STUDY OF THE SURFACE MICROSTRUCTURE OF CERAMIC FLOOR TILES WITH NON-SLIP PROPERTIES

(1) O. Ruiz, (1) F. Sanmiguel, (2) C. Gargori, (2) G. Monrós, (3) Ruth Lahoz, (3) Isabel de Francisco

(1) TORRECID S.A. Alcora (Spain).

(2) Department of Inorganic and Organic Chemistry.

Universidad Jaume I, Castellón (Spain).

(3) Laboratorio de procesado de materiales por láser.

Instituto de Ciencia de Materiales de Aragón – CSIC. Zaragoza (Spain).

1. INTRODUCTION

The use of ceramic flooring in public spaces, outdoor settings and areas subject to damp and liquids is becoming more and more widespread and consequently, the demands made of it by the market are increasingly restrictive. Indeed, regulations have appeared that set the minimum standards such flooring is required to meet depending on its end use. In Spain, the Technical Building Code in its Basic Document SU (Safety in Use) – Section SU 1 (Safety in relation to risk of falls) uses a Slip Resistance (Rd) value to classify floor types and their location. Thus, if the Rd value is equal to or less than 15, it is categorised as Class 0. Floors with Rd values of between 15 and 35 are categorised as Class 1, values of between 35 and 45 are Class 2, and values over 45 are categorised as Class 3.

By taking the place where the floor is to be laid into account, the Technical Building Code stipulates the minimum floor Class acceptable for each use as follows:

Dry indoor areas:

- Surfaces with a slope of less than 6%. Class 1
- Surfaces with a slope equal to or greater than 6% and stairs. Class 2

Wet indoor areas such as bathrooms, kitchens, WCs, indoor swimming-pools, etc:

- Surfaces with a slope of less than 6%. Class 2
- Surfaces with a slope equal to or greater than 6% and stairs. Class 3

Indoor areas where, apart from water, other types of agents may be present (grease, lubricants, etc), such as industrial kitchens, abattoirs, car-parks, areas for industrial use, etc. Class 3

Outdoor areas. Swimming-pools. Class 3

Apart from the afore-mentioned technical and regulatory conditions, it should also be remembered that these non-slip properties must also be accompanied by suitable decorative characteristics so that the end product is acceptable to the ceramic flooring market.

2. AIM

The aim of this paper was to assess surface microstructure of various non-slip ceramic floors obtained by different methods: refractory particles, surface treatment using hydrofluoric acid, a specific ceramic additive to create non-slip surfaces, and laser-treated surfaces.

Apart from assessing the surface microstructure, the study also looks at how each different type of surface treatment affects the aesthetic or decorative character of the piece, particularly with regard to questions such as the transparency of the applied surface treatment, smoothness, and stain-resistance.

3. EXPERIMENTAL PROCEDURE

3.1. Materials and equipment.

The base material on which the various surface treatments were applied was a standard matt glaze composition for porcelain tile.

The surface of this body was treated with several materials:

- Refractory particles: two cases were studied, one with grit particles and the other with corundum. In both cases, the particles were applied prior to firing of the ceramic body.
- Ceramic additive, also applied onto the glazed body prior to firing.
- Different concentrations of hydrofluoric acid solutions applied onto the fired glazed body.

Laser-treated surfaces were also developed, specifically using two types of laser: firstly a TruMark 6230 solid-state green Nd:YVO_4 laser and secondly, a less powerful Rofin-Sina E20 PowerLine solid-state Nd:YVO_4 unit.

The resulting surfaces were characterised by means of the following techniques:

- Non-slip capacity

  The non-slip capacity was measured by two test parameters, namely the slip-resistance value, also known as Rd, and the coefficient of friction or COF.

  In accordance with the recommendations of the Technical Building Code, slip resistance (Rd) was measured using the pendulum test described in standard ENV-12633:2003.

  The static Coefficient of friction, or COF, was measured in accordance with the provisions of ASTM standard C1028-96.

- Roughness

  In order to measure surface roughness, the conventional method with a pick-up and a Kosaka Laboratory Ltd SM-3 roughness meter was used.

- Confocal optical microscopy

  The equipment used was a Sensofar PLμ 2300El microscope which combines interferometry and the confocal technique in the same unit and was used in this paper to study surface profile. The light source was an LED emitting a 460nm wavelength. The unit had high lateral resolution ranging between 0.935 µm for lower magnification levels (10X) to 0.311 µm for the greatest magnification (100X). This high lateral resolution enabled surface roughness to be assessed not only in 3D topography but also in 2 dimensions.

- Stain resistance and visual assessment

  Stain resistance was assessed in accordance with ISO standard 10545-14.

  Visual assessment consisted of comparing the influence of the surface application on a decorated piece, using as a reference the same decorated piece without a surface application.

