

Developing Novel Materials to Increase Opacity Performance of the CaO-Al₂O₃-SiO₂ System in Ceramic Coatings

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29.04.2019 Geliş/Received, 14.11.2019 Kabul/Accepted

Abstract

The era we live in is the age of rapid changes. Turkey is a developing country with increasing needs. As in other countries, the main axis of development inevitably constitutes the construction sector. This motivation is a common for the ceramic industry; however it should be focused on the whitening agents used on ceramic tiles with the view of their contribution on the cost including imported ingredients. In this study, a novel whitening agent is formulated by introducing native raw material compositions to reduce costs in ceramic tiles production. To characterize the whitening agent, chemical structures of the raw materials were firstly carried out with particle size, X-ray diffraction (XRD), and X-ray fluorescence (XRF) analyses. Zircon, aluminum and silicon oxide were obtained based on the regarding chemical analyzes in the content of introduced raw materials. In addition, the XRD analysis reveals that grain sizes of zircon, corundum, spinel (Li, Ti), baddeleyite and gibbsite are in between 1.50-2.00 µm.

Keywords: ceramic, zirconium, whitening, aluminum oxide, characterization, mineralogy.

Seramik Kaplama Malzemelerinde CaO-Al₂O₃-SiO₂ Sisteminde Kullanılacak Örtücülük Performansını Arttırıcı Yeni Malzemelerin Geliştirilmesi

Öz

İçinde yaşadığımız çağ, hızlı değişimlerin çağıdır. Türkiye de artan ihtiyaçları olan gelişmekte olan bir ülkedir. Diğer gelişmekte olan ülkelerde olduğu gibi, ana gelişme eksenini kaçınılmaz olarak inşaat sektörü oluşturmaktadır. Bu motivasyon seramik endüstrisi için de ortak bir unsurdur, ancak ithal edilen malzemelerin maliyete katkısı göz önüne alınarak seramik karolarda kullanılan beyazlatıcılara odaklanması gerekmektedir. Bu çalışmada maliyet azaltma çalışmaları kapsamında seramik üretiminde fiyat ve miktar açısından önemli bir girdi olan Zirkonun yerine kullanılmaya başlanan ithal beyazlatıcının yerli kompozisyonları elde edilmesine katkı sağlayacak beyazlatıcı karakterizasyon çalışmaları tamamlanmıştır. İlk

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aşamada kullanılan hammaddelerin kimyasal analizleri, tane boyutları (mastersizer) , X-Işın difraksiyonu (XRD) ve X-Işını floresans (XRF) analiz çekimleri yardımı ile kimyasal, fiziksel ve mineralojik analizleri tamamlanmıştır. Kimyasal analizlerinde zirkon silikat, alüminyum oksit ve silisyum oksit saptanmıştır. Ayrıca tane boyutlarının $d_{50}=1,50$ ile μm - $2,00$ μm arasında olduğu X-Işın difraksiyonu (XRD) mineralojik analizlerinde ise zirkon, korundum, spinel (Li ,Ti), baddeleyite, gibbsite varlığı da görülmüştür.

Anahtar Kelimeler: seramik , zirkon , beyazlatıcı , alüminyum oksit , karakterizasyon, mineraloji

1. Introduction

While some parts of the ceramic raw materials are available, zircon silicate which is used for white color and providing opacity, is not produced in our country and all zircon silicate is imported from other countries. In the ceramic sector, zircon is used for production of tile, vitrified materials, dinner ceramics, ceramic health tools as well as for production of glaze and frit needed for fabrication of ceramic materials (Zucca, 2013).

All the materials used as replacement for zircon in the recipe are called as whitening agent. These materials are purchased directly or through the seller representatives from other countries. White, nontransparent glazes of fast-fired wall tiles are made opaque by the zirconia (ZrO_2) present in the frits. Zircon plays an important role in providing to the wall and floor tile glaze. Zircon (ZrSiO_4) is increasingly reducing the amount of use due to both high costs and the rapid depletion of reserves even alternative glaze systems are looking for ways to get rid of it completely (Pekkan, Karasu 2009).

The grain size of the zircon demanded for producing glaze and engobe is $9 \mu\text{m}$ zircon ($d_{50}=1.2-2 \mu\text{m}$) (Synders et al., 2005).

In this study, the mineralogical and chemical composition and grain size of the whitening agents used in tile coating were investigated by using XRD, XRF, classical chemical melting method and Mastersizer.

2. Materials and Method

In this study, characterization of different whitening agents was tried to be defined. While physical and chemical tests give information about the material, it will shed light on the domestic whitening studies to be carried out in the future.

