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Production of translucent ceramics containing diopside-akermanite phases by fast firing

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In this study, research was made on the production of white and translucent ceramics with a low water absorption and high resistance using waste dolomitic sepiolite, cullet and calcite through fast firing under operational conditions. For this purpose, 4 different recipes were prepared. The recipes were first dry ground and shaped with a dry pressing method. The shaped samples were then fired in a fast firing kiln at 1140 °C for 70 minutes. Strength, water absorption, porosity and color measurements were made on the fired samples as well as mineralogical and microstructural examinations. Consequently, diopside and amorphous phases and diopside and akermanite based ceramic structures were produced using the waste materials through fast firing at 1140 °C. L* values of the fired samples were found to be between 92.30 and 95.40. In the samples with the akermanite and diopside phases, the ratio of dissolution was found to be higher in acids than samples containing the diopside and amorphous phases. Consequently, highly white and translucent ceramics with a low water absorption capacity were obtained using the waste materials used through fast firing.

Key words: Diopside, Akermanite, Sepiolite, Translucent ceramic, Fast firing.

Introduction

Diopside is a very important phase in glass ceramics, ceramic products and for biomedical applications. There are many studies on this topic in the literature [1-3]. Diopside is a calcium and magnesium silicate with the chemical formula $CaMgSi_2O_6$ [4]. Diopside crystals are formed in glass ceramics to be used as a frit, which is prepared at 1450-1500 °C [5, 6]. Most of the raw materials, particularly quartz, may not liquify when ceramics are subjected to a fast firing process. This prevents crystallization in the structure and accordingly, the desired characteristics cannot be obtained. For this reason, the selection of proper raw materials is very important in fast firing practices [7]. Fröberg et al. [8], in their study, stated that diopside and wollastonite crystals may be formed in operational kilns through fast firing at 1215 °C (for 60 minutes). In order to obtain a high whiteness value [*L**-value (lightness)] in ceramics, raw materials should not contain any pigments or ZrO_2 is added to the structure in specific quantities. The later process, however, causes a rise in the cost. For this reason, many studies have been made on glazes with diopside in order to increase the opacity and *L**-value in ceramic glazes [9, 10]. In ceramic products, particularly porcelain products, low water absorption, high resistance, whiteness and translucency are very important characteristics. In addition to these characteristics, the firing time is also very important. However, when porcelain products are fired through traditional methods, long periods are required for firing. Instead, production of a ceramic within a short period and at very low temperatures is quite important in terms of capacity and profitability [11, 12]. The most important point with fast firing is to ensure the desired crystallization. Studies have been performed on sintering, crystallization and chemical resistance of diopside glazes, which are formed in ceramics at different firing speeds [13, 14]. However, the number of the studies on production of diopside-based white translucent ceramic structure through fast firing at low temperature is quite limited.

Sepiolite is a non-swelling, lightweight, porous clay with a large specific surface area. Unlike other clays, the characteristic particles of sepiolite have a needle-like morphology. The high surface area and porosity, as well as the unusual particle shape of this clay account for its outstanding sorption capacity and colloidal properties that make it an important material for a wide range of purposes. The material described as "dolomitic sepiolite", which contains over 50% sepiolite, constitutes the biggest portion of the volume in an upper sepiolite bed. The color of dolomitic sepiolites varies from white to light beige and beige according to the sepiolite content and their unit

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Table 1. Chemical analyses of the raw materials used (in wt %)

	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	SO_3	LOI
Sepiolite	0.07	0.07	11.01	23.36	0.82	0.32	39.51	0.01	0.36	24.46
Waste Glass	10.60	0.08	8.46	2.86	4.54	0.09	72.93	0.04	0.13	0.16
Calcite	0.65	0.06	52.84	0.09	1.50	0.06	1.51	0.01	0.59	42.48

volume weights decrease [15]. Dolomitic sepiolite is quite important in production of diopside-based ceramics due to melting capacity at lower temperatures. When dolomitic sepiolite is sintered, CaO-MgO-SiO_2-based enstatite and diopside phases are formed [16].

The aim of this study is to produce CaO-MgO-SiO_2-based translucent ceramics with a low water absorption and a high level of whiteness through the fast firing of 4 different mixtures. These mixtures are composed of sepiolite that are available in a factory stockyard as waste (-1 mm), cullets and calcite, and fast fired at 1140 °C for 70 minutes. Today, waste utilization is quite important for both environmental protection and energy saving purposes. Therefore, using waste materials as the main ingredients increases the importance of the study.

Materials and Methods

In this study, dolomitic sepiolite, which is used for production of cat litter and stocked as a waste under 1 mm, cullet and calcite were used in order to produce diopside-based ceramics. The major components were determined by X-ray fluorescence using a Spectro X-Lab 2000 spectrometer. Chemical analyses of the raw materials used are given in Table 1.

4 different recipes, which contained dolomitic sepiolite, calcite and cullet, were prepared in order to produce diopside-based ceramics. Chemical analyses of the recipes prepared are given in Table 2.

