STUDY OF WEAR RESISTANCE OF PORCELAIN GLAZED TILES BY THE PEI METHOD: EFFECT OF GLAZE TYPE AND CORUNDUM ADDITION

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RESUMEN

Nowadays, beyond aesthetics, durability and safety in use have been highlighted in the selection of ceramic tiles by the consumer. Therefore, industry providers must specify adequately the location and applicability of their products. In this sense, this study sought to obtain a glaze that promotes the increase in wear resistance of ceramic tiles without producing changes in aesthetic characteristics such as brightness, colour and texture. In the work, two glaze matrices were selected with regard to the boron content of their compositions, and the glazes were reinforced by corundum particles. A 2^k+1 full factorial design was selected, resulting in nine formulations. The corundum mass fraction and particle size and glazes were the factors of the design (DoE). Wear resistance, change in gloss and lightness, hardness and surface roughness were determined for all formulations. The abrasive wear resistance was measured by PEI method in accordance with ISO 10545. Gloss and colour variation were determined by colorimetry. Hardness was determined by Vickers microindentation, and surface roughness by the Ra profile. The results show some noticeable flaws in the PEI method, ranging from the test procedure to the evaluation of the results, the latter being susceptible to the individual capacity of wear perception. The PEI method does not take into account factors that are noticeable for the user, such as the loss of brightness. The ANOVA analyses have shown that the glaze with the higher boron content was least resistant to wear and presented

the highest variation in brightness due to the degradation of the tile surface. The change in lightness – which affects visual analysis in the PEI method – was minimized by a low boron content and small particle size of the corundum reinforcement. The surface roughness was lower for a combination of boron glaze with lower corundum content, probably due to a polishing effect. The hardness results had no statistical significance and were not analysed.

1. INTRODUCTION

With the advancement in printing and decoration technologies applied to ceramic tile surfaces, the wide applicability of these products is gaining prominence and, in addition to their aesthetics, durability and safety of use stand out as technical characteristics. For the consumer, the durability of ceramic tiles is related to the change in their surface characteristics. If the surface of a ceramic tile remains unchanged or presents only visually imperceptible changes, a more competitive product is produced, expanding its local use [1-3].

With regard to surface resistance and appearance, the PEI method is by far the most widely used for measuring the abrasive wear suffered by ceramic tiles in their service location. However, because of the subjectivity involved in the analysis of the results, this method alone does not ensure the applicability and suitability of a ceramic tile for its intended use. Therefore, a further analysis of the surface characteristics relating to the results of the PEI method is necessary in order to define the ceramic tile durability [2-5].

Among many features, abrasion resistance stands out because of the importance of specifying the place of use for a given floor covering. Ceramic tiles for floors are under constant abrasive wear, it being extremely important that they keep their aesthetic characteristics unchanged over a satisfactory period of use. Therefore, there is a need to search for materials which provide surfaces with more resistance to abrasive wear, assuring more security and precision in the specification of the places of use for these coverings [4-7].

The PEI method, the most widely used technique to measure the wear resistance of ceramic tiles, has been widely criticized due to the subjectivity involved in the evaluation procedure of the results. Thus, the surface characteristics of ceramic tiles that can be used as parameters for measurement and the understanding of the properties that affect the user perception of wear has been the subject of research by industries around the world [1-5, 8-10].

The resistance to abrasive agents is of paramount importance for ceramic tiles whose use is intended for floors. For this application, the ceramic material must present higher surface hardness and greater resistance to abrasive wear. Regarding glazed tiles, to raise the hardness of glazes, composites are used, where a crystalline phase, usually of greater hardness, is contained in a glassy matrix. These composites can be obtained in two ways: 1) the use of frits and raw materials that crystallize during firing, or 2) the introduction of small crystals in powder form, added together with the frits in the compositions of glazes [1-4].

