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Investigation of porosity of ceramic tiles by means of image analysis method

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Amount, size and distribution of porosity are among the important factors which affect physical and mechanical properties of ceramic tiles. In this study, the effect of flux variation in porcelain tile recipes and different firing conditions were investigated. X-ray diffraction and Rietveld analyses were used to determine how fluxes affect the phases of samples. In the consequence of these analyses it was found that changing the variation of fluxes and different firing conditions increased liquid phase amount and densification hence the amount and size distribution of porosity decreased. Image analysis method was used to determine the amount and morphology of porosity of porcelain tiles and the results were compared with Archimedes method, Helium pycnometer. Parallel between the amount of porosity determined through image analysis and the amount determined through Archimedes test and helium pycnometer and the possibility of determining the size distribution and morphology of porosity showed that this new method is advantageous.

Key words: Image analysis, Porcelain tile, Porosity.

Introduction

Porcelain tile has increasingly become a widely-used ceramic product in recent years. According to ISO 10545, various features of porcelain tile such as high amount of abrasion resistance (< 205 mm^3), the low water absorption value (< 0.5%), high bending strength (> 27 N/mm^2), resistance to frost and chemicals gained it a significant place in the sector [1].

The relationship between mechanical strength, stain resistance of ceramic materials and the size of porosity, and volume has been the subject of various studies. Amoros *et al*. [2] studied the amount of porosity of porcelain tile samples in different grinding conditions after sintering and they determined that insufficient grinding conditions formed large porosity in the body after sintering; therefore stain resistance was adversely affected. Dondi *et al*. [3] indicated that the most important variables affecting the stain resistance are size and amount of porosity in porcelain tile microstructure after polishing. Kobayashi *et al*. [4] investigated the effect of different firing temperatures on bending strength of the porcelain. In their study, they showed that spherical and small-size porosity in microstructure had a positive impact on the strength and an increment in the amount of porosity decreased strength exponentially.

The porosity is connected to the liquid phase during firing [5] and is affected by the transformations that occur during sintering. For this reason, selection of components and fluxes that affect the microstructure phases and alkaline amounts are important [6]. The microstructure of ceramic materials is composed of crystals, liquid phase and porosity. Fluxing raw materials in recipes decrease the temperature of the liquid phase formation and the viscosity of the glassy phase [7-12]. The fluxing components used as auxiliary components to facilitate the sintering of ceramic product and the formation of liquid phase is potassium feldspar, sodium feldspar and calcium feldspar. Other fluxing raw materials are nepheline syenite, dolomite, wollastonite and talc [13-15]. When talc is added to body even in small percentages (2-5%), it contributes to production of dense ceramic products with low water absorption (porcelain tiles) producing low-melting- point eutectic mixtures via alkaline feldspars [16].

Sintering a material leads to formation of closed porosity and open porosity which is connected to the surface. Mass density of bodies and open porosity are determined through Archimedes method in accordance with Eq. (1) and Eq. (2). According to this method, the density is calculated based on dry weights of fired samples (W_d), weights in water after 4 hours of boiling (W_w) and wet weights after cleaning the surface (W_s).

$$\textit{Bulk density} \frac{w_d}{w_w - w_s} \tag{1}$$

$$\textit{Open porosity}\ (\%)\ \frac{w_w - w_d}{w_w - w_s} \times 100 \tag{2}$$

A certain amount of helium gas is sent from a reference volume to the cell including the sample and the gas is forced enter from one side and exit from the

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other side. The system is at atmospheric pressure at this time [17]. Proportion of the amount of sample put in the cell to the value of volume obtained from helium pycnometer gives theoretical density (ρt) as in Eq. (3).

$$V_x = \frac{(PV_{sys} + P_{sys}V_r - P_sV_s - P_rV_r)}{P_{sys} - P_s} \quad (3)$$

where, V_x= the volume of unknown material

V_s= known volume

V_r= known volume of reference cell

P_s= the measured pressure in sample cell after the cover of the cap has been closed

P_r= the changed pressure of reference cell the volume of which is known [18].

The bulk density determined through Archimedes method and theoretical density determined by Helium pycnometer is used in Eq. (4) for the total porosity analysis in Helium pycnometer.

$$\text{Total porosity (\%)} = \frac{(\rho_t - \rho_b)}{\rho_b} \times 100 \quad (4)$$

where *P(%)* is the total porosity ρ_t is the theoretical density (g/cm^3) and ρ_b is the bulk density of the sample [17].

