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Development of a Cost-effective Opacifier Alternative to Zircon for Porcelain Floor Tile Engobes

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Abstract

In this study, different opacifier recipes were designed and replaced with zircon in the engobe recipe which was ball milled and applied to the floor tiles by a glaze applicator and fired in an industrial fast-firing regime. It has been shown that the opacity and the water absorption of the engobe was increased due to the increase in alumina content. The water absorption and shrinkage of the engobes were balanced by adding frit and zircon to the recipes. The tazheranite phase formation was observed with the addition of frit with TiO_2 content resulting in a more yellowish appearance of the engobe. The increase in Al_2O_3 content suppressed tazheranite formation and decreased the opacity. The addition of albite to the recipe improved the sintering behavior of the engobes which resulted in decreased water absorption and increased shrinkage. It was observed that decreasing the alumina particle size resulted in decreased opacity as well as water absorption while increasing the shrinkage. It has been shown that the amount of zircon in engobe recipes could be reduced by 80% and a cost reduction of 18% is possible by optimizing the refractoriness-water absorption balance with the frit/Al_2O_3 ratio while keeping the opacity in the preferred levels.

Porselen Yer Karosu Engobları için Uygun Maliyetli Zirkon Alternatifi Opaklaştırıcı Geliştirilmesi

Özet

Bu çalışmada, endüstriyel hızlı pişirim rejimlerinde pişirilmek üzere porselen ve yer karosu engob reçetelerindeki zirkona alternatif olarak kullanılabilecek farklı opaklaştırıcı reçeteleri oluşturulmuş ve bilyalı değirmenlerde öğütülerek, sır aplikatörü ile uygulanmıştır. Alümina içeriğindeki artışa bağlı olarak engobun su emiliminin yanı sıra opaklığının da arttığı gösterilmiştir. Reçetelere frit ve zirkon eklenerek engobların su geçirgenliği optimize edilmiştir. TiO_2 içerikli frit ilavesi tazheranit fazı oluşumuna ve engobun daha sarımsı bir görünmesine neden olmuştur. Al_2O_3 içeriğindeki artış tazheranit oluşumunu baskılamış ve opaklığı azaltmıştır. Reçeteye albit ilavesi, engobların sinterleme davranışını iyileştirmiş ve bu da su emiliminin azalmasına ve büzülmenin artmasına neden olmuştur. Alümina partikül boyutunun küçültülmesinin, engobun küçülmesini arttırırken su emiliminin yanı sıra opaklığının da azalmasına neden olduğu gözlenmiştir. Opaklığı tercih edilen seviyelerde tutarken frit/ Al_2O_3 oranı ile refrakterlik-su emme dengesinin optimize edilmesiyle engob reçetelerindeki zirkon miktarının %80 oranında azaltılabileceği ve %18 maliyet azalmasının mümkün olduğu gösterilmiştir

1. INTRODUCTION

Porcelain ceramic tiles are strong sintered ceramic materials, which have moderate mechanical properties, such as high hardness, wear, and bending resistance.[1] The very low water absorption and superior appealing aesthetics of porcelain tiles make them ideal materials for outdoor applications.[2] Due to these technical and aesthetic features, porcelain tile production increases every year.[3] The continuous increase in the production of ceramic tiles has led to an increase in the need for large quantities of raw materials used in the production process.[4]

Engobe is an inert intermediate layer of 100–300 µm thickness between the glaze layer and the ceramic body in ceramic tiles.[5] Engobe is used to reduce imperfections on the tile surface and improve the compatibility between the ceramic tile and glaze coating.[6,7] One of the most important features of engobes is that they provide waterproofing to the ceramic tile. Since water permeability is caused by the porosities, engobe layer fills those pores and provide a waterproof layer on ceramic tile. Therefore, watermarks on the tile surface can be eliminated by increasing the thickness of the engobe and thus reducing the amount of porosity, which also improves opacity.[8,9]

Glass-ceramics are polycrystalline materials produced by the controlled nucleation of the glass matrix and the growth of the formed crystals. Crystal structures in ceramic products significantly affect thermal, mechanical and chemical properties.[10] In ceramic tiles, the opacity resulted as the reflection and scattering of light caused by the difference in the refraction between the formed crystals and the glass matrix.[11] Glazes containing zircon can be considered as glass-ceramic glazes due to the promotion of nucleation by zircon.[12] The dispersion of zircon crystals has a significant effect on the scattering of light. The amount of homogeneous zircon clusters obtained by using a zircon-based frit is higher than glazes using zircon as a raw material in the recipe directly.[13] Anorthite $Ca(Al_2Si_2O)$ is a crystalline phase consisting of isomer needle-shaped grains that causes an increase in opacity. It is a good option to use glazes containing TiO_2 (rutile refractive index: 2.76 and anatase refractive index: 2.52) with high refractive indices compared to typical porcelain glazes (refractive index: 1.50–1.55) as an opacifier.[14] The presence of TiO_2 in ceramic glazes acts as a nucleator forming the rutile and anatase phases. The anatase phase is preferred because the rutile phase causes an increase in the yellow color in the glaze and thus degrade aesthetic features. Glazes with multiple anatase crystal structures in smaller crystals can be developed by delaying crystal growth with Sb and Nb additions. K_2O is preferred instead of Na_2O to provide a blue-white color that has better appealing aesthetics.[15]