- X-ray diffraction
- Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX)

3.2. Refractory particle-based non-slip systems.

3.2.1. Experimental procedure.

The use of grit particles, either on their own or mixed with other refractory particles such as corundum, zircon, etc., has to date been the traditional method of producing non-slip floor tiles. Therefore, initially, two surface treatments were studied, one using corundum and the other grit. The procedure consisted of spraying suspensions with grit and corundum onto porcelain bodies coated with a standard matt glaze. These were then fired in a standard porcelain tile cycle to a maximum temperature of 1200ºC.

3.2.2. Results.

The non-slip properties were analysed on the matt base glaze and on the two applications. The following table shows the Rd and COF values obtained:

	BASE GLAZE	GRIT	CORUNDUM
Rd	25	50	60
COF	0.39	0.94	1.20

Table 1. Rd and COF values.

On the basis of the Rd values, according to the Technical Building Code, the standard matt base glaze would be categorised as a Class 1 floor, while both the grit and corundum treated surfaces would qualify as Class 3 floor tiles. Likewise, the COF values for the treated surfaces also reveal a significant improvement over the standard matt surface.

With regard to roughness, the matt glaze has a Ra value of 4.5µm, while the grit and corundum tile surfaces gave readings of 13µm and 30µm respectively, which indicates that applying these particles to the base glaze increases surface roughness considerably, as is noticeable simply by touch.

Confocal optical microscopy was used to characterise both treated surfaces and the standard matt glaze. Figures 1, 2 and 3 illustrate the images produced. As one can see, the standard matt glaze has a fairly smooth surface, in line with its low Ra values. The grit-covered surface reveals significant plateau-like elevations with a height of around 3.5 micrometres, which account for its high Ra, Rd and COF values. The corundum-treated surface reveals sharper, crest-like elevations, with a serrated arrangement that accounts for its even higher Ra, Rd and COF values.

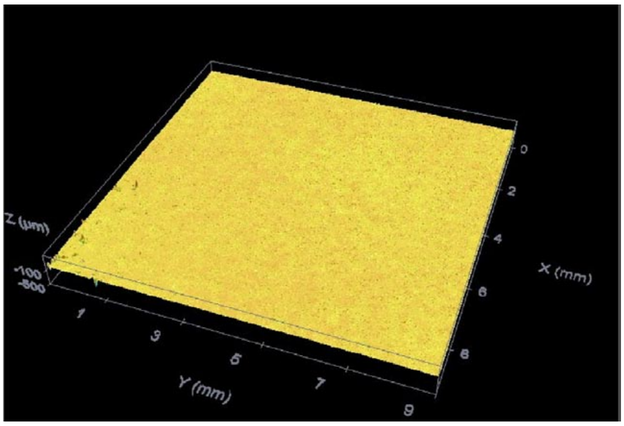


Figure 1. Confocal optical microscopy of the matt base glaze.

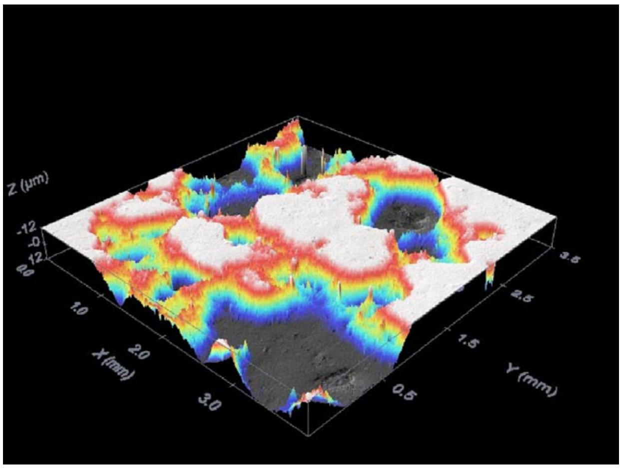


Figure 2. Confocal optical microscopy of the surface with grit.