Table 2.1 The types of whitening agents

COMPANY	MATERIAL
SILPO	SILPO GLK
AMC	ZIRKUOX MEDIUM
AMC	ZIRKUOX MED KFG
AMC	ZIRKUOX EXTRA-2
REMIX	WG-41
GUZMAN	ZA-40

The chemical compositions of the raw materials were determined with a XRF spectrometer (Panalytical Axios). Samples were prepared as fused beads for XRF. Fused beads were created by mixing a finely powdered (<63µm) sample with a flux (lithium tetraborate /metaborate mixture) in a flux /sample ratio of 10:1 and then heated to 1050°C in a platinum crucible. The powders were heated up to 1000°C for 1 h to determine the loss of ignition as weight difference before and after heating.

The grain size analysis, 1 gram of sample was dissolved in water and analyzed in Malvern 3000 in liquid form.

X-ray powder diffraction patterns were recorded at room temperature with a Panalytical X'pert Pro MPD diffractometer using Cu K α radiation and the X'Celerator Detector on diffracted beam. XRD data were collected in a Bragg Brentano (θ/θ) vertical geometry (flat reflection mode) between 3° and 70° (2 θ) in steps of 0.02°2 θ and step-counting time of 1 s. The X ray tube operated at 40 kV and 30 mA. 1/2° divergence slit, a soller slit (0,04 rad) and a 10 nm fixed mask were mounted in the incident beam pathway. The software High Score Plus (v.6.0) for peak identification and automated search-match was used to analyze the resulted of diffraction patterns. The quantitative analyses have been carried out by the combined Rietveld-Reference Intensity Ratio (R.I.R) method as explained by Young (1995).

3. Results and Discussion

3.1 XRF Analysis and Chemical Compositions

As shown in Table 3.1, chemical structures of whitening agents are given as percentage. After quantitative scanning with XRF, the analyzes were completed with classical chemical melting. The results showed that ZrO₂ was 20-33% in 5 whitening agents. It is determined that the Al₂O₃ ratio is higher than the ZrO₂ ratio and it consists mainly of Al₂O₃ + ZrSiO₄.

Table 3.1. % Chemical analysis results

Chemical Analysis	ZIRKUOX EXTRA-1	ZIRQUAX MED KFG	ZIRQUAX MED	ZIRQUAX EXTRA-2	WG-41	ZA-40
L.O.I*	3,62	0,48	0,5	0,41	0,94	1,01
SiO ₂	12,18	20,86	16,19	11,31	16,9	16,62
Al ₂ O ₃	55,02	47,33	49,73	64,53	49,77	49,07
TiO ₂	0,18	0,17	0,15	0,07	0,15	0,16
Fe ₂ O ₃	0,01	0,01	0,01	0,01	TRACE	0,01
CaO	2,23	0,19	0,1	0,06	0,09	0,07
MgO	1,65	0,23	0,24	0,3	0,25	0,25
Na ₂ O	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
K ₂ O	0,01	0,02	0,01	0,01	TRACE	TRACE
ZrO ₂	24,95	30,35	33,12	23,36	31,98	32,44

*Lost on ignition

The functions of the zirconium silicate and alumina can be described as below.

Zirconium Silicate: Zirconium silicate forms are used in varying particle size distribution. It is a very good opacifier. Zirconium silicates are used as opacifiers in glazes fired between 940 and 1300 °C. Only a part of the zirconium silicate joins the other components while the other part remains its own. The associated part increases the crack resistance of the glaze. Zirconium also has a color stabilizer effect (Sacmi, 2009).

Zirconia is used sometimes as heating agent, sometimes used as abrasion resistant machine parts, such as cutting devices and extrusion molds, due to its high hardness and abrasion resistance, are sometimes seen as indispensable materials in ceramic coatings for oxidation and thermal barrier due to their high chemical stability (Tokgöz, 2008; Shockelford and Doremus, 2008).

Alumina (Al₂O₃): Calcined alumina or alumina hydrate, taken from feldspars, kaolin and corundum. When used in appropriate proportions (4 to 8%) in low-grade glazes, provides increase in viscosity, bending strength, resistance to acids, decrease in tendency to devitrification (crystallization), expansion coefficient, increase in improved opacity. The amount of Al₂O₃ involved in the glaze is reduced or increased based on the fusing temperature of the glaze. The matt and satin surface glaze contains a high amount of Al₂O₃. But glossy surface glazes contains small amount. The amount of Al₂O₃ added to the glaze also depends on the grain size distribution. If the particles are small, the amount to be added decreases and the larger the particle size, amount of Al₂O₃ increases. Due to the fact that it is an amphoteric substance, this oxide is combined with basic oxides to combine with silica. It is therefore the most effective stabilizer (Kaya, 2010). Since whitening agents are recommended by companies as zircon alternatives, they can be preferred as long as their prices are below the zircon price. This enables firms to produce whitening agents by using materials that are cheaper than zircon. Al₂O₃ is used to increase whiteness alongside zircon.