The superior technical properties of zircon make it the material of choice in the ceramic industry. Thanks to its high refractive index, it provides opacity to ceramic tiles. Another advantage of zircon in ceramic tiles is that it increases the chemical and surface abrasion resistance of ceramic tiles.[16] The zircon consumption in the ceramics industry is much higher than in other industries. Zircon consumption is increasing gradually, but its production cannot increase enough (Figure 1). The zircon resources in the world are gradually decreasing, and this causes the prices to increase.

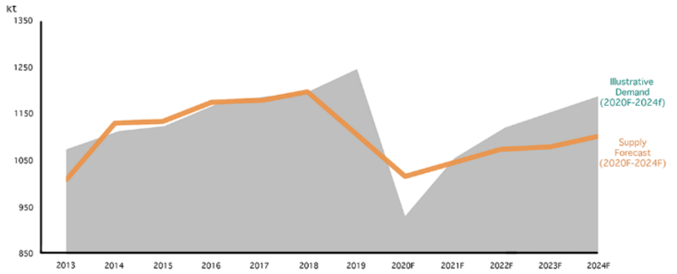

Figure 1. Global zircon supply and demand outlook.[17]

The aim of this study is to develop a cost-effective alternative opacifier to zircon by adjusting the refractoriness-opacity values of engobe recipes. For this purpose, different engobe recipes were examined depending on the variation of Al_2O_3-frit ratios.

2. METHODS

The porcelain engobe recipe determined as a standard is shown in Table 1.

Table 1. Porcelain engobe recipe.

Material	Supplier	Wt. %
Flux frit	Akcoat	15-20
Opaque frit	Akcoat	15-20
Kaolin	Kaolin	10-15
Clay	Etili	10-15
Zircon Mo	Bitossi	5-10
Quartz	Pomza	20-25
Alumina	Eti	5-10
Feldspar	Straton	10-15

The seger formulation of the tested opacifier recipes instead of zircon in the standard engobe recipe and the resultant engobe recipe is given in Table 2 and Table 4, respectively. The substitution of Al_2O_3 content with a frit containing CaO-TiO_2 is investigated in recipes W1-W2-W3, while the substitution of Al_2O_3 with albite and CaO-MgO-ZrO_2 containing frit is investigated in recipes W4-W5-W6 and W7-W8-W9, respectively. The effect of Al_2O_3 grain size is investigated in recipes W3-W10-W11.

Table 2. Seger formulations of opacifiers

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	ZrO_2	TiO_2
W1	5.77	19.15	-	0.36	0.64	-	2.8	0.36
W2	4.28	5.17	-	0.3	0.7	-	1.03	0.38
W3	4.68	8.93	-	0.31	0.69	-	1.51	0.38
W4	5.06	6.11	-	0.44	0.56	-	1.19	0.3
W5	5.25	4.22	-	0.53	0.47	-	0.97	0.24
W6	5.38	2.92	-	0.59	0.41	-	0.82	0.21
W7	2.58	3.48	0.04	0.14	0.37	0.45	0.86	-
W8	2.88	6.03	0.04	0.15	0.37	0.44	1.18	-
W9	3.71	13.18	0.04	0.19	0.35	0.42	2.08	-
W10	4.68	8.93	-	0.31	0.69	-	1.51	0.38
W11	4.68	8.93	-	0.31	0.69	-	1.51	0.38

Table 3. Al_2O_3 grain sizes used in recipes

Recipe	Al_2O_3 Grain Size (μm)
W1	75
W2	75
W3	75
W4	75
W5	75
W6	75
W7	75
W8	75
W9	75
W10	4
W11	120