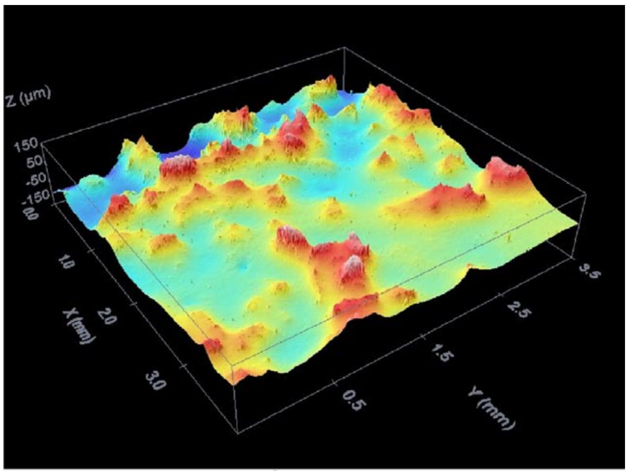
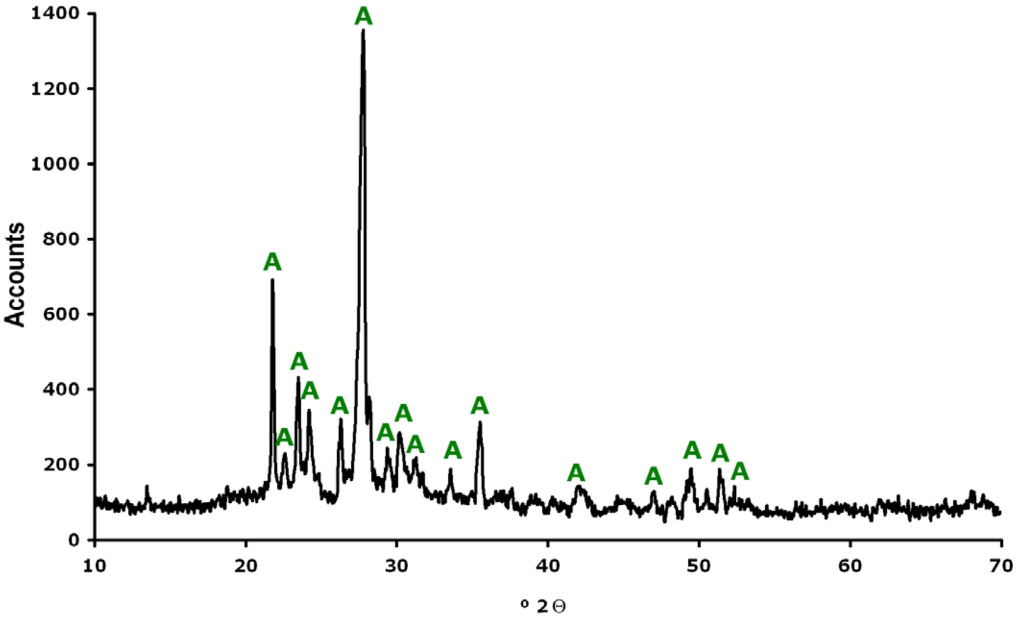


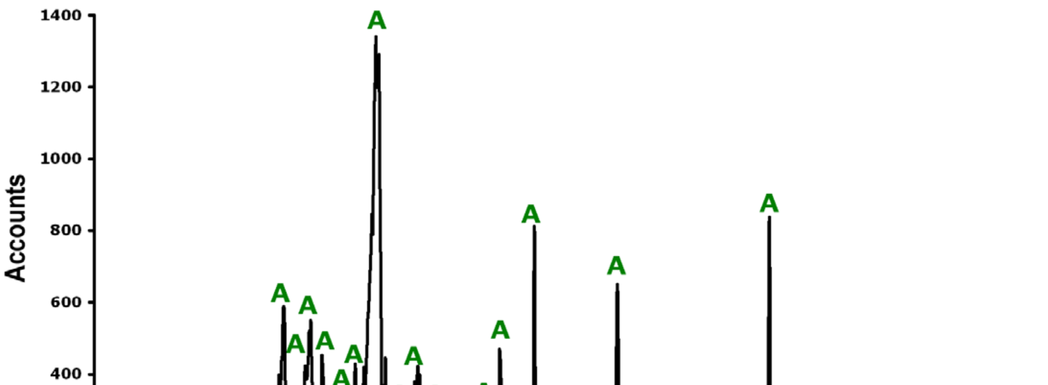
Figure 3. Confocal optical microscopy of the surface with corundum.

With regard to X-ray diffraction crystallography, analysis of the surface with the grit application revealed peaks of anorthite ($CaAl_2Si_2O_8$) from the base glaze, whereas diffraction analysis of the surface treated exclusively with corundum revealed an anorthite ($CaAl_2Si_2O_8$) and a corundum (Al_2O_3) phase.

