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Reducing the Amount of Zircon by Using Alternative Frit Compositions in Fast Firing Floor Tiles Ceramic Engobe Recipes

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Abstract

In this study, engobe recipe containing diopside phase ($MgCaSi_2O_6$) providing opacity and whiteness to engobe was produced by reducing zircon ($ZrO_2.SiO_2$), which increases recipe costs. Zircon was gradually reduced (5%, 3%, 0% by weight) from recipes. Four different frit compositions were studied. The reference recipe was optimized according to the percentages of SiO_2, Al_2O_3, CaO, MgO percentages calculated by Seger formulation. Recipes has standards of under 63 µm grain size, 1500 g/L density, 45 g that turned in the mill and with a spray application to 30x60 tiles and sintered standard regime (1205°C - 1210°C) for 60 minutes. X-Ray Difraction (XRD) method, dilatometer device, Scanning Electron Microscope (SEM), spectrophotometer and glossmeter were used for characterization.
It can be explained by EDX analysis and XRD phase analysis that the diopside phase is obtained in the SEM images of the new engop recipes and that decrystallization does not occur above 1100ºC. In addition to the diopside phase, the formed anorthite phase also appears to support opacity. The whiteness (L^*) value of the recipe closest to the standard in terms of surface properties was 83.64 and its brightness was 2.1. It is seen that the thermal expansion coefficient of the recipe ($69.8x10^{-7}$/K @ 400ºC) approaches the thermal expansion coefficient of the masse. ($70.2x10^{-7}$/K @ 400ºC).

Hızlı Pişirim Yer Karosu Seramik Engop Reçetelerinde Alternatif Frit Kompozisyonları Kullanılarak Zirkon Miktarının Azaltılması

Özet

Bu çalışmada, reçete maliyetlerini artıran zirkon ($ZrO_2.SiO_2$) azaltılarak, opaklık ve beyazlık sağlayan diopsit fazı ($MgCaSi_2O_6$) içeren engop reçeteleri üretilmiştir. Zirkon, kademeli olarak azaltılarak (ağırlıkça %5, %3, %0) değirmene ilave edilmiştir. Dört farklı frit kompozisyonu çalışılmıştır. Referans reçete, Seger formülasyonu ile hesaplanan SiO_2, Al_2O_3, CaO, MgO yüzdelerine göre optimize edilmiştir. Reçeteler 63 µm tane boyutu altında, 1500 g/L yoğunluk, 45 g standartlarında olup, değirmende döndürülerek 30x60 ebatlı karolara sprey ile uygulanmış ve standart rejimde (1205°C-1210°C) 60 dakika sinterlenmiştir. Karakterizasyon için X-Ray Difraction (XRD) yöntemi, dilatometre cihazı, Taramalı Elektron Mikroskobu (SEM), spektrofotometre, glossmetre kullanılmıştır. Yeni engop reçetelerinin SEM görüntülerinde diopside fazının elde edildiği ve 1100ºC'nin üzerinde dekristalizasyonun gerçekleşmediği EDX analizi ve XRD ile yapılan faz analizi ile açıklanabilmektedir. Diopsit fazına ek olarak, oluşan anortit fazının da opaklığı desteklediği görülmektedir. Yüzey özellikleri açısından standarda en yakın reçetenin beyazlık (L^*) değeri 83.64, parlaklığı 2.1 olarak ölçülmüştür. Reçetenin termal genleşme katsayısının ($69.8x10^{-7}$/K @ 400ºC), massenin termal genleşme katsayısına ($70.2x10^{-7}$/K @ 400ºC) yaklaştığı görülmektedir.

1. INTRODUCTION

Zircon is the basic element that provides the opacity and gives the white color in traditional glazes and engobes. Opacity in engobes is achieved by adding zircon or frit component to engobe composition during milling and a combination of both methods. Despite its low industrial cost among the general opacity providers, zircon has the highest cost due to using at the amount of 9 11 wt % and constitutes the cost of 55 60% of the engobe recipe.[1,2]

Natural diopside $CaMgSi_2O_6$ is a mineral of the pyroxene group. Its melting point i s 1390°C~ it possesses a high electrical conductivity, and a low temperature coefficient of linear expansion. Upon heating, diopside does not decompose, does not shrink, and does not lose mass. In compositions with clay minerals diopside forms high melting eutectics.[3] Alteration of CaO/MgO ratio affects the opacity and whiteness of engobe and glaze.[4] The formation of the crystalline phase depends on the amount of diopside. The addition of diopside leads to the formation of anorthite phase. The vitreous phase increases diopside. When quartz inte nsely dissolve in the melt, anorthite is synthesized.[5] Removal of zircon from the recipe is achieved by optimizing the CaO/MgO ratio.[6]

In this study, diopside phase evaluated to promote the opacity and whiteness by reducing the amount of zircon content in engobe recipes.

2. METHODS

Standard engobe recipe is G3 that has properties of under 63 μm particle size and 1500 g/L density. 45 g engobe drops on each tile. First, standard recipe was obtained according to raw materials. Table 1 shows oxide ratios of standard recipe calculated by Seger formulation. For the comparison, different frit compositions were used as shown in Table 2.