The introduction of crystalline particles in a glass matrix tends to reduce the wear due to the higher hardness of the reinforcing particles. However, the adhesion forces between the particles and the glass matrix must be sufficiently strong to prevent pull-out of the reinforcing particles. The chemical interactions depend primarily on the chemical composition of the phases and the firing cycles (temperature and time) [1-5].

The reinforcing materials have characteristics that differ greatly from the glass matrix and usually are refractory and stable, making the interaction between the matrix and the surface of the particles difficult. When this interaction does not occur, the crystals are easily pulled out of the matrix when the glaze suffers abrasion wear and therefore the use of these crystals becomes inefficient. This interaction depends on the crystalline material and the composition of the glaze [1-3].

The glaze should present enough viscosity to wet the surface of the crystal particle and so that the crystals can be solubilized in the glass matrix, resulting in good adhesion of the particles to the glaze matrix. In this case, there is an increase in the wear resistance of the glaze since there is formation of a vitreous-crystalline composite [1-4].

Therefore, this work deals with the effect of glaze characteristics and corundum addition on the wear resistance of porcelain glazed tiles. The wear resistance is analysed using the PEI method, as described by the EN 10545 standard, and the PEI results are compared with other techniques like brightness and lightness variation, hardness and surface roughness.

2. MATERIALS AND METHODS

In this work, a full factorial experimental design was used for analysis and presentation of the results. Three factors were the variables under study: glaze matrix, reinforcement particle size and reinforcement mass fraction. These factors were varied at two levels, plus a central point, resulting in a 2^k+1 factorial design, i.e., three factors varied at two levels each, plus a central point, forming a block with nine experiments.

Corundum (alumina) was used as reinforcement with two particle sizes, D_{50}=12μm and D_{50}=24μm. The central point was a mix (50/50 wt.%) of both reinforcements. The mass fractions of the reinforcements (corundum) were 5 wt.% and 15 wt.%, with 10 wt.% as central point. Regarding the glaze matrix, some works have shown that an increase in the boron oxide (B_2O_3) content has resulted in better abrasion resistance than glazes without B_2O_3 in their composition. Two frits were selected as matrices, one with a high boron content (B) and another frit without boron oxide (NB). The central point was a mix (50/50 wt.%) of both frits (B/NB).

Table 1 shows the chemical composition (XRF) of both frits. The main difference between the frits is the presence of zinc oxide in frit NB, which is absent in frit B. Frit NB also has a higher content of alkaline (Na_2O and K_2O) and earth alkaline (CaO) oxides than frit B. In turn, frit B contains boron oxide, which is absent in frit NB.

Frit	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	BaO	ZnO	B_2O_3
B	68.0	7.1	6.5	0.5	1.6	1.5	1.0	0.1	12.4
NB	60.3	6.1	13.1	3.1	4.1	1.4	0.3	9.8	-

Table 1. Chemical composition of the frits used in the study (wt.%).

Glazed porcelain tiles (45 cm x 45 cm) were selected as substrate for this study. The tiles were collected directly from the production line. Each composition was applied in the form of paste by screen printing (55 mesh, commonly used for protective glazing). The compositions were formulated as ceramic inks using ethylene glycol as vehicle, with a ratio of 1:1 with the dry mixture. Nine compositions were made by varying the factors previously described. The decorated samples were fired in a roller kiln with a cycle of 37 minutes and 1215 °C maximum temperature. The tiles were placed in the centre of the furnace entrance in order to prevent possible temperature variations in relation to the sides. All formulations were fired in the same condition, and the samples were subsequently cut to 10 cm x 10 cm size for the abrasion test and other characterization tests of the ceramic surface.

The porcelain tiles were subjected to abrasive wear according the PEI method (EN 10545). For each composition six samples were tested, which were subjected to four stages of surface abrasion: 100, 150, 600 and 1500 cycles. The specimens were evaluated according to the procedure described by the standard, following the visual assessment for PEI classification.

The variation in brightness (ΔG) and lightness (ΔL*) presented by the glazed surface of the tiles after the abrasion test was measured in comparison with the non-abraded areas of the tiles. The measurements were performed using a spectrophotometer (d8 geometry, 400 to 700 nm, D65 light) at four points on the abraded area. The average results were used.