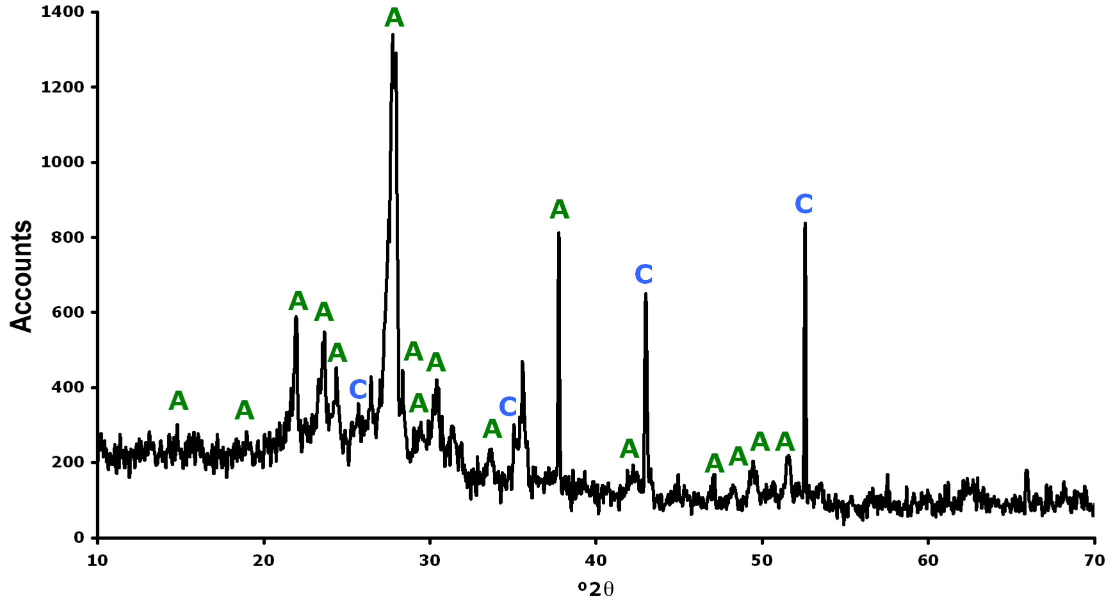
SEM tests show that the surface with a grit application has grit particles integrated to a certain extent in the glaze, of a size that varies between 200 and 600 micrometres. In the surface wit corundum, the SEM tests indicate the presence of partially integrated particles in the glaze in the shape of tips protruding from the surface.



A: Anortithe ($CaAl_2Si_2O_8$)
Figure 4. X-ray diffraction of the matt base glaze.



A: Anortithe ($CaAl_2Si_2O_8$)
Figure 5. X-ray diffraction of the glaze with the grit application.



C: Corundum (Al_2O_3). A: Anorthite ($CaAl_2Si_2O_8$).
Figure 6. X-ray diffraction of the glaze with the corundum application.

On the basis of this initial study, a few early conclusions can be drawn:

- Applying refractory materials such as grit of Corundum enables Class 3 floor tiles with non-slip properties to be produced from Class 1 tiles with a standard matt glaze. However, the limited degree to which such materials can be integrated and the excess relief means that the surface has to be altered excessively to reach Rd values of over 45, thereby causing significant roughness. Furthermore, a certain loss of surface smoothness and aesthetic qualities in the end tile has also been noted.
- From a microstructural point of view, the applied refractory particles integrate to a certain extent into the glaze to create plateau or crest-like elevations of about 3.5 micrometres in height.

3.3. Alternative non-slip systems.

3.3.1. Experimental procedure.

As mentioned in the previous section, the use of refractory particles enables high Rd values to be obtained but at the expense of sacrificing surface smoothness and aesthetics of the treated tile.

In view of this situation, in recent years, the ceramics sector has devised alternative solutions that strive to achieve surfaces that are both pleasant to the touch and aesthetically appealing. First, the application was studied of different concentrations of hydrofluoric acid to fired porcelain tiles with a standard matt glaze. For this, 4 solutions of HF acid with variable concentrations were prepared: 48% (referenced HF1), 36% (HF2), 24% (HF3) and 12% (HF4). Once the solution had been applied, it was left for 15 minutes, after which time, the entire surface was rinsed in abundant water before proceeding to characterise it.

The second case was based on applying a ceramic additive, widely-used in the present ceramic sector as a non-slip solution. For this purpose, the additive was sprayed onto the unfired porcelain body with the standard matt glaze. Specifically, two different grammages were applied: 150g/m^2 (test N1) and 200g/m^2 (test N2), prior to subjecting the pieces to a standard porcelain tile firing cycle.

The third approach consisted of treating the standard matt glaze with two types of laser under three different operating conditions. All three tests, referenced L1, L2 and L3, used the laser to generate a matrix design of lines on the fired glazed body. The following table shows the treatment conditions for each test. As can be seen, the test started with the least aggressive conditions (tests L1 and L2) using a less powerful laser (1064nm) before proceeding to more aggressive treatment (L3) using a 532 nm green laser.

In all three tests, the laser was set to provide 100% output. However, the firing frequency was altered over a range of 5 kHz for the 1064nm laser and 25 kHz for the 532nm unit. Treatment rate with the 1064 nm laser was also studied under two different settings, first with a slower rate of 10 mm/s and then 10 times faster, while the green laser was used directly at the fastest speed. Finally, the distance between the lines created on the design was varied between 0.4mm for tests L1 and L2 and 0.2mm for test L3.

	TEST L1	TEST L2	TEST L3
Type of laser	1064nm PowerLine	1064nm PowerLine	532nm Green laser
Frecuency (kHz)	5	5	25
% Power	100	100	100
Speed (mm/s)	100	10	100
Gap between lines (mm)	0.4	0.4	0.2

Tabla 2. Laser test conditions.