Table 1. Oxide ratios of standard G3, Z1, Z10, Z12, Z13 recipes calculated by Seger formulation by XRF (wt%).

Oxide Ratio	G3	Z1	Z10	Z12	Z13
SiO_2	60.05	61.73	52.81	55.85	57.11
Al_2O_3	19.97	19.68	26.47	21.01	21.71
TiO_2	0.24	0.26	0.11	0.23	0.32
Fe_2O_3	0.29	0.26	0.20	0.23	0.29
CaO	1.26	3.56	4.16	3.86	3.52
MgO	0.35	1.83	4.46	3.64	3.16
Na_2O	4.59	4.84	4.75	4.81	4.41
K_2O	0.42	1.51	2.78	1.21	1.19
P_2O_5	0.02	0.02	0.01	0.02	0.02
SO_3	0.03	0.03	0.04	0.04	0.05
B_2O_3	0.62	0.62	0.90	0.78	0.62
ZnO	0	0.21	0.36	0.00	0.00
ZrO_2	12.14	5.42	2.94	8.33	7.58
BaO	0.01	0.01	0.00	0.01	0.01
SrO	0.00	0.01	0.00	0.00	0.01
Total	100	100	100	100	100

Frit-1 that is used in standard recipe is not capable for formation of diopside crystalline because of CaO and MgO amount. Especially, frit-2 and frit-4 has high SiO_2, CaO, MgO and promote diopside phase. Frit-3 has high ZrO_2.

Table 2. Chemical analysis of frit composition by XRF (wt%).

Chemical Analysis	Frit-1	Frit-2	Frit-3	Frit-4
SiO_2	49.5	60.1	52	65.59
Al_2O_3	17.5	8.2	6	8.6
TiO_2	0	0	0	0.01
Fe_2O_3	0	0	0	0.01
CaO	5	12.8	0	11.2
MgO	1	6.8	8	7.2
Na_2O	14	2.8	14	1.19
K_2O	0	0.8	3	5.2
P_2O_5	0	0	0	0
SO_3	0	0	0	0
B_2O_3	3	0	4	0
ZnO	0	0	0	1
ZrO_2	10	8.5	13	0
BaO	0	0	0	0
SrO	0	0	0	0
Total	100	100	100	100

After the recipes were determined, they were milled during 50 minutes, applied on 30x60 size tiles with spray and sintered at 1205-1210°C during 60 minutes in roller continuous furnace. Totally, 13 which recipes were studied.

3. RESULTS AND DISCUSSION

Chemical analyses of frits by XRF, phase analyses by XRD, microstructure analyses and EDX by SEM and dilatometer for determining thermal expansion coefficient were investigated at Ceramic Research Centre in Eskişehir Technical University.

3.1. X Ray Diffraction Results

XRD method was used to detect diopside phase and the other crystalline phases analysis with Rigaku Rint 2200 (with Cu-K_α radiation). Figure 1 shows the XRD pattern of Z1 sample. After sintering, diopside phase was apparent in the engobe. Diopside, which makes it possible to decrease the sintering temperature and to improve the physicochemical properties and whiteness of engobe. In addition, anorthite phase also formed. In literature, when the vitreous phase amount increases diopside phase at elevated temperature and quartz intensely dissolve in the melt and anorthite is synthesized.[5]

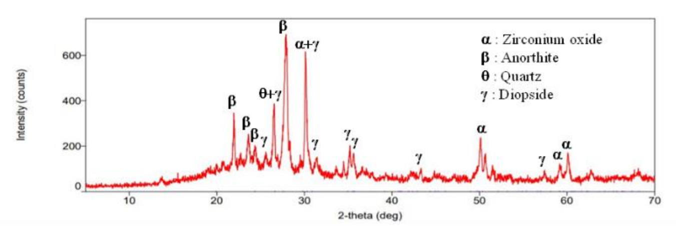

Figure 1. XRD pattern of Z1 sample.

3.2. Microstructural Investigation

Scanning Electron Microscopy (SEM) ZEISS SUPRA 50VPwas used for imaging microstructure of samples. The SEM images (Figure-2) were examined, diopside crystallization in Z1, Z12, Z13 samples was completed and particles are homogeneously distributed throughout the structure. Diopside particles are similar to zircon particles as shape and size. Those recipe compositions had present common frit composition of frit-2. However, microstructure of Z10 sample did not possess crystalline diopside phase that has similar properties. Z10 had the region where CaO and MgO phases that come from other raw materials in the recipe (Table-1) are high as an agglomerate. Agglomeration result can be explained that diopside phase formed during sintering was depleted when the temperature rises over 1100°C in the case the absence of supporting materials to crystallization.