3.2. Grain Size

The determination of the grain size distribution of the materials to be used is important in the phase transformation of materials against the heat, and behavior in the prescription. Another condition is the conversion of the tetragonal (and cubic) zirconia phase at high temperature into the monoclinic phase at room temperature and its relevance to the particle size of zirconia. According to many sources, if tetragonal zirconia is pure and greater than a certain (critical) size, it returns to room temperature as a monoclinic phase. (Rendtorff et al., 2009; Garrido et al., 2006; Ebadzadeh and Ghasemi, 2002; Zhao et al., 2003). The grain size distribution of the whiteners used alternative to the zircon should be close to the grain size distribution of the zircon used. Relativity of the grain size distribution of materials with water sorption and color measurements (L, a, b values) of the will be examined separately.

Table 3.2. Grain size of zircon

Grain Size	d50	d90
Zr MO	1,53	4,77

Table 3.3 Grain size distribution of the whitening agent samples

GRAIN SIZE	d50	d90
ZIRKUOX EXTRA-1	2,26	12,44
ZIRQUAX MED KFG	2,74	14,79
ZIRQUAX MED	2,14	10,85
ZIRQUAX EXTRA-2	2,61	14,33
WG-41	1,95	8,64
ZA-40	1,78	8,78

When the particle size distribution analyzes were examined, it was seen that the d50 values of the samples ranged from 1.2 to 2.7 μm . The d50 value for the zircon used in ceramic ranges from 1.5 to 2.5. (As shown in Table 3.2). It is seen that Table 3.3 d50 value of 4 of 6 samples is within this range and 2 of them are within 2-3 μm range. Although the range of 2-3 μm is an acceptable range, samples with values above this are excluded from the acceptance criteria. The d90 value of the zircon used should be 9 μm . When the results of the samples are examined, it is seen that only 2 materials are in desired size. D90 value of 4 samples is over 10 μm .

The desired size of the grain size distribution is important for the more uniform distribution of the material in the recipe and the grinding time.

The effect of grain size distribution on glaze surfaces is shown in Figure 3.1.

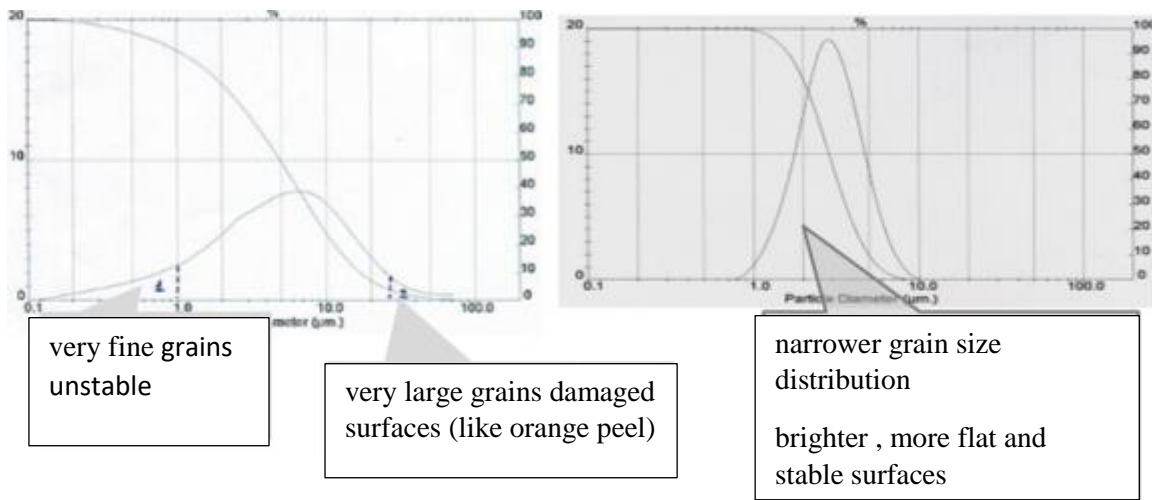


Figure 3.1 Effect of particle size distribution on surface performance

3.3 Structural Properties

XRD phase analysis of whitening agent samples are given in Table 3.4 These analyzes showed that whitening agents were mostly corundum. Apart from corundum, zircon and dolomite were detected in a sample and information was obtained about the mineralogical content of the materials.