The variation of surface roughness of the samples was measured with the aid of a portable profilometer. The measurements were made on the abraded area and compared with the non-abraded areas of the tiles. The aim was to determine the influence of the variables under study, as described above, on the surface roughness of the samples, and this on the visual perception of wear according the PEI method. The average roughness (Ra) was used for data analysis. The average length measured by the profilometer was approximately 4 mm.

Glaze hardness was measured by the Vickers microindentation test using a diamond indenter with a pyramidal shape against the surface of the glaze under controlled load and loading rate conditions. For each sample, measurements were taken at five, randomly distributed points, and the procedure was repeated three times. When analysing the results the outliers were disregarded. The average results were used.

Each composition was formed as a small cylinder (5 mm height and 5 mm diameter) and sintered in an industrial roller kiln together with the decorated tiles, ensuring the same heat treatment for all samples. After firing, the samples were cut in order to examine the microstructure of the composite. The bodies were then analysed by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

Table 2 presents the results of abrasion resistance by the PEI method, hardness by Vickers microindentation, surface brightness, lightness variation and roughness for the factorial design study. Each result was analysed individually.

Run	Frit	Al_2O_3 (wt%)	Al_2O_3 (μm)	PEI	ΔG	ΔL*	HV (GPa)	Ra (μm)
1	NB	5	12	3	-10	0.21	63.1	1.30
2	NB	5	24	3	-10	0	59.6	0.67
3	NB	15	12	3	-6	0.67	65.0	1.31
4	NB	15	24	2	0	0.07	67.7	1.45
5	B	5	12	2	-2	-0.01	63.8	0.63
6	B	5	24	2	-2	0.32	56.0	0.58
7	B	15	12	2	-2	0.05	63.8	0.88
8	B	15	24	2	-2	0.10	63.0	0.68
9	B/NB	10	18	2	0	-0.07	53.5	0.76

Table 2. Results for the full factorial 2^3+1 design.

For the PEI method, eight samples were tested for each of the nine runs. By analysis of variance for the determination of surface abrasion by the PEI method (Table 3), it is clear that the only statistically significant factor is the type of frit. The p-factor, which indicates the reliability of the system, is 0.095, indicating a 90.5% reliability of the results for the influence of the type of frit on the surface abrasion of the tiles determined by the PEI method. The most influential factor in the determination of surface abrasion by the PEI method is determined by the Fisher (F) value, which indicates the largest source of variation. The experimental F (from the results) must be greater than the tabulated F for the hypothesis (H_0) of the variability factor be true, that is, the higher will be the significance of the tested model.

Factor	SS	dF	MS	F	p
Frit type	1.125	1	1.125	9.0	0.095
Corundum mass fraction (wt%)	0.125	1	0.125	1.0	0.423
Corundum Particle size (μm)	0.125	1	0.125	1.0	0.423
Frit × % corundum	0.125	1	0.125	1.0	0.423
Frit × D_{50} corundum	0.125	1	0.125	1.0	0.423
% corundum × D_{50} corundum	0.125	1	0.125	1.0	0.423
Error	0.250	2	0.125		
Total	2.000	8			

Table 3. ANOVA for the determination of surface abrasion by the PEI method.

Where: SS is the sum of squares, dF are the degrees of freedom; MS is the mean square, F is the Fisher test and p is the reliability.

Thus, the only factor that is statistically significant for determining the abrasion by the PEI method is the type of frit and, therefore, the value was determined graphically from the average results for the PEI test depending on the type of frit, for 95% confidence intervals, Figure 1. Frit B, with the higher boron oxide content, shows the lowest values for the PEI test. This result is surprising because it shows that the frit envisioned as the most suitable for forming an adequate composite presents the lower PEI values, displaying more wear.