3.3.2. Results.

As in the previous study of refractory particles, the non-slip capacity afforded by the various treatments was assessed by measuring the Rd and COF values. Table 3 shows the results obtained.

TEST	Rd	COF
Matt base glaze	25	0.39
HF1	65	0.87
HF2	59	0.81
HF3	60	0.84
HF4	60	0.82
N1	52	0.71
N2	63	0.85
L1	25	0.36
L2	37	0.56
L3	56	0.76

Table 3. Rd and COF values.

As one can see, treating the surface with hydrofluoric acid led to high Rd and COF values and consequently significant non-slip properties (Class 3 according to the Technical Building Code). Test N1 and N2 using the ceramic additive give high Rd and COF values, thereby enabling the end surface also to be categorised as Class 3.

With regard to the laser treatments, the operating conditions are determinant for the end Rd and COF value obtained. Thus, the least powerful operating conditions (L1) do not provide any acceptable non-slip capacity with low Rd and COF values of 25 and 0.36 respectively. Using the same laser (1064nm) but with more aggressive operating conditions, both the Rd and COF values improve to reach 37 and 0.56 respectively. Finally, when the most powerful laser with its subsequent higher ability to alter the surface is used, an Rd value of 56 is achieved, which is classifiable as a Class 3 surface, accompanied by a high COF rate (0.76).

The following table summarises the resulting roughness measured for all the systems:

TEST	Ra (μm)
Matt base glaze	4.5
HF1	4.6
HF2	4.6
HF3	4.5
HF4	4.6
N1 (150g/m^2)	1.3
N2(200g/m^2)	5.7
L1	2.5
L2	4.2
L3	6.8

Table 4. Roughness values.

As can be seen, the acid treatment does not alter the roughness of the matt base glaze.

In Test N1, roughness is reduced as the actual ceramic additive is integrated into the surface, thereby smoothening it. However, by increasing the dose (N2), accumulations of the material begin to build up and increase roughness.

As far as the laser treatment is concerned, when the least powerful operating conditions are used (L1), roughness is actually reduced because the treatment only affects the areas of the glaze with a slight relief, so that the surface is on the whole smoother. As operating conditions are made more aggressive, the laser's ability to erode the surface grows and therefore roughness increases (L3).

Confocal optical microscopy studies of the topography of the various treated surfaces show that, as indicated by the measured Rd values, the surfaces treated with HF acid do not display high surface roughness (figure 7).

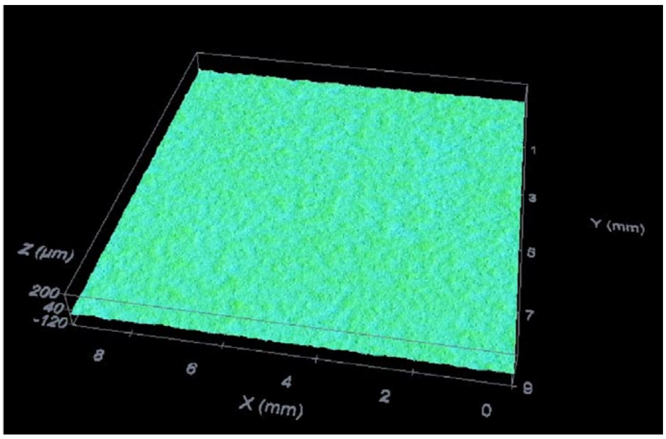


Figure 7. Confocal optical microscopy of surface HF1.

With regard to the pieces treated with the additive in tests N1 and N2, the surface with the lightest coating (N1) is found to be fairly smooth, which enhances the notion that the additive integrates with the base glaze to provide a surface that is actually smoother than at the outset. However, when the weight of the additive coating is increased (N2), a more significant alteration of the surface with greater irregularities and unevenness is observed, which accounts for the higher Rd values obtained.

Laser treatment causes a significant change to the surface profile depending on the laser operating conditions. Thus, test L1 (less aggressive) leads to a micro-relief of separated dots without actually forming lines that represents a rather insignificant modification of the surface. Test L2 (with the same laser but under more aggressive operating conditions) allows well differentiated lines to be distinguished in a well-defined, repetitive matrix. Finally, test L3 displays a square pattern of very sharp relief. This design, together with the most powerful laser (532nm), enables the highest non-slip capacities to be achieved, as well as the surfaces with the highest roughness values. However, visual inspection of the laser-treated surfaces shows that the treatment not only modifies the roughness of the surface but also affects the aesthetic decoration of the tile by causing increased opacity and colour tone changes.