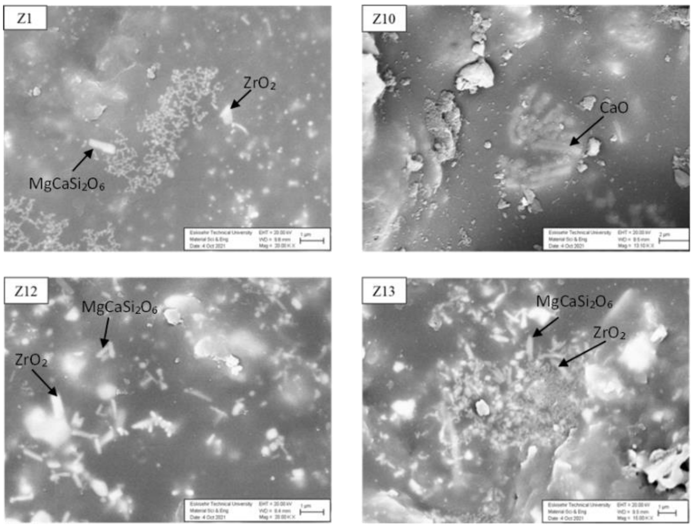

Figure 2. Back scattered SEM images of Z1, Z10, Z12, Z13 samples fired at the same conditions, 1205 1210ºC, 60 min.

3.3. Dilatometer Results

The thermal expansion coefficient measurements were made with the NETZSCH 402PC dilatometer. Generally, thermal expansion coefficient of engobe is 75.6 x 10^{-7}/K at 400°C for standard G3 at factory. Thermal expansion coefficient of engobe which developed at AKGÜN Ceramic laboratories was measured 69.8 x 10^{-7}/K at 400°C. Thermal expansion coefficients of the body and engobe converged as seen in Table 3. That is the factor to decrease internal stress and act to prevent possible deformation and defects.

Table 3. Thermal expansion coefficients of standard G3 and Z1 engobe

Samples	α300 x10^{-7}	α400 x10^{-7}	α500 x10^{-7}
STD G3 Engobe	73.5	75.6	78.5
Z1 Engobe	69.0	69.8	71.2

3.4. Color properties

Spectrophotometer was used for color measurement and glossmeter device was used for gloss. It determined by chromatic coordinates; L*, a*, b*values were measured for the engobe recipes. In addition, the success of the opaque structure expected to be obtained by gloss measurement was evaluated quantitatively. The L^*, a^*, b^* values and gloss values of sample are shown in Table 4 in detail.

Table 4. Spectrophotometer and glossmeter values of G3, Z1 Z13 engobe samples.

Recipes	L^*	a^*	b^*	Gloss
G3	85.94	-0.03	-0.42	1.8
Z1	76.98	0.55	-1.58	2.8
Z2	76.76	0.52	-1.55	3.2
Z3	73.61	0.78	-2.11	2.4
Z4	74.30	0.56	-1.63	2.5
Z5	71.04	1.13	-1.97	2.8
Z6	77.27	0.63	-2.55	2.8-3.1
Z7	71.43	1.15	-2.37	0.7-1.2
Z8	73.54	0.83	-2.65	1.9-3.0
Z9	77.70	0.64	-3.12	0.7-1.5
Z10	79.72	0.52	-2.81	1.5
Z11	80.11	0.50	-3.14	1.9
Z12	82.87	0.35	-2.60	2.2-2.4
Z13	83.64	0.21	-1.77	2.1

Table 5. Spectrophotometer values of engobe samples having different liter weight (1400, 1500 and 1600 g/L) and different particle size sieve residue (0.80 g, 2.84 g).

	L^*	a^*	b^*
0.80-1400g/L	84.02	0.15	-4.08
2.84-1400g/L	83.07	0.28	-4.23
0.80-1500g/L	83.59	0.23	-4.33
2.84-1500 g/L	84.60	0.19	-4.10
0.80-1600 g/L	85.87	0.07	-3.78
2.84-1600 g/L	86.16	0.08	-3.73

L^* value indicates whiteness and if it approaches to 100, whiteness increases. Standart and new engobe recipes were about 85 and all recipes were close to 1.8 of gloss as can be seen on the Table 4.

Determining surface properties of engobe with different density and different sieve residue, also effects of them on the final product should not be ignored. The Table-5shows that whiteness increases by increasing density and amount of sieve residue.

4. CONCLUSIONS

Frits with high SiO_2 and Al_2O_3 ratios and high CaO and MgO ratios, facilitating diopside phase formation, were added to the recipe.

As can be seen from the XRD result, obtaining the diopside phase as well as the formation of the anorthite phase increased the advantages to be obtained from the recipe.

The color measurement value increased in terms of whiteness with the increase in the density and amount of the engobe applied on the tile. Especially in recipes where frit-2composition is used, color measurement and opacity values provided the standard.

Bringing the thermal expansion coefficient of the new engobe recipe closer to the body will eliminate the possible crack formation especially encountered in large sized tiles.

As a result of the study, the frit-2 composition was determined as the new standard and its suitability for mass production was determined.

Last but not least;

- Although the standard recipe had 15 wt % zircon, that value was reduced to 5 wt % zircon in Z12 and Z13 recipes.
- As a result, overall decrease in recipe cost is about 66%.
- Decreasing of zircon from the recipe was achieved by optimizing the CaO/MgO ratio.

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