Although the higher concentration of boron in Frit B contributes to lowering the surface tension of the glaze on the surface of the corundum particles and thereby facilitating the interaction between the reinforcement and the matrix, the matrix characteristics highlight the synergistic effect expected from the presence of reinforcement particles. In the absence or at low concentrations of network modifiers, boron atoms present trigonal coordination with oxygen. The trigonal coordination negatively alters the properties of the glaze, resulting in a material of lower hardness, which may be indicative of a lower wear resistance. The nuclear magnetic resonance (NMR) technique that could determine the state of coordination of boron in the frits was not available for this work.

Figure 1. Average scores for the PEI test depending on the type of frit (±95%).

For the brightness variation, four samples were tested for each of the nine runs. In the ANOVA for the variation of surface brightness (Table 4), once again the only factor that is statistically significant is the type of frit, with p-factor of 0.186, indicating that the reliability of the results is 81.4% for the influence of this factor on the determination of the surface brightness of the tiles. Figure 2 shows the value of the average results for the variation of brightness depending on the type of frit.

Factor	SS	dF	MS	F	p
Frit type	40.5	1	40.5	3.941	0.186
Corundum mass fraction (wt%)	24.5	1	24.5	2.384	0.263
Corundum Particle size (µm)	4.5	1	4.5	0.438	0.576
Frit × % corundum	24.5	1	24.5	2.384	0.263
Frit × D_{50} corundum	4.5	1	4.5	0.438	0.576
% corundum × D_{50} corundum	4.5	1	4.5	0.438	0.576
Error	20.6	2	10.28		
Total	123.6	8			

Table 4. ANOVA for the determination of surface brightness variation (ΔG).

Figure 2 shows that the highest brightness variation occurs to Frit B, i.e., the frit with the higher boron content, regardless of size or fraction of the corundum particles added. A greater brightness variation normally is related to greater wear. The EN 10545 standard stipulates that the brightness should not be used as a parameter to determine surface abrasion. The higher change in brightness related to the samples with boron frit can be explained by the anomalous behaviour of boron glazes. The boron frits tend to have low surface tension, good chemical resistance and higher hardness. However, the properties of the glaze can be modified by the coordination number of the boron atom, which in turn tends to change depending on the other elements incorporated into the glass structure, as mentioned previously, causing low abrasion resistance and thus greater change in the brightness of the samples.

Also, the appearance of surface cracks, as well as exposure of closed porosity, or even heterogeneities in the glaze matrix may interfere with the light path and thus change the perception of wear. However, further studies are needed in order to quantify the degree of interference of these properties on the perception of wear in different use conditions. The interaction between the reinforcement and the glaze tends to reduce the porosity of the composite; however, the application (decoration) process can also affect the microstructure and thus the final strength of the glaze. According to standard EN 10545, changes in brightness should not be considered in the PEI classification. However, in real use this change is noticeable, which shows the unreliability of the method for determining the durability of the material by the standard.

Figure 2. Average scores for the surface brightness variation depending on the type of frit (±95%).

For the lightness variation, four samples were tested for each of the nine runs. The ANOVA for the lightness variation (Table 5) shows that the interaction between type of frit and average particle size of corundum is the only factor that is statistically significant (p-factor of 0.123) with a reliability of the results of 87.7%. The results for brightness variation can be plotted as contours, from a response surface for the factors type of frit and average particle size of corundum, Figure 3.

Factor	SS	dF	MS	F	p
Frit type	0.030	1	0.030	1.083	0.407
Corundum mass fraction (wt%)	0.017	1	0.017	0.618	0.514
Corundum Particle size (µm)	0.023	1	0.023	0.834	0.457
Frit × % corundum	0.060	1	0.060	2.148	0.280
Frit × D_{50} corundum	0.177	1	0.177	6.389	0.127
% corundum × D_{50} corundum	0.056	1	0.056	2.025	0.291
Error	0.055	2	0.028		
Total	0.418	8			

Table 5. ANOVA for the determination of surface lightness variation (ΔL).*

Figure 3 shows the effect of the interaction between type of frit and average particle size on brightness variation. The highest brightness variation occurs for the combination of non-boron frit with the smallest particle size of corundum. In turn, the lowest brightness variation values occur for the combination of boron frit with the smallest particle size of corundum or non-boron frit with the largest particle size of corundum. These results are probably associated with the interface formed between the glaze matrix, provided by the frit, and the corundum reinforcement.