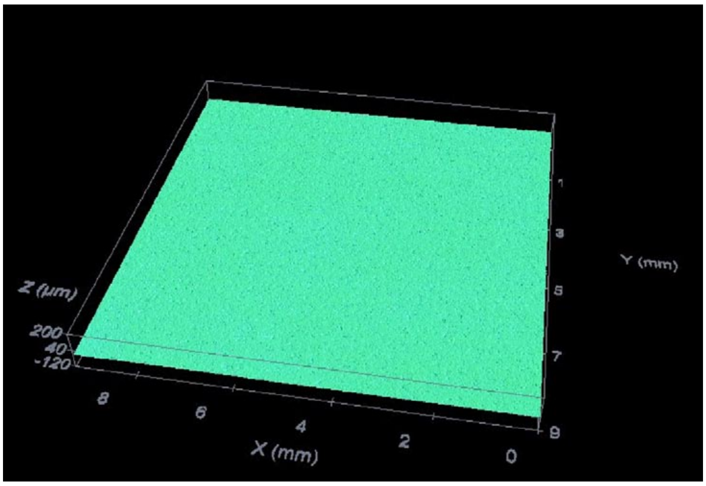


Figure 8. Confocal optical microscopy of surface N1.

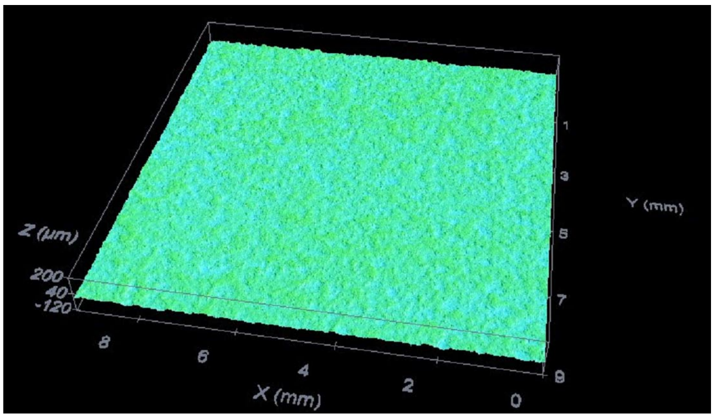


Figure 9. Confocal optical microscopy of surface N2.

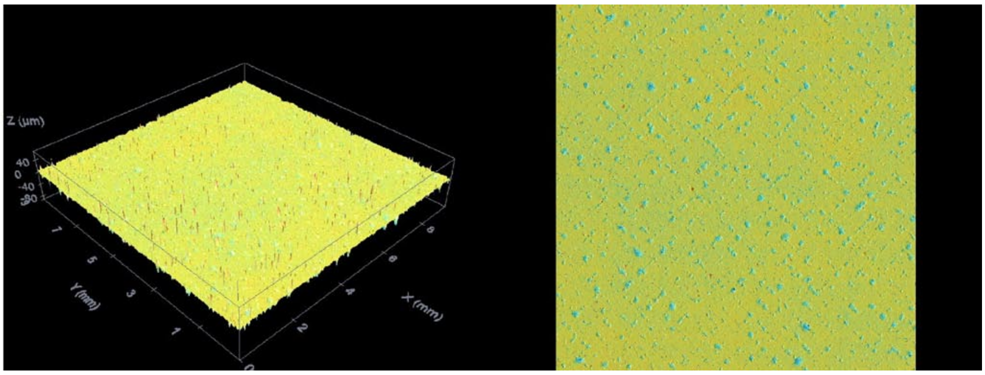


Figure 10. Confocal optical microscopy of surface L1 in 3D and 2D.

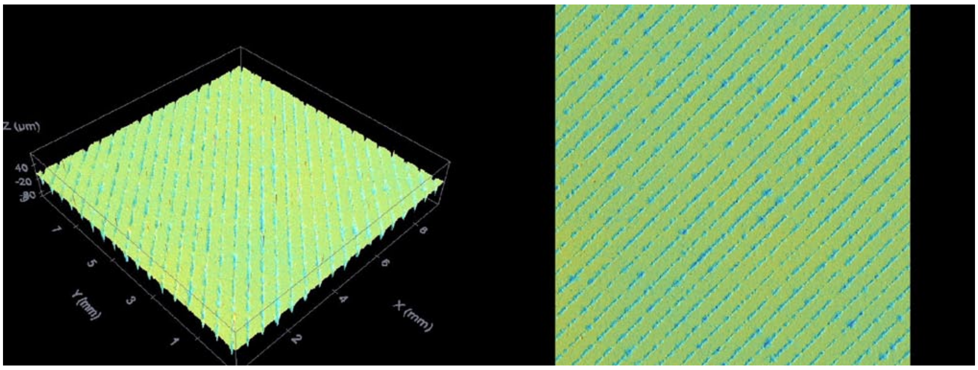


Figure 11. Confocal optical microscopy of surface L2 in 3D and 2D.

