EFFECT OF BaO AND Al_2O_3 RATIO ON SURFACE CRYSTALLIZATION OF PORCELAIN TILE GLAZE

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ABSTRACT

Conventional anti-slip glazes consist of increased tile surface roughness by incorporating hard particles embedded in a glassy matrix, which degrades aesthetics and cleanability. This study aims to achieve a smooth tile surface with high slip resistance without compromising aesthetics and cleanability by controlling the crystallization of the glaze. It was observed that replacing the barium matt frit with Al_2O_3 resulted in increased corundum crystallization. On the other hand, SEM analysis showed that increasing barium matt frit promotes the rectangular-shaped celsian crystals. Although the surface roughness was increased with more Al_2O_3 content, there was no significant change in slip resistance, while the aesthetics were degraded due to the opacity of the Al_2O_3 particles. Staining resistance decreased with increasing Al_2O_3 content. It is shown that a smooth tile surface with acceptable slip resistance is possible by optimizing the crystallization of the glaze and hard particle incorporation.

1. INTRODUCTION

Porcelain tiles are one of the most widely used products in construction, and they are produced from inorganic materials including silica, alkaline, and hard materials [1]. They can be classified according to the raw materials mixture, firing cycle, porosity, water absorption, and composition of the glaze that is applied on the surface [2]. Among ceramic tiles, porcelain tiles are preferred due to their high wear resistance, long-lasting service life, mechanical properties, and chemical and stain resistance. The composition of the glaze plays a major role in tile use, as well as surface texture and aesthetic appearance [3,4].

Porcelain tiles are mostly preferred in indoor and public areas where high technical performance and safety are required because of their excellent technical characteristics. Among the surface textures, anti-slip glazed porcelain tiles are one of the best candidates for wet and contaminated floors [5].

The demand for ceramic floorings in public areas has recently increased, especially for ceramic tiles that have higher slip resistance as a basic safety requirement [6]. The EU Construction Products Regulation No. 305/2011 requires non-slip coverings in areas where slip-fall accidents might occur [7]. In terms of safety, the slip resistance of tiles is a significant measure for areas with heavy pedestrian traffic as well as for wet, slippery, and contaminated floors [8].

Slip resistance and surface roughness are required to prevent slipping, especially in wet, contaminated floor conditions. Surface roughness is an important property affecting both the surface's cleanability and slip resistance [9,10]. There are several factors affecting surface roughness, such as particle size distribution of the glaze, the thickness of the engobe and the glaze layer, as well as the application type of the glaze [11]. There are several studies to increase slip resistance and surface roughness of porcelain tiles especially used in external areas, such as poolsides, pavements, and garden pathways. The conventional studies consist of increasing surface roughness by incorporating hard particles such as alumina, quartz, and crushed frits [12,13]. However, excess incorporation of alumina or crushed frit results in an increased opacity that influences decorative and aesthetic properties negatively.

In this context, this study aims to obtain a smooth tile surface by achieving high slip resistance, without compromising aesthetics and cleanability, by controlling the crystallization of the glaze. For this purpose, different matt slip-resistant glazes were prepared with varying amounts of barium oxide (BaO) and aluminum oxide (Al_2O_3). The correlation between crystallization and microstructure, as well as surface roughness, staining resistance and slip resistance were examined.

2. MATERIAL AND METHODS

A commercial barium matt frit (Akcoat, Türkiye) and industrial raw materials (kaolin, albite, dolomite, clay, nepheline) were used to produce ceramic glaze. The corundum amount was changed within different ratios (5, 15, 25, 35, and 45 wt.%) by replacing barium matt frit in the formulation. The chemical composition of the frit and glazes is given in Table 1 and Table 2, respectively. The glaze formulations were weighed at 300g and wet milled with alumina balls for 20 min. The glaze slip was applied to the green porcelain tile surface by spraying. The glazed porcelain bodies were dried at 110 °C for 30 minutes and then fired at 1210 °C for 58 minutes in an industrial fast-firing regime.