Considering the frits, the non-boron frit is more refractory than the boron frit, which may have hindered the interaction between matrix and reinforcement, resulting in the corundum particles not being embedded in the glaze matrix, and possibly having a greater surface exposed to abrasive action. As in the PEI method the change on the ceramic surface is evaluated only visually it may differ in relation to the observer because of individual colour perception. Also, human eye sensitivity to certain colours, place of observation and even eyestrain can interfere in the results. Therefore, the need to use quantitative methods which allow the acceptable colour variation to be measured becomes evident.

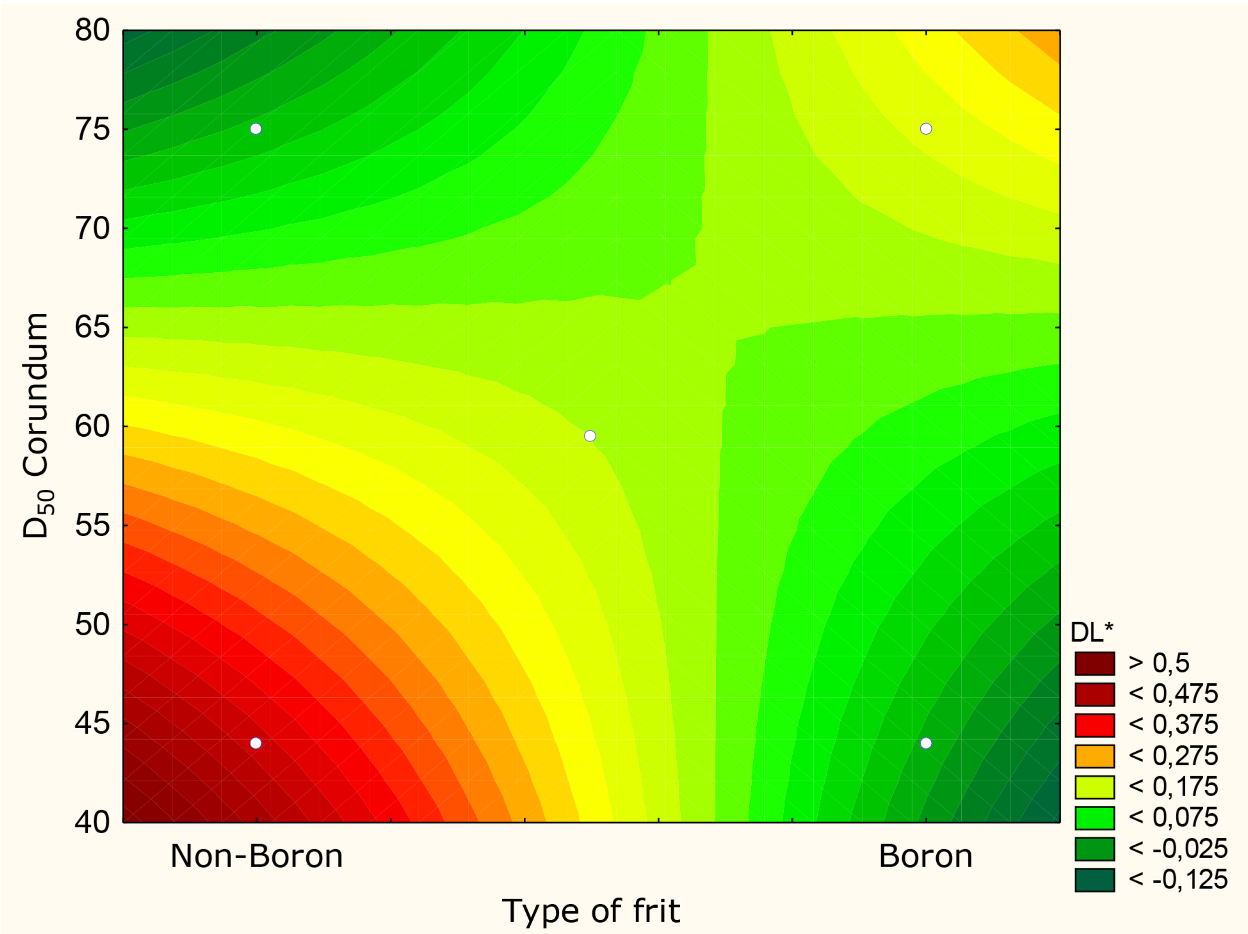

Figure 3. Contour curve for the surface lightness variation (R^2=0.87).

By the analysis of variance for Vickers hardness by microindentation (Table 6), no single factor is statistically significant, given the values of F and p. Thus, this property will not be analysed.

Factor	SS	dF	MS	F	p
Frit type	966	1	966	0.256	0.663
Corundum mass fraction (wt%)	3642	1	3642	0.965	0.429
Corundum Particle size (μm)	1126	1	1126	0.298	0.640
Frit × % corundum	118	1	118	0.031	0.876
Frit × D50 corundum	759	1	759	0.201	0.698
% corundum × D50 corundum	2175	1	2175	0.576	0.527
Error	7546	2	3773		
Total	16331	8			

Tabla 6. ANOVA para la dureza Vickers por microindentación.

There was wide variation in hardness for the glazes measured by Vickers microindentation, even for the large number of measurements made. The hardness measurement could indicate which of the studied factors – type of frit, mass fraction of corundum and corundum particle size –would have more effect on the hardness of the glaze, and thus the resistance to abrasive wear.