The mercury porosity is used to measure porosity size distribution. The mercury is forced to enter the network structure and porosity size distributions with a diameter of 360-0.003 mm can be determined in this device [17]. However, the mercury porosimeter can not be widely used because of its high cost, difficulty in supplying the mercury, its effects on the environment, and of the fact it can solely investigate bulk sample.

In recent years, image analysis method has become a more easy-to-use analysis method owing to the development of computer image processing and image analysis software programs. The particle size, porosity size and distribution can be measured by using images taken from optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM). The images must be taken from a high-voltage back scattered electron with the best resolution [17]. On the images obtained through back scattered electrons which are taken from polished surface of the sintered tiles via SEM phase regions are coloured percentage of these regions are measured.

When the coloured regions are proportioned to uncoloured regions, investigated porosity or crystal amount can be determined. The colored regions show the percentage of porosity. The percentage of porosity calculated by image analysis program (SCANDIUM) is shown in Eq. (5).

$$\text{\% Porosity} = \frac{A_{porosity}}{A_{total}} \times 100 \quad (5)$$

where $A_{porosity}$ is porosity area, A_{total} is all the area [17].

In literature, only a few studies related to the use of image analysis method in ceramics are available. Mahdavi *et al*. [19] compare the X-ray diffraction (XRD) and image analysis method to determine the percentage of crystallization in two different glass-ceramic samples based the cordierite. Due to the fact that there is not a significant difference between the two methods, it is concluded that image analysis technique can be used to measure the percentage of crystalline phase. Mannesson *et al*. [20] use image analysis method in their study to determine the particle size distribution which is important in terms of technological properties of WC cutting tool material. Also, Kang *et al*. [21] study on the images taken from the optic and electron microscope through image analysis method in determining the amount, size and shape of carbide in materials with high amount of metal carbide. The obtained results are described in relation to features such as hardness and toughness. Diogenes *et al*. [22] have made a statistical analysis between the visual inspection and image analysis method for the samples sintered magnesite and low carbon steel, and image analysis method has been proved to provide faster and give more accurate results.

In this study, the amount of total alkali and firing conditions are changed in porcelain tile body, size and morphology of porosity was examined using Archimedes method, Helium pycnometer and image analysis.

Experimental Procedure

The clays, feldspar, pegmatite and talc for ceramic tile body were used in experimental studies and chemical analysis of the modified raw materials is given in Table 1. The total alkali content of used raw material was low. Thus clays, pegmatite was kept constant to see what kind of an effect talc of rich alkali will inflict on the body. Instead of feldspar, a talc of 2%, 4% and 6% weight was added and the total alkali contents of the recipes were changed (Table 2). Raw materials used in recipes were wet-grounded in ball mill until the sieve balance of 63 μm reached the required value of 2.5-3.0, then the slips obtained were dried in an oven at around 110 °C, humidified at a level of 7% (7 wt.% moisture content) and finally sieved

Table 1. Chemical analysis of raw materials (wt.%).

Raw materials	*L.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Feldspar	2.00	72.50	15.39	1.11	2.01	0.18	4.64	1.89
Talc	9.32	55.34	0.68	0.25	0.61	33.75	–	–

*L.I: loss of ignition.

Table 2. Prepared recipes.

Number of recipes	Feldspar	Talc	Total Alkaline amount
1	14	0	7.07
2	12	2	7.58
3	10	4	8.09
4	8	6	8.61

down to 1 mm before forming. Rectangular samples, 100 × 50 × 8 mm in size, were prepared by uniaxial pressing at a forming pressure of 37 MPa (Gabbrielli Press). The samples shaped were sintered at 1200 °C/ 30 min. (floor tile regime) and at 1205 °C / 40 min. (porcelain tile regime). The effect of variation of fluxing raw material and firing temperature/time on phases of samples were determined by XRD and Rietveld analysis while porosity features were examined through Archimedes method, helium pycnometer and image analysis. Phase analyzes were investigated by XRD (Rigaku Rint 2200) between 10-70 ° at 40 kV and 30 mA current. The amount of crystalline phases was calculated by Maud software in the Rietveld method [23]. The bulk density, open and total porosity of sintered samples was determined according to Eqs. (1-4). Tile samples were cut for image analysis method and they were polished via an automatic polishing device (Strues-Tegra Force 5). Microstructure of the samples whose surface polished was examined by SEM Zeiss EVO 50 EP. The back scattered electron images were examined by Scandium image analysis program. The amount of porosity was determined according to Eq. (5) and the size distribution of porosity was scaled as different micron ranges in the program according to the colored regions.

