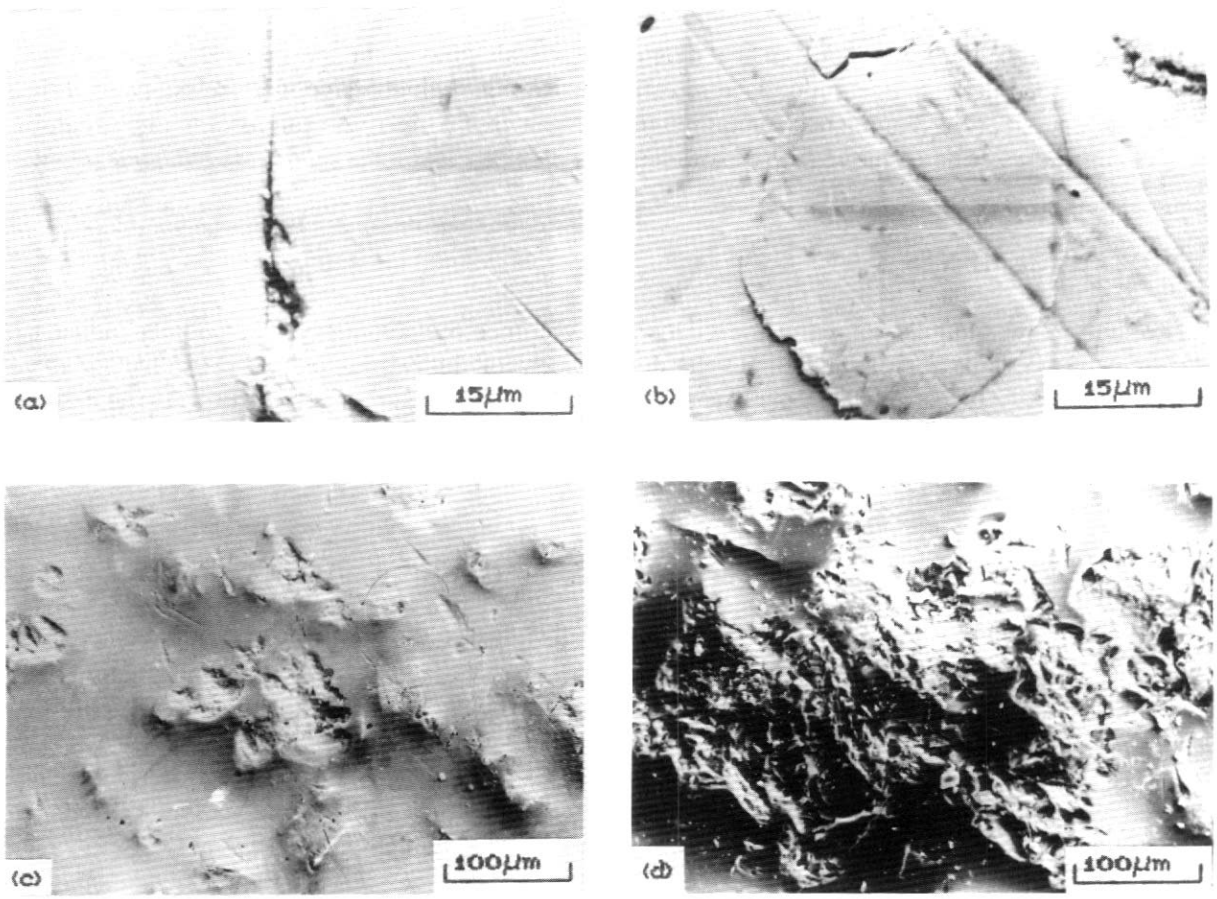


Figura 9. *Micrographs of the abrased sample surfaces obtained by scanning electron microscope. (a) grooving formation; (b) lateral crack formation, (c) holes formation, $fv\beta = 0.273$, $d\beta = 47.74\mu m$, $\lambda = 22.35\mu m$; (d) holes formation, $fv\beta = 0.300$, $d\beta = 83.0\mu m$, $\lambda = 105.32\mu m$.*

5. CONCLUSIONS

- The porosity of the studied ceramic glaze layers increases with the increasing of the zircon particle volumetric fraction , particularily for those compositions with higher zircon particle sizes, although the mean free path has been higher for a same volumetric fraction.

- The obtention of low porosity is a factor which contributes for the abrasing resistance increasing by the PEI - visual evaluation method, since the staining test is directly related with this factor.

- The abrasion resistance (material loss) measured by the rugosimeter increases with the volumetric fraction increase, and with the zircon particle size reduction and mean free path.

- The abrasive wear mechanism analysis based on the lateral fracture mechanism by indentation has shown to be suitable to auxiliate on the fracture mechanism understanding with material removal of vitreous materials .

- The utilization of the reflected light technique - model POZ -01 , developed in this work for the quantification of the effects originated from the visual analysis of the abrasive wear, is a complementary tool for the diagnosis of the abrasive wear evaluation of ceramic glazes.

- At last, it is important to sign that from a practical view point the microstructural design concept can help in a ceramic glaze selection that needs high abrasive wear resistance. In this case, the size, the volumetric fraction and the mean free path of the reinforcing phase can be optimized relating to the abrasive particle sizes.

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