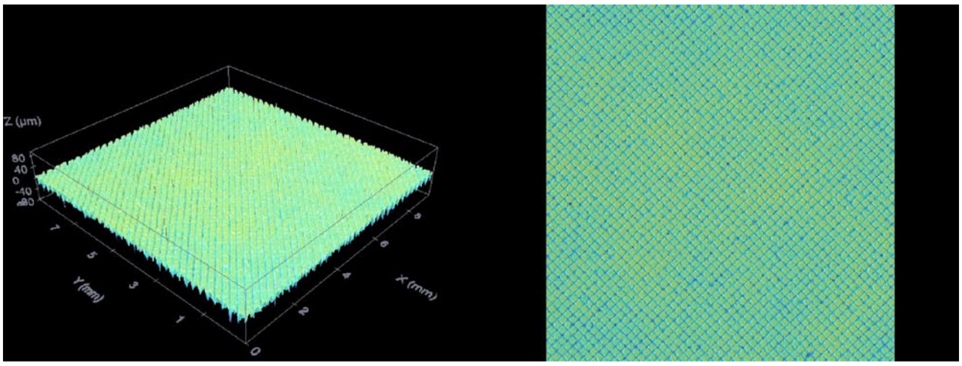


*Figure 12***.** *Confocal optical microscopy of surface L3 in 3D and 2D.*

An important factor to bear in mind when assessing a floor tile is its stain resistance capacity. The following table shows the results obtained according to ISO standard 10545-14:

TEST	STAIN RESISTANCE
Matt base glaze	Class 5
HF1	Class 2
HF2	Class 2
HF3	Class 2
HF4	Class 2
N1 (150g/m^2)	Class 5
N2(200g/m^2)	Class 5
L1	Class 5
L2	Class 4
L3	Class 4

Table 5. Stain resistance.

Glazes treated with hydrofluoric acid do not give good results as, according to ISO standard 10545-14, they only achieve Class 2, due to the fact that the treatment leads to a loss of glaze surface and to greater porosity. Treatments with the ceramic additive, as well as laser test L1, do not affect the resistance to stains and qualify as Class 5, the same as the matt base glaze. Finally, laser test under operating conditions L2 and L3 reduce resistance to stains slightly and are categorised as Class 4.

In the application of the ceramic additive, a light grammage (test N1) does not affect the aesthetic appearance of the tile, which remains the same as the original reference model. When the grammage is increased to 200g/m^2 (N2), a slight surface opacity (a milky appearance) can be seen, which affects the aesthetic value of the tile. No loss of tactile smoothness is perceived with either grammage.

With regard to laser treatments, it should be noted that high-density energy applied to the surface modifies it significantly, producing changes of colour in the glaze.

X-ray diffraction crystallography of all three treatment systems does not reveal any changes to the phases detected in the standard base glaze and also identifies anorthite, as shown in figure 13.

However, scanning electron microscopy does reveal significant morphological changes in both the HF acid and laser treatments (figure 14). In the former, a significant loss of glaze surface can be seen as a result of the acid attack. In the laser treated tile, surface morphology is seen to acquire a groove pattern caused by the laser ablation process.

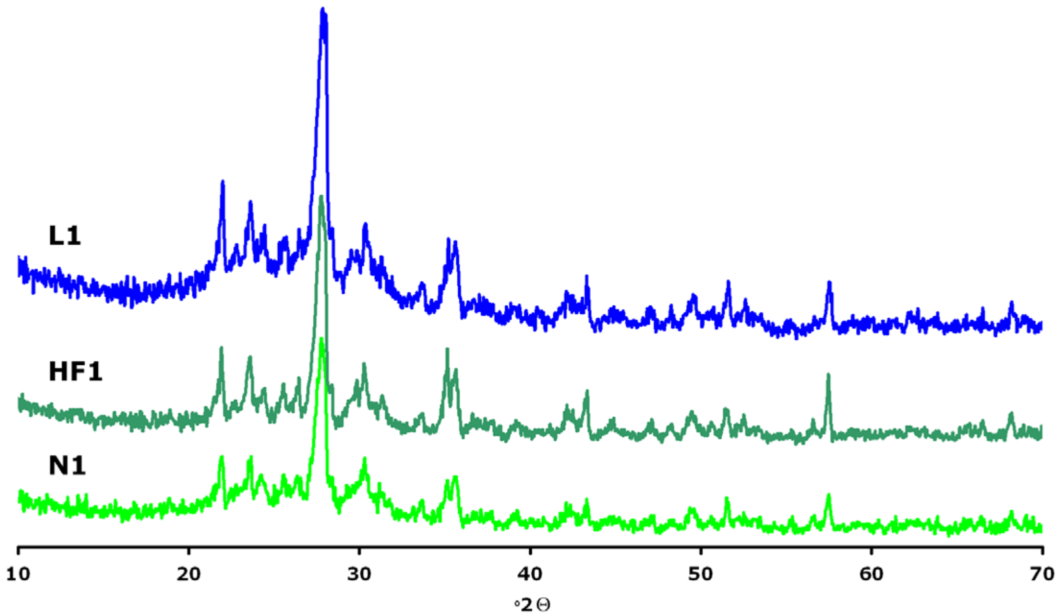


Figure 13. Diffractograms of the glazes with N1, HF1 and L1 treatments.