Table 4. Seger ratios of engobes recipes

	SiO_2/Al_2O_3	Basic Oxide	Stabilizer	Acidic Oxide	ZrO_2
STD	4.68	1.00	1.19	5.98	0.38
W1	3.72	1.00	1.45	5.61	0.21
W2	3.98	1.00	1.34	5.57	0.20
W3	3.85	1.00	1.40	5.59	0.20
W4	3.97	1.00	1.35	5.60	0.20
W5	4.11	1.00	1.31	5.60	0.20
W6	4.25	1.00	1.27	5.60	0.20
W7	3.96	1.00	1.32	5.44	0.21
W8	3.83	1.00	1.38	5.50	0.21
W9	3.71	1.00	1.44	5.57	0.21
W10	3.85	1.00	1.40	5.59	0.20
W11	3.85	1.00	1.40	5.59	0.20

The investigated opacifier recipes were weighed and milled in an alumina ball mill for 30 minutes. The slurries were dried at 200 °C for 2 hours and the resultant powders were ground in an agate mortar. The recipes were weighed by using opacifiers instead of zircon in the porcelain engobe recipe, which is accepted as a standard. The resultant engobe slurries were milled in ball mills until a sieve residue of 45 μm was achieved between 0-1%. The densities of the engobe slurries were adjusted to 1780 gr/l and applied to the tile surfaces with an applicator of 0.8 mm thickness. The porcelain tiles were dried at 200 °C for 10 minutes. The dried tiles were then fired in an industrial fast-firing regime of 1205 °C for 58 minutes. L-a-b color values were determined by a spectrophotometer (Conica Minolta, CM 600d). To measure the water absorption and shrinkage values, engobe recipes were dried and sieved through a 500 μm sieve. 80 grams of powder is used to press tablets with a size of 5x10 cm and fired in the same firing regime as the tiles. The shrinkage was calculated by measuring the dimensions of the tablets before and after the firing. For the water absorption test, tablets were weighted and then kept in boiling water for 2 hours. After the boiling, their weight was measured again and the % water absorption was calculated from the weight difference before and after the boiling. XRD analysis was employed to evaluate crystallization (D8 Eco, Bruker).

3. RESULTS AND DISCUSSION

The L-a-b color values of the engobes are given in Table 5. It was observed that the opacity values of the opaficier were the same or close to the standard. Recipes with high Al_2O_3 content have higher L values. The opacity value decreases depending on the increase in the frit amount and albite amount, but the opacity value is higher although the frit amount in the W8 recipe is higher than the frit amount in the W9 recipe. Depending on the decrease in Al_2O_3 grain size, the opacity (L) value decreases slightly. Increasing the amount of CaO-TiO_2 frit resulted in increased yellowness (b). W2 recipe with the highest amount of TiO_2 has the highest yellowness value. Depending on the increase in the amount of frit containing CaO-MgO-ZrO_2, the blue value increases, and the yellowness value increases due to the decrease in the frit/Al_2O_3 ratio. It was observed that the blue color value of the W10 recipe with the lowest Al_2O_3 grain size was higher, which indicates that the blue color intensity increases with decreasing Al_2O_3 grain size. The opacity value in W1-W4-W8-W9-W11 recipes is higher than 90, which was acceptable for the current application. W1-W9-W4 recipes have the highest amount of Al_2O_3. Due to the high Al_2O_3 grain size in the W11 recipe, it is more opaque than the opacifier recipe containing the same amount of frit. In addition, the frit/Al_2O_3 ratio in the W9 recipe is determined to be optimum, since the opacity value increases due to the homogeneous distribution of the zircon in the frit.