For the average roughness, four samples were tested for each of the nine runs. The ANOVA for the average roughness Ra (Table 7) shows that the only factors that have statistical significance are the type of frit and marginally the mass fraction of corundum added, with p factors of 0.116 and 0.259, respectively, indicating a reliability of the results of 88.4% and 74.1% for the influence of these factors on the average roughness (Ra) of the tiles. The results for average roughness can be plotted as contours, from a response surface for the factors type of frit and mass fraction of corundum, Figure 4.

Factor	SS	dF	MS	F	p
Frit type	0.480	1	0.480	7.178	0.116
Corundum mass fraction (wt%)	0.162	1	0.162	2.428	0.259
Corundum mass fraction (wt%)	0.068	1	0.068	1.023	0.418
Frit × % corundum	0.024	1	0.024	0.362	0.609
Frit × D50 corundum	0.007	1	0.007	0.108	0.774
% corundum × D50 corundum	0.048	1	0.048	0.718	0.486
Error	0.134	2	0.067		
Total	0.924	8			

Table 7. ANOVA for the average roughness (Ra).

Figure 4 shows that the smallest roughness occurs for the boron frit combined with the smallest fraction of corundum added. In turn, the higher values of roughness occur for the combination between the non-boron frit and the largest mass fraction of corundum. Usually, the larger roughness values are associated with a strong abrasion of the surfaces being worn. However, after a strong initial abrasion, indicated by higher values of Ra, it is possible that the surface is smoothed – lower values of Ra – with continued wear, because of the "polishing" effect of the surfaces.