Raw material	SiO_2	Al_2O_3	CaO	MgO	Ka_2O	Na_2O	BaO
Barium Matt Frit	40-45	13-17	3-7	0-2	0-2	0-2	33-38

Table 1. *Chemical composition (wt.%) of the commercial frit*

Sample	SiO_2	Al_2O_3	CaO	MgO	Ka_2O	Na_2O	BaO	B_2O_3
R1	44.8	20.5	6.5	2.7	1.1	3.1	18.8	1.9
R2	40.4	30.0	6.0	2.5	1.1	3.0	15.0	1.6
R3	35.9	39.5	5.6	2.3	0.9	2.9	11.2	1.2
R4	31.5	48.9	5.1	2.1	0.9	2.9	7.5	0.8
R5	27.1	58.5	4.7	1.9	0.8	2.9	3.8	0.4

Table 2. *Chemical composition (wt.%) of the developed glazes*

XRD analysis was used to evaluate crystallization (D8 Eco, Bruker). Scanning Electron Microscope (SEM) was used to investigate the microstructural and morphological evolution of the crystalline phases (FEI Quanta FEG 450). Surface roughness of the glazed surfaces was measured with a hand-held surface profilometer (Time group, TR200), taking the Ra and Rz values. Ra is the average roughness of the glazed surface and Rz is the difference between the deepest valley and the tallest peak in the glazed surface. The stain resistance of the glazed surfaces was determined according to the ISO 10545-14 standard [14]. Slip resistance was measured with the pendulum test method according to the BS-7976 standard and it was referred to as the pendulum test value (PTV) [15]. The colorimetric values of the surface were measured by using a spectrophotometer (Konica Minolta, CM 600d) according to the CIE Lab space, expressed as L* (lightness), a* (red, green), b* (blue, yellow).

3. RESULTS AND DISCUSSION

Fig. 1 shows the phase transformation behavior of the glazes after the firing process. It was observed that the main crystalline phase is Celsian ($Ba_{0.8}Al_{1.6}Si_{2.4}O_8$, PDF #04-011-0793) at 26.66° (2θ) for R1 and R2. When the BaO ratio decreases, celsian peak intensity tends to decrease. Conversely, increasing the Al_2O_3 ratio promoted the formation of Corundum (α-Al_2O_3, PDF #00-046-1212) crystals at 35.15° (2θ). As seen in Figure 1, the corundum crystal pattern became sharper and more intense for R3, R4 and R5. Albite ($Na_{0.685}Ca_{0.347}Al_{1.46}Si_{2.54}O_8$, PDF #01-083-1939) was also detected at 27.80° (2θ), as a secondary phase. Moreover, it was observed that the albite crystal patterns gradually became stronger as the BaO ratio decreased.