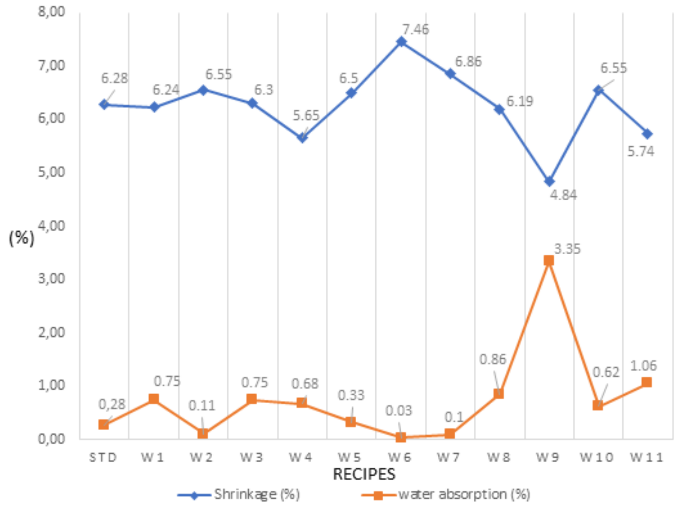

Figure 2. Shrinkage and water absorption of investigated engobe recipes

Figure 2 shows the water absorption and shrinkage values of the investigated engobes. Depending on the increasing amount of Al_2O_3 and Al_2O_3 grain size, the amount of water absorption increases and the amount of shrinkage decreases. This is attributed to the decreasing sinterability of the engobes. Since Al_2O_3 has higher refractoriness, sinterability decreases as Al_2O_3 content increases which results in decreased shrinkage and increased water absorption. Depending on the increase in the amount of frit and albite, the amount of water absorption decreases and the shrinkage increases. This is attributed to the improved sinterability due to the increased amount of highly fluxing albite and frit in the recipe. The recipes with the lowest water absorption values and the highest shrinkage values are W2-W5-W6-W7. The low water absorption value in the W2-W7 recipes can be explained by the increased amount of frit, and the low water absorption value in the W5-W6 recipes can be explained by the increased albite amount. As the refractoriness of the engobe recipes decreases, its sinterability is increased and thus the amount of water absorption decreases, whereas the shrinkage increases. The water absorption and shrinkage values in the recipes with Al_2O_3 grain size of 4 µm and 75 µm were close to the standard. It was observed that there were very large deviations in the recipe with 120 µm grain size Al_2O_3.

Table 5. Color values of engobe surfaces

Recipe	CIE Lab. Space	
STD	L	90.3
	a*	-0.3
	b*	2.07
W1	L	90.13
	a*	-0.38
	b*	2.08
W2	L	89.7
	a*	-0.37
	b*	2.42
W3	L	89.74
	a*	-0.38
	b*	2.15
W4	L	90.23
	a*	-0.42
	b*	2.17
W5	L	89.22
	a*	-0.44
	b*	2.03
W6	L	89
	a*	-0.43
	b*	2.08
W7	L	89.81
	a*	-0.36
	b*	1.76
W8	L	90.36
	a*	-0.38
	b*	1.94
W9	L	90.21
	a*	-0.47
	b*	2.23
W10	L	89.41
	a*	-0.44
	b*	1.86
W11	L	90.03
	a*	-0.43
	b*	2.25

The results of the XRD analysis performed on the engobe recipes are given in Figure 3. The same phases are seen in all samples, but differences in peak intensities are observed. Zircon has the highest intensity in the standard recipe since its zircon content was higher. The peak intensity of the Tazheranite phase increased with the increasing amount of TiO_2 containing frit, while it is decreased when the amount of albite and Al_2O_3 increased. Increasing the CaO ratio resulted in increased peak intensity of the anorthite phase. ZnO was added to engobe recipes as a reference material for semi-quantitative analysis.

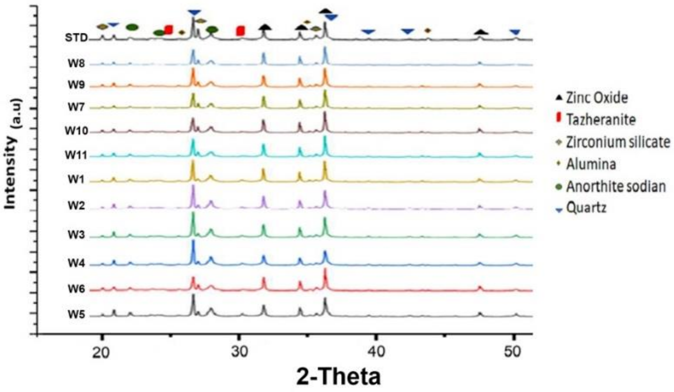

Figure 3. XRD patterns of investigated engobe samples

4. CONCLUSIONS

In this study, a cost-effective opacifier alternative to zircon was developed for floor tile engobes. It was observed that the opacity of the engobes, as well as the water absorption, increases with increasing refractoriness. The addition of frit and albite successfully compensated for the increased refractoriness, but the opacity decreased. An opacifier recipe equivalent to zircon was obtained with clustered zircon oxide grains and the anorthite ($CaAl_2Si_2O_8$) phase formation by using a frit in CaO-MgO-ZrO_2 glass system. The formation of tazheranite phase ($CaTiZr_2O_8$) was observed due to the increased amount of CaO-TiO_2 containing frit. It was observed that increasing the amount of Al_2O_3 resulted in a decrease in the formation of this phase. It has been shown that the amount of zircon in the engobe recipe can be reduced by 80% and the cost reduction of 18% is possible by changing the frit/Al_2O_3 ratio in engobe recipes.

- It has been shown that, with the frit/Al_2O_3 ratio, the zircon ratio in engobe recipes can be reduced the recipe can be made cheaper.
- It was observed that the opacity, as well as the water absorption of the engobe was increased due to the increase in alumina content.
- The tazheranite phase ($CaTiZr_2O_8$) formation was observed resulted in a more yellowish appearance of the engobe.
- The addition of albite to the recipe improved sintering behavior of the engobes which resulted in decreased water absorption and increased shrinkage

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