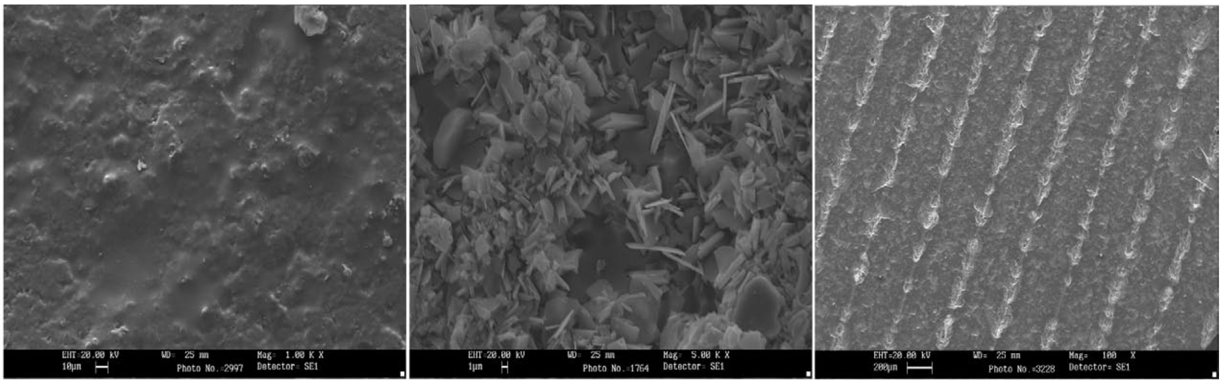


Figura 14. Imágenes MEB del esmalte mate estándar, prueba HF1 y prueba L2.

4. CONCLUSIONS

On the basis of the results set out above, the following conclusions can be drawn:

Grit and corundum:

- The use of refractory materials such as grit and corundum enable non-slip surfaces with high Rd and COF values to be obtained, which, according to the Technical Building Code are categorized as Class 3.
- The limited degree to which the particles integrate with the surface and the high-relief observed imply that, in order to achieve Rd values above 45, the surface needs to be excessively modified, which in turn causes significant roughness and reduced aesthetic properties.

HF:

- A 12% solution of HF acid is sufficient to achieve Rd values above 45 (Class 3).
- However, high Rd and COF values are associated with a reduction in aesthetic properties and stain resistance.
- Chemical treatment with hydrofluoric acid produces a loss of glaze surface, though surface roughness does not increase.

Laser treatment:

- Physical treatment by laser radiation in low-energy operating conditions produces low Rd values and reduces roughness by smoothening the surface.
- To develop surfaces with a higher non-slip capacity (Class 3), the laser has to be used at higher power ratings, which then produces destruction of the surface with a loss of the decorative finish compared to the original piece.

Ceramic additive:

- Applying a ceramic additive to the surface, even with low grammages (150g/m^2), allows high non-slip capacities (Class 3) with reduced roughness to be achieved and therefore enables very smooth surfaces to be created.
- At low grammages (150g/m^2) the non-slip additive integrates well without creating opacity and thus not affecting the aesthetic character of the floor tile.
- Higher grammages (200g/m^2) lead to high Rd and COF values. However, they also lead to a significant increase in roughness and opacity, thereby affecting the aesthetic characteristics of the tile.

REFERENCES

[1] Código Técnico de Edificación. Real Decreto 314/2006 (B.O.E. 28.03.2006).

[2] Norma Europea Experimental UNE-ENV 12633. Enero 2003. Asociación Española de Normalización y Certificación – AENOR.

[3] Standard Test Method for Determining the Static Coefficient of Friction of Ceramic Tile and Other Like Surfaces by the Horizontal Dynamometer Pull-Meter Method. C1028-96. American Society for Testing and Materials – ASTM.

[4] Norma UNE-EN ISO 10545-14 "Baldosas Cerámicas. Parte 14: Determinación de la resistencia a las manchas". Asociación Española de Normalización y Certificación – AENOR.

[5] Influencia del vidriado base en la desvitrificación de granillas. F. Sanmiguel y col. Congreso Qualicer 2000.

[6] Laser Ablation. A. Sappey & N. Nogar. Springer-Verlag. 1994.

[7] Laser Material Processing. Steen, W.M. Springer – Verlag. 1998 (3rd edition).