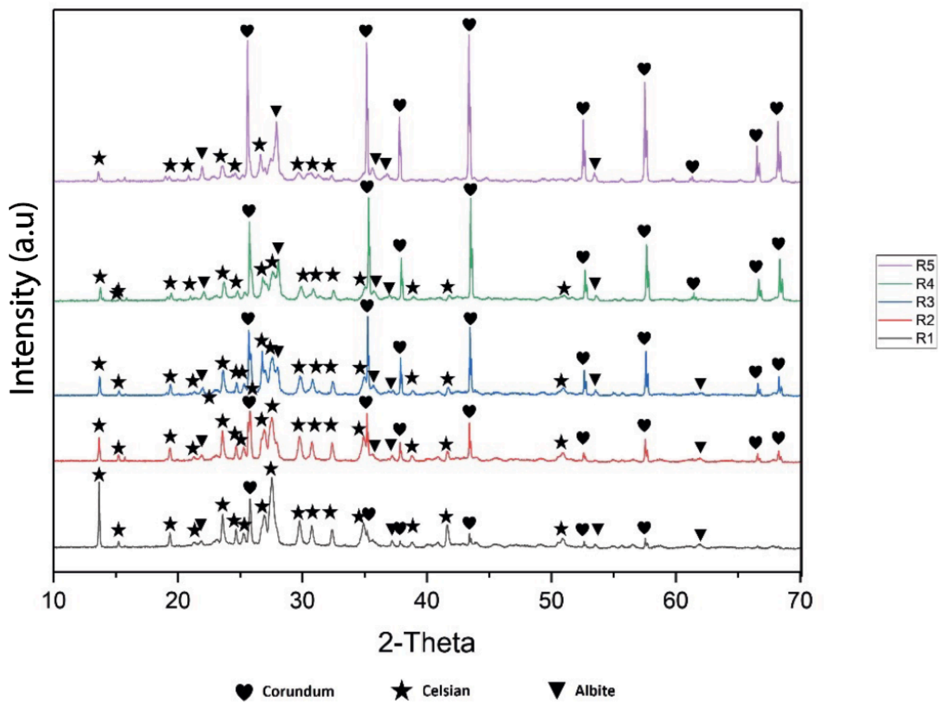

Figure 1. *XRD pattern of phase transformation behavior in the glazes*

The effect of the Al_2O_3 and BaO ratio on glaze microstructure is examined in Figure 2 at 2000x magnification. It is seen that, after the sintering process, the glaze devitrified into rectangular, monoclinic Celsian crystals with an increasing BaO ratio. Barrachina et al. reported a rectangular-shaped uniformly spread celsian crystal in their anti-slip enamel study [16]. Celsian crystal size and distribution gradually decreased with increasing Al_2O_3 ratio. Moreover, the increment and decrement of crystal peak intensity in the XRD pattern of crystals matched the variation in celsian and corundum crystallite size. Additionally, it was seen from Figure 2 that coarser corundum crystals were distributed inside the matrix. Therefore, when the Al_2O_3 ratio reached above 30%, the structure became porous due to coarser and unshaped corundum crystals on the surface (Fig.2c-Fig.2e). Consequently, the celsian crystals could not be distributed homogenously into the glaze matrix because of the porous structure and lack of glassy matrix when the Al_2O_3 ratio increased.

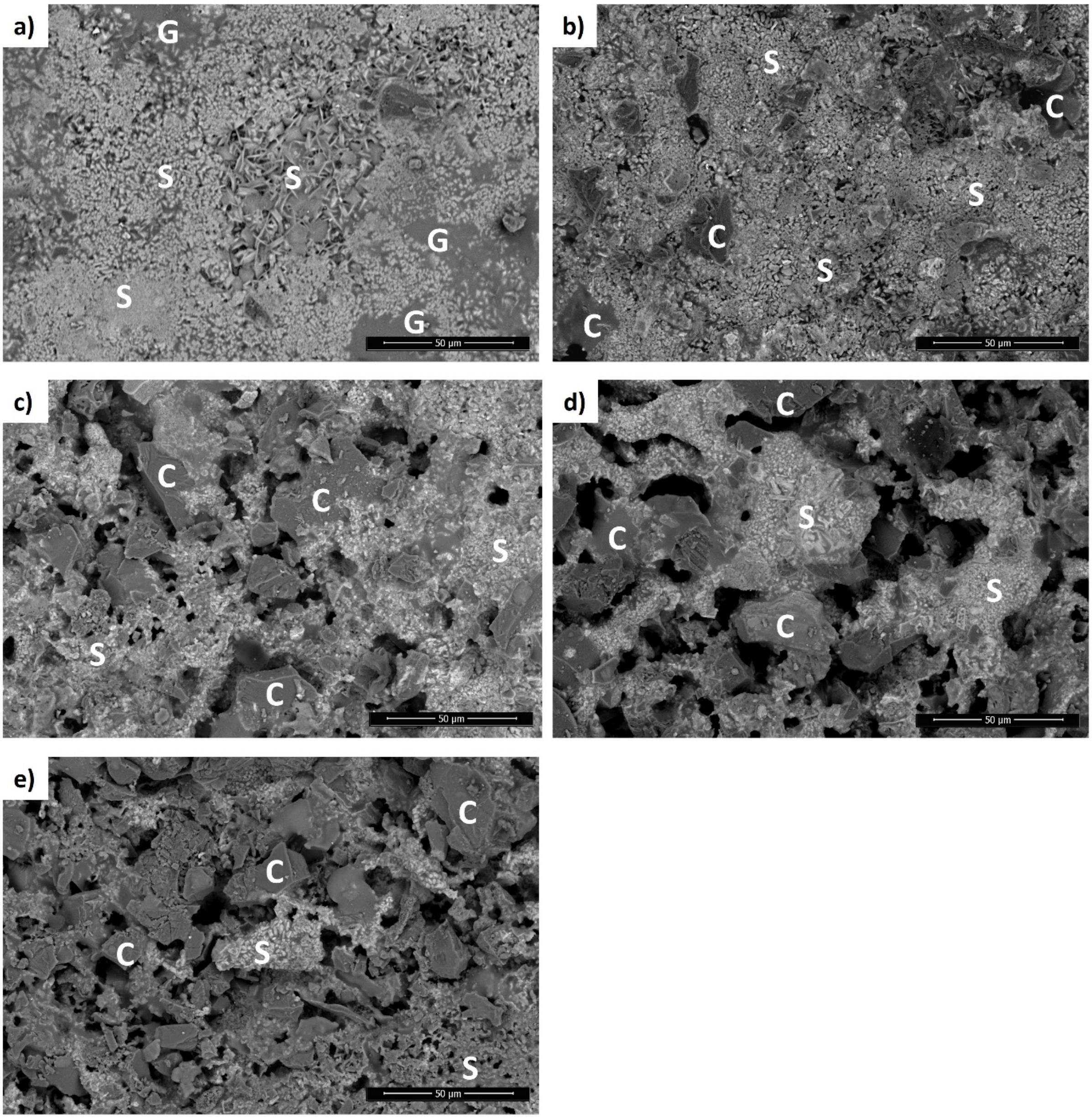

Figure 2. *BSE-SEM images of the samples at 2000x magnification a) Sample R1, b) Sample R2, c) Sample R3, d) Sample R4, e) Sample R5 (**G:** Glassy matrix, **C:** Corundum, **S:** Celsian)*