These recipes were dry ground in ball-type jet mills. As sepiolite possessed rheological problems in wet grinding, dry grinding was preferred. Particle size analysis was conducted using a Malwern laser particle size analyzer. The ground samples were moisturized at 5% through a spraying method and shaped on line with the dimensions of 100 mm × 100 mm × 5 mm using a Gabrielli hydraulic press through a dry pressing method with a pressure of 400 kg/cm^2. The samples were dried at 110 °C. Then, they were fired in operational kilns (for earthenware) through fast firing at 1140 °C for 70 minutes. The XRD analyses of bulk and fired samples were performed using a Rigaku miniflex diffractometer with Cu-K_α radiation in the range of 2θ between 2 and 70 °.

The Archimedes method was used for determining the water absorption (ISO 10545-3), bulk density, density and porosity values of the fired products. The strength values were measured (ISO 10545-4) by a Gabrielli three point bending instrument.

Color measurements were carried out using a Minolta 3600d spectrophotometer and the chromatic coordinates were expressed as L*, a*, b*.

Morphology and microanalysis of fired samples were determined by SEM/EDX. SEM studies were carried out with a Zeiss Supra 50 VP instrument, after leaching with a 10% HF solution and covering the sample surfaces with gold. Afterwards, the images of fracture surfaces were obtained.

In the test of resistance against acids and alkalis, 10% NaOH and HCI solutions were prepared and the samples were separately boiled in these solution at 95 °C for 2 hours. Then, weight losses were measured and given in percentages according to the initial weight.

Table 2. Chemical analyses of the mixtures prepared (in wt %)

Wt. %	R1	R2	R3	R4
Na_2O	4.48	4.62	4.76	4.89
K_2O	0.09	0.09	0.09	0.09
CaO	20.14	19.87	19.61	19.36
MgO	16.53	16.21	15.90	15.62
Al_2O_3	2.65	2.70	2.74	2.78
Fe_2O_3	0.26	0.25	0.25	0.25
SiO_2	55.83	56.24	56.62	56.99
TiO_2	0.02	0.02	0.03	0.03

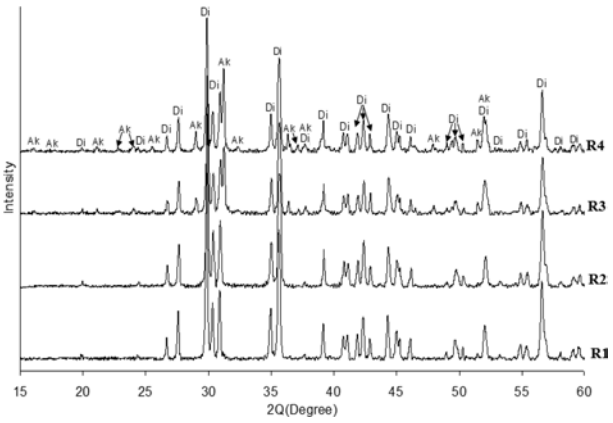

Fig. 1. XRD patterns of the samples, which were fast fired at 1140 °C.

Results and Discussion

Mineralogical analysis

XRD analysis of the fired samples indicated that "diopside [Ca(Mg, Al)(Si, Al)$_2$O$_6$], akermanite [$Ca_2MgSi_2O_7$] and amorphous phases were present (Fig. 1). It was

Table 3 . Technological properties of fired samples

	R1	R2	R3	R4
Total shrinkage (%)	12.01	12.30	12.45	12.54
Firing strength (kg/cm^2)	78.30	83.70	102.30	118.50
Apperent density (g/cm^3)	2.20	2.35	2.50	2.52
Water absorption (%)	10.20	5.50	0.44	0.10
Apperent porosity (%)	23.20	13.40	0.70	0.20
Solubility in HCl (%)	0.78	0.31	2.18	2.22
Solubility in NaOH (%)	0.50	0.28	0.13	0.14
L*	92.39	93.91	94.95	95.40
a*	1.37	1.33	0.83	0.77
b*	1.23	0.28	2.10	3.04

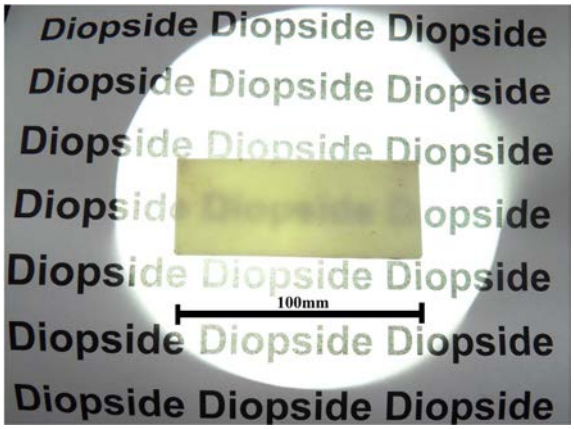

Fig. 2. The transparency of the sample given as R4.

observed that diopside crystals were formed in the R1 and R2 recipes as well as the amorphous phase in limited quantities. In the R3 and R4 recipes, both akermanite and diopside phases were detected although the former forms at higher temperatures.