Results and Discussions

XRD and Rietveld analyses were performed to determine the effect of variation in the alkali ratio on phases. The phases obtained in samples were given in Figure 1 and the amount of phases was shown in Table 3. The phases of the samples are albite, mullite and quartz in 1205 °C/ 40 min. firing conditions. The amount of glassy phase produced during firing varies according to alkaline-earth alkaline oxide content and ratios. The variation of total alkali amount and firing conditions especially the increase of the dwell time led to the dissolution of quartz and albite, and thus increased the amount of glassy phase. high amount of the quartz dissolved passed to glassy phase instead of creating mullite crystal. Therefore the amount of mullite crystal did not change significantly.

The amounts of porosity detected by Archimedes method, helium pycnometer and image analysis and size distribution of porosity analyzed by image analysis are shown Table 4. The variation of distribution, size and shape of porosity in sintered tiles are investigated in electron images scattered back through Zeiss Evo 50 scanning electron microscope (SEM) in image analysis program. Back scattered electron image from each sample is analyzed three times by image analysis program (Scandium). SEM images investigated are shown in Fig. 2. The regions marked with green colour represent the porosity in images. The data is provided for each on the diameter of porosity based on Scandium program. According to these datas, as 0-5 μm, 5-15 μm and 15-30 μm the ranges are determined depending on the choice of user and calculated percentages of the ranges. It is observed that the amount of glassy phase changes and the amount of porosity reduces depending on the increase in the amount of total alkali in the samples. When the amounts of porosity (%) is examined

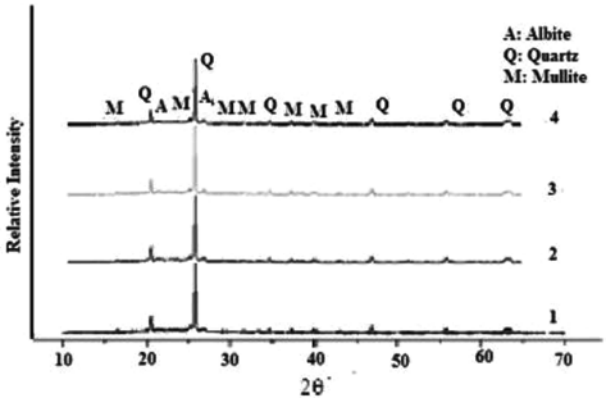

Fig. 1. Phase analysis of samples.

Table 3. Results of quantitative analysis of samples on different firing conditions 1205 °C/40 min. and 1200 °C/30 min.

Samples	Quartz	Albite	Mullite	Glassy Phase
1205 °C/40 min.				
1	36.38 ± 0.29	4.85 ± 0.24	7.87 ± 0.25	50.89 ± 0.93
2	30.96 ± 0.23	4.24 ± 0.22	7.91 ± 0.23	56.88 ± 0.86
3	28.76 ± 0.26	1.51 ± 0.23	8.15 ± 0.27	61.56 ± 0.89
4	26.86 ± 0.24	1.15 ± 0.21	6.83 ± 0.24	65.16 ± 0.84
1200 °/30 min.				
1	31.08 ± 0.29	7.37 ± 0.29	6.93 ± 0.28	54.63 ± 0.74
2	31.83 ± 0.24	7.29 ± 0.24	7.49 ± 0.23	53.39 ± 0.89
3	30.48 ± 0.28	5.26 ± 0.25	6.98 ± 0.25	57.27 ± 0.90
4	27.85 ± 0.23	3.93 ± 0.23	6.19 ± 0.25	62.04 ± 0.89

Table 4. Porosity amount (%) of samples and size distribution of porosity by means of image analysis.

Samples sintered a)at 1200 ºC/30 min. b)at 1205 ºC/40 min.	Archimedes method	He pyncnometer	Image analysis	Size distribution of porosity (%)		
				0-5 μm (%)	5-15 μm (%)	15-30 μm (%)
1 a	11.41	14.09	11.71 ± 1.13	80.7	17.2	1.7 > 30 μm: 0.2
2 a	8.87	11.25	5.73 ± 0.41	86.7	12.5	0.6
3 a	5.70	5.90	4.75 ± 0.46	89.3	10.2	0.8
4 a	4.59	5.02	5.99 ± 0.59	82.2	16.6	0.1
1 b	7.40	11.30	9.28 ± 2.28	94.3	3.6	1.2 > 30 μm: 0.6
2 b	4.87	6.75	4.57 ± 0.76	96.3	3.6	–
3 b	1.01	4.18	4.23 ± 0.65	85.5	13.8	0.6
4 b	0.49	4.16	5.72 ± 0.77	88	12	–