Figure 3 shows the results of PTV and surface roughness of glazed surfaces with varying Al_2O_3 ratios. Sample R1 has resulted in 41 for PTV and Ra 2.150±0.1, Rz 9.091±0.1 for the roughness value. Figure 2 indicates clearly that the smaller rectangular crystals in the glassy matrix of sample R1 provided decreasing PTV and surface roughness. In contrast, a combination of the rectangular and coarser corundum crystal on the surface reached 89 for PTV of slip resistance behavior for sample R2. When the Al_2O_3 ratio was increased to 30%, the PTV value and surface roughness increased rapidly to 89 and Ra 3.301±0.1, Rz 16.597±0.1, respectively. When the Al_2O_3 ratio increased from 30% up to 58.46%, slip resistance and surface roughness of the samples increased slightly. Sample R5 which has the lowest BaO ratio and the highest Al_2O_3 ratio reached the highest slip resistance value of 92 and surface roughness of Ra 4.039±0.1, Rz 19.440±0.1, respectively.

Vermol et al. observed that the corundum incorporation and increased slip resistance caused design tonality to decrease due to the higher opacity on the surface [5]. It was seen that as the corundum crystals occurred at the surface with the increasing Al_2O_3 ratio, slip resistance and surface roughness increased because of the porous structure. As a result, the Pendulum Test Value of 36+ shows a low slip potential surface according to the BS 7976 standard. Therefore, the results show the surfaces have a low slip potential surface [15].

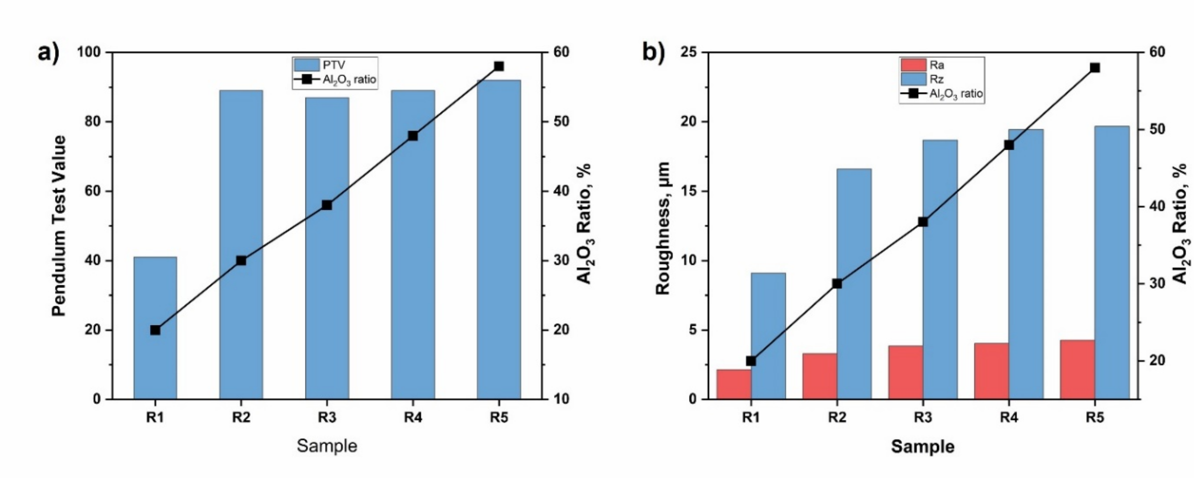

Figure 3. *Pendulum test and surface roughness values at different Al_2O_3 ratio*

Figure 4 shows the stain resistance class of the glazed surfaces. Sample R1 resulted in Class 5 referred to as the best cleanability on the surface according to ISO 10545-14 standards thanks to the lower surface roughness. The surface's poor cleanability may be explained by considering a pore-rich structure and higher surface roughness. This was shown clearly in the SEM images of sample R1, which has a finer crystal-rich structure, and of sample R5, which has a pore-rich structure. Also, greater surface roughness due to the increased Al_2O_3 ratio resulted in poor stain resistance. Increased formation of finer rectangular crystals on the surface ensured the cleanability of the surface.