Table 3.4 XRD phase analysis results of whitening agents

XRD Phase Analysis	ZIRKUOX EXTRA-1	ZIRQUAX MED KFG	ZIRQUAX MED	ZIRQUAX EXTRA-2	WG-41	ZA-40
Corundum	68%	44%	65%	49%	65%	64%
Zircon	16%	49%	33%	50%	33%	34%
Feldspat		7%				
Dolomite	14%					
Gibbsite						2%
Others	2%		2%	1%	2%	

According to the XRD and chemical analysis results of Zirquox Med KFG material, it was seen that this material is $ZrSiO_4$ when the 49% Zircon crystal and 20,86% SiO_2 contents were taken into consideration. Since the corundum is 44%, we can say that the material is a corundum based material.

When the XRD and chemical analysis results of Zirquox MED material are examined, it is seen that this material is mostly corundum.

When the XRD and chemical analysis results of Zirox Extra 2 material are examined, it is seen that this material is mostly corundum as well.

When the XRD and chemical analyzes of WG-41 sample were examined, this material was identified as $ZrSiO_4$ considering the 65% corundum from XRD pattern, silica and zirconium contents from the chemical analysis.

It is seen that the material of Guzman ZA 40 is mostly corundum. According to the chemical analysis, it is observed that it has approximately 49.07% Al_2O_3 and about 32.44% zircon. It can also be said that it is $ZrSiO_4$ because of its silicon content. We can call this material corundum.

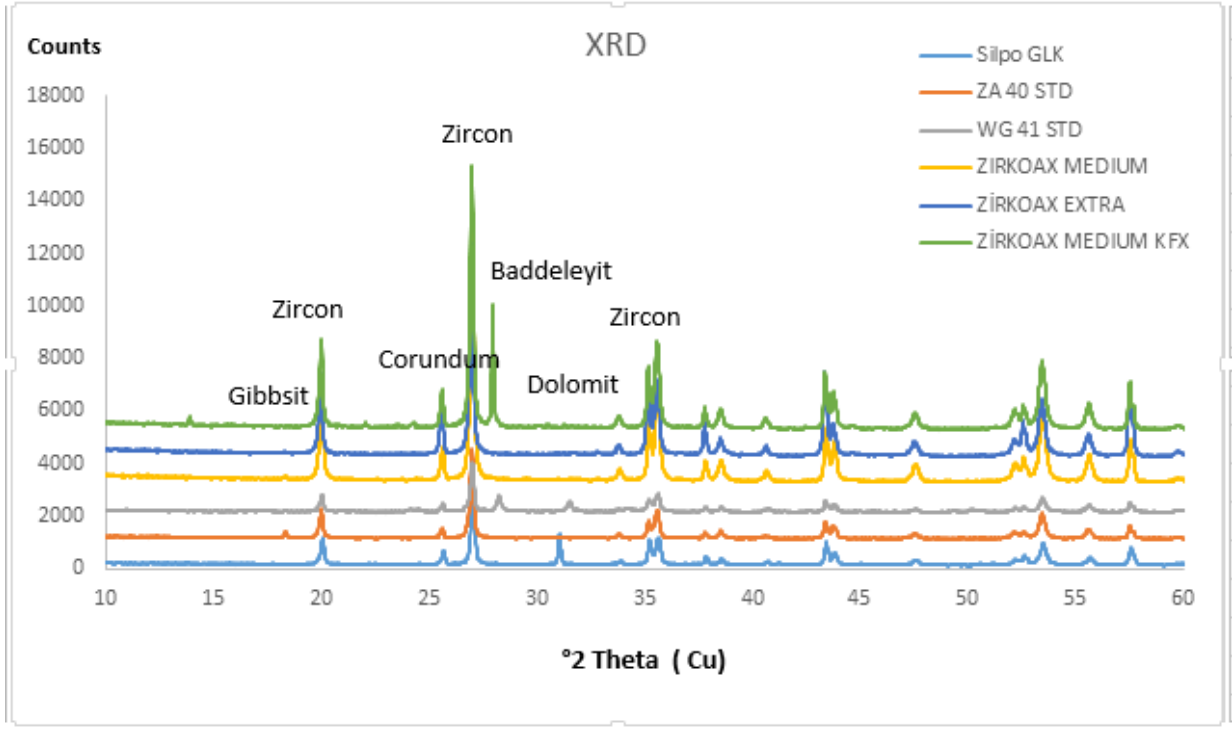


Figure 3.2 XRD results

4. Conclusion

In this study, characterization of imported whitening agents was determined. It was observed that 4 of 6 whitening mineralogical minerals composed of corundum with 50-65% ratio. In general, these materials were found to contain $ZrSiO_4$ and they contained a small amount of different minerals in their structure. Alternative materials studies related to many raw materials used in the ceramics industry and especially the materials that imported are carried out and will continue. These studies should be continued in order reduce the cost and produce alternative materials. In this context, in the future, the characterization studies will be very important for the purpose of domestic production.

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