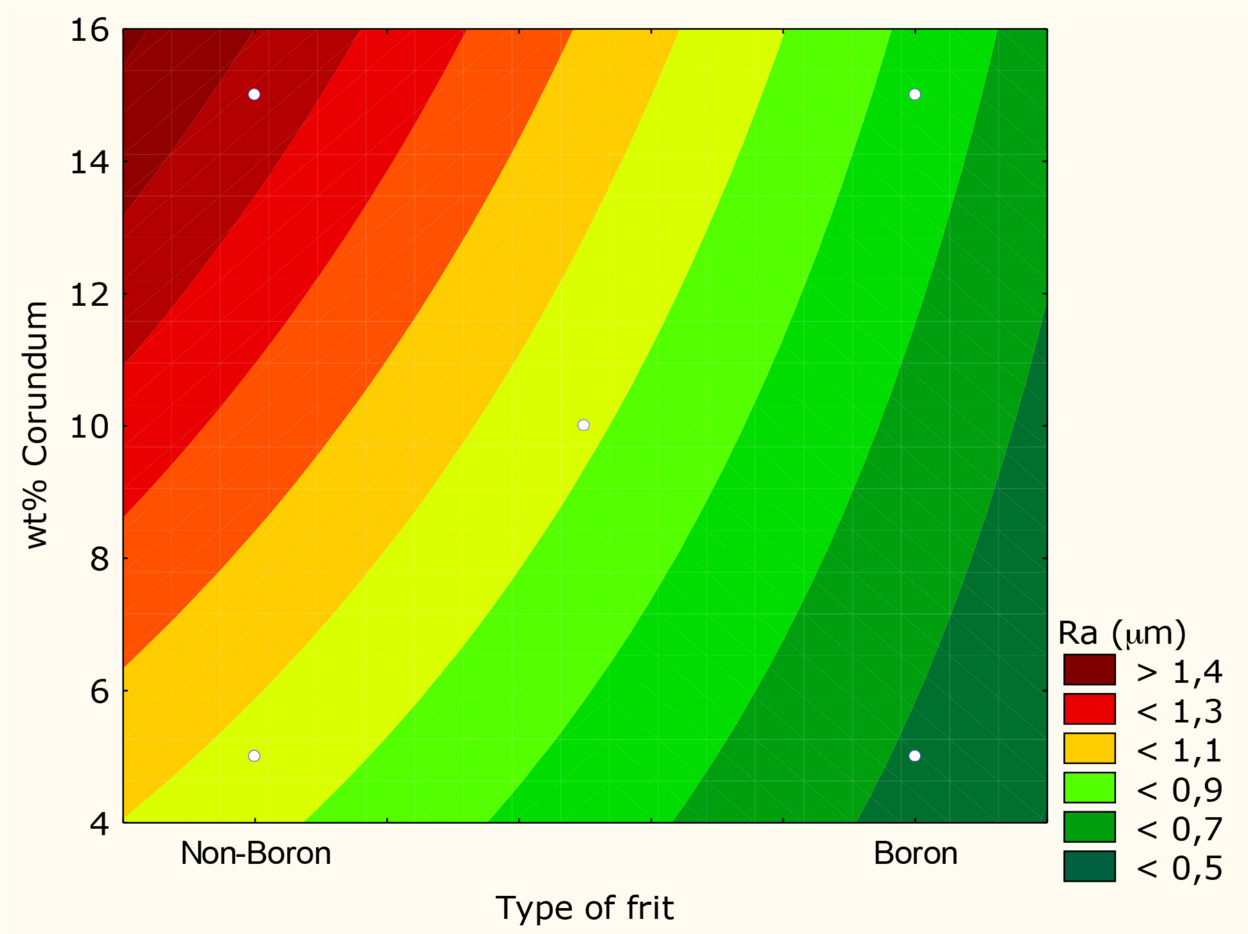

Figure 4. Contour curve for the average roughness (R^2=0.85).

According to Pierse and Hiorns (2003), the roughness magnitude that affects the optical behaviour of a surface is much smaller than the wavelengths of the visible region of the spectrum so that the relationship between brightness and roughness does not involve the size of the latter. This can be verified in the present study, since the non-boron frit that had greater roughness variation also showed less variation in brightness. As a result, roughness does not significantly affect the brightness of the samples and therefore the perception of the abraded region, since the non-boron frit was the one that showed the best results in wear resistance according to the visual analysis of the PEI method.