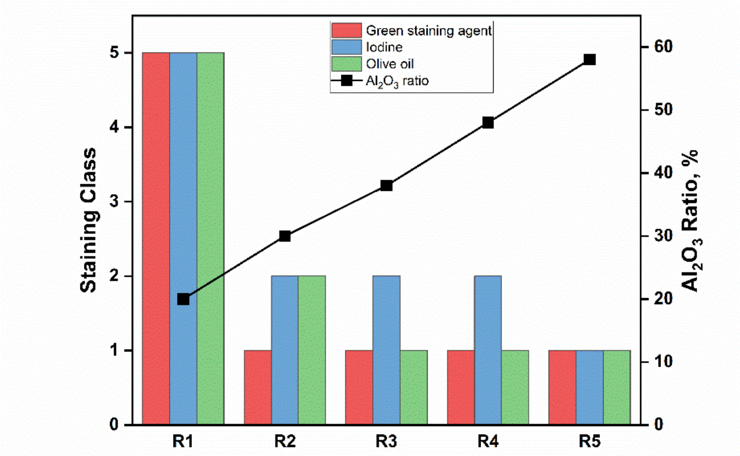

Figure 4. *Visual representation of the results of surface resistance to stains with varying Al_2O_3 ratios*

The colorimetric values of the surfaces are given in Figure 5. The highest BaO ratios showed the lowest L* value and higher a* and b* values on the surface, which positively affects color perception. On the contrary, the lowest BaO ratio caused the a* and b* values of the surface to decrease, as seen in Figure 5. Overall, the L* values of the samples increased gradually with the increasing Al_2O_3 ratio due to the higher corundum crystal formation. Also, several studies showed that excessive incorporation of alumina tends to increase the opacity of the surface.

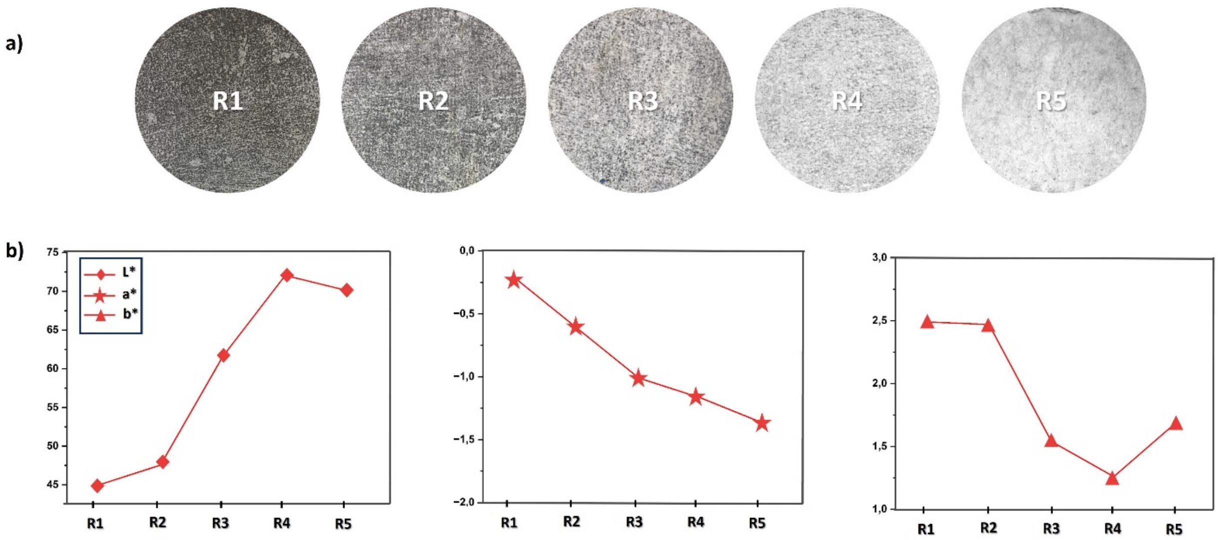

Figure 5. *a) Glazed surfaces of digitally printed porcelain tile b) graphical representation of colorimetric values of samples defined as L*, a*, b*.*

4. CONCLUSION

It was observed that increasing the Al_2O_3 ratio promoted corundum crystals, while increasing the BaO ratio promoted Celsian crystals. The presence of rectangular-shaped celsian crystals on the surface provides the best cleanability, which resulted in Class 5. The higher amount of Al_2O_3 caused a pore-rich structure on the surface as well as increased surface roughness, so that it caused poor cleanability of the glazed surfaces. In addition, the resulting corundum crystals caused surface opacity to rise. In conclusion, it was observed that, by controlling the crystallization of the glaze, a smooth tile surface with high slip resistance can be obtained without compromising surface aesthetics and cleanability.

5. REFERENCES

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