Physico-mechanical properties

In addition to an increase in fired shrinkage values in the recipes, the density values also increased. However, there was only a slight increase in the R3 and R4 recipes (Table 3). As the density increased, the water absorption and apparent porosity values decreased. In the R3 and R4 recipes, no structural deformation was detected with water absorption values in the range of 0.44% and 0.10%. While strength values varied from 78.30 to 118.50 kg/cm^2, the R4 recipe had the highest value at 118.50 kg/cm^2 (Table 3).

Dissolution in acids and alkalis

The dissolution level of R1 and R2 recipes in acid and alkali solutions was limited and dissolution occurred in the glassy structure rather than the diopside crystals. In the R3 and R4 recipes, in which akermanite and diopside were formed together, the dissolution was

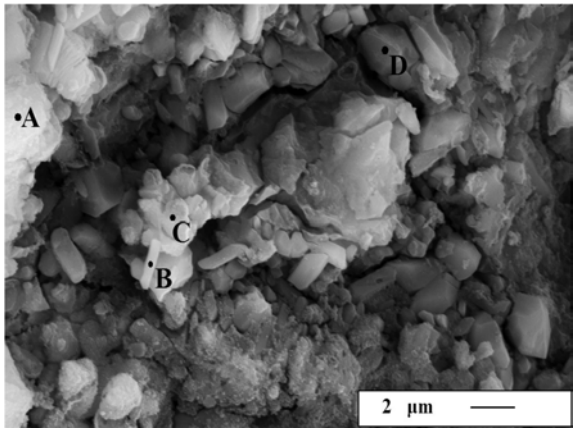

Fig. 3. Fracture surface image of R4 recipe.

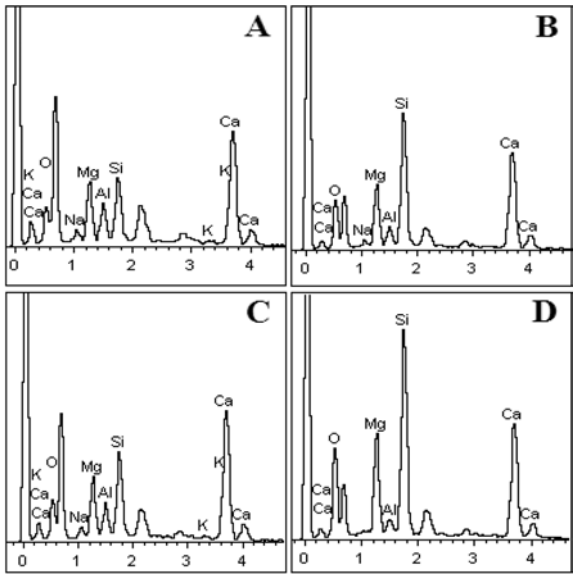

Fig. 4. EDX analysis of the points marked in SEM image in Fig. 3.

higher in acids although dissolution was low in a basic environment. In the R3 and R4 recipes, it was found that the dissolved crystals were akermanite as diopside crystals were stable in acidic and basic environments (Table 3).

Colour properties

L* values of the fired recipes varied from 92.30 to 95.40 and the highest value, 95.40, belonged to the R4 recipe (Table 3). These recipes had a high level of whiteness. The whiteness of the R1 and R2 recipes with a single diopside phase was found to be lower than those of the R3 and R4 recipes, in which both the diopside and akermanite phases were formed together. The transparency of the R4 recipe (thickness 4 mm) is shown in Fig. 2.

Microstructural properties

The crystal sizes of the R4 recipe, which was fired at 1140 ºC for 70 minutes, were found to be approximately ~1-2 µm in the fracture surface of the SEM image. It

was determined that diopside was formed as two different crystals through SEM/EDX studies. The first type of crystal was rod-shaped crystals with a length of 2 μm and a width of 0.5 μm (represented as B in Fig. 3). The other crystals were small prismatic diopsides, which were smaller than 1 μm (represented as D in Fig. 3). In Fig. 3, A and C points represent akermanite crystals. The F content, which remained as a residue even after the samples were seared in HF, was reflected in the EDX peaks. Higher CaO ratios from the analyses performed in A and C points shows that these points are also akermanite crystals (Fig. 4).

Conclusions

Samples composed of sepiolite, calcite and cullet, were dry ground with no noticeable problem. Since dry grinding is more cost-efficient than wet grinding, this result seems to be important for mass production. Diopside and an amorphous phases were developed in the R1 and R2 recipes and diopside and akermanite phases were developed in the R3 and R4 recipes through fast firing at 1140 °C (for 70 minutes). In addition, the structures obtained had a high level of whiteness and translucency. In the R1 and R2 recipes, which contained diopside and amorphous phases, acidic or basic dissolutions were detected in very low quantities and the dissolution was related to the glassy phase. In the R3 and R4 recipes, which contained akermanite and diopside, acidic dissolution was found to be high. It was observed that akermanite was dissolved in acid at higher quantities when compared to alkalis.

The results of this study was found to be quite important for ceramic factories since highly white and translucent structures can be produced through fast firing using waste materials such as cullet and sepiolite.

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