Finally, Figure 5 shows the microstructural analysis of the samples by scanning electron microscopy (SEM). Because of the sample preparation method, the SEM samples are thicker than the glaze layer applied on the ceramic substrate and therefore the amount of porosity observed in the SEM specimens is different from the glaze samples. Observing the micrographs, Fig 5, a high porosity is noticeable for all formulations. Corundum particles are well dispersed in the glaze matrix producing a homogeneous glaze. The composition without boron (F1, on the left) had larger pores, as compared with the boron glaze (F6, on the right).

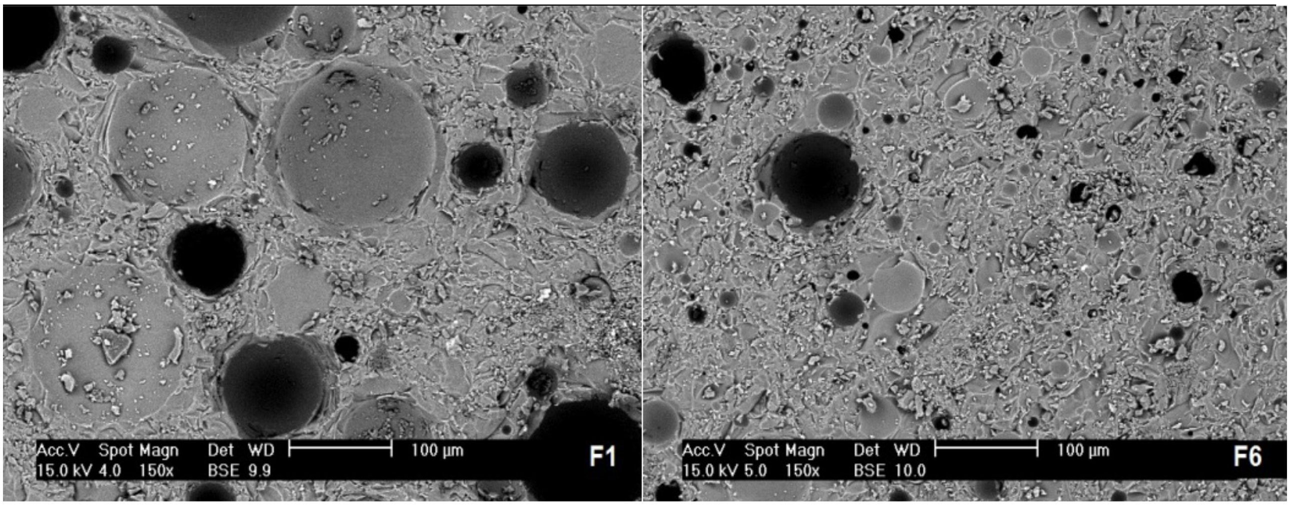

Figure 5. SEM micrographs of the ceramic glazes containing corundum particles: F1) non-boron frit (left); F6) boron frit (right).

4. CONCLUSIONS

The present study highlights the importance of quantifying the properties that significantly affect the perception of wear. The frit used in the glaze matrix presented significant statistical influence on the results of abrasion resistance for each factor under analysis. The loss of gloss is not considered in the PEI classification method (EN 10545), but the gloss variation is one of the most evident characteristics generated by the wear of a glaze. In this work, the frit showing the lowest wear resistance according to the PEI method presented the higher brightness variation.

The use of corundum particles was unsatisfactory in the improvement of the glaze surface wear resistance because the interaction between the glaze matrix and the corundum reinforcement was impaired. Therefore, the development of a more resistant glaze without the use of particulate reinforcement can provide a more homogeneous microstructure and greater resistance due to the presence of crystalline phases instead of the introduction of immiscible particles.

Finally, the standard used to determine the abrasion resistance of glazed ceramic tiles, EN 10545/7, is not suitable. The method of assessment, susceptible to individual perception of wear, ignores factors and conditions of use that are noticeable by the user, such as the loss of brightness. Studies intended to qualify wear resistant products have sought a method of measuring the wear resistance which is closest to the actual conditions the glaze layer is subjected to, considering the loss of brightness and colour variation, measured by colorimetry.

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