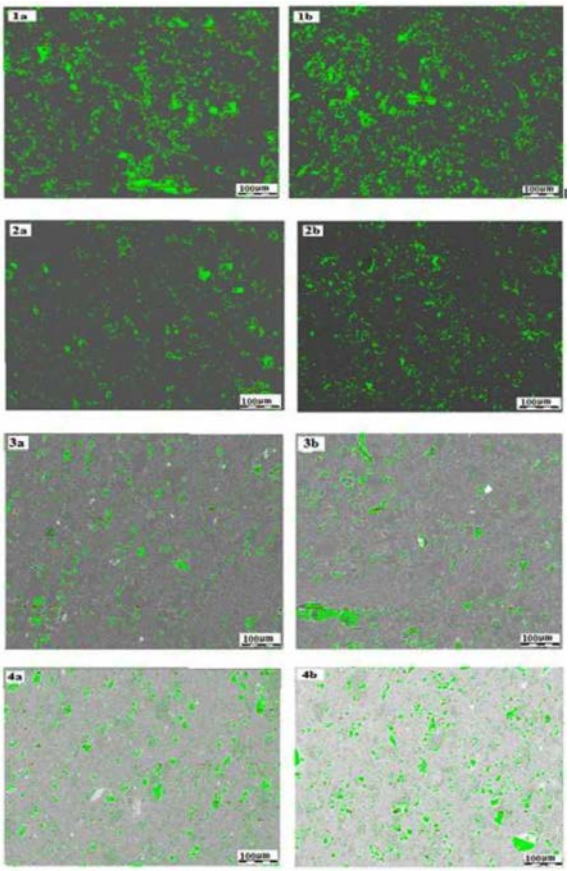

Fig. 2. Back scattered electron image of samples a) at 1205 ºC/40 min and b) 1200 ºC/30 min.

it is observed that in all three methods measured porosity values decrease with the increase of total alkali content and dwell time in firing conditions.

While the calculation in Archimedes method is performed depending on the amount of water entered into the open porosity of samples, in helium pycnometer method the calculation is performed depending on the gas entered into the porosity with help of pressure. For this reason the porosity values determined by the Archimedes method are lower than the values obtained through helium pycnometer as reflected in Table 4.

The differences between the values determined by helium pycnometer and image analysis method especially in sample 4, Table 3 is considered to occur for this reason. As seen in Table 3 as the amount of talc increases, the amount of quartz, albite crystals decreases in both firing conditions. The amount of mullite of the non added sample (1) reached 7.87 ± 0.25 and 6.93 ± 0.28 respectively, while it reached 7.91 ± 0.23 and 7.49 ± 0.23 for the sample 2 in different firing conditions. This situation is suggested that total alkaline amount up to 7.58% depend on the amount of talc is affect on increment of mullite crystals. High amount of alkaline content provides forming high amount of glassy phase, dissolving crystals and closed pores swells. These closed pores are opened by polishing during the preparation of samples for electron microscopy examination. For this reason the porosity results of image analysis are higher than the results of helium pycnometer especially for sample 4.

In image analysis method, the possibility to make different interpretations about the amount of porosity because of the factors such as grain pull out due to the polishing of electron microscope samples and the fact that images obtained are two-dimensional may change the results. As a consequence, the gap left by a certain amount of glassy phase while leaving the surface during polishing may be misinterpreted as porosity. In order to eliminate these differences more than one analysis should be made on a large number of images, and the results should be given with the standard deviations. The amount of porosity obtained by different methods is generally in parallel with each other when the results evaluated with the standard deviations.

Also, the porosity size distribution determined by image analysis method in the in the table 4 table is examined, the interval with the largest percentage of porosity size distribution is of 0-5 μm range and in the standard, even if it is small, there is a porosity size larger than 30 μm. The absence of porosity greater than 30 μm except for sample 1 in samples in both the firing conditions is shown the increment of total alkali amount and the amount of glassy phase is effective on large

porosities. As dwell time increases, the amount of porosity with 5-15 μm size increases but the amount of porosity with 0-5 μm size decreases. The results presented shown that distribution of porosity size of the same samples changes substantially in different dwell times. In this respect, image analysis method is advantageous when compared to other methods since it shows how and at which interval of the amount of porosity the amount of porosity and morphology change.

Conclusions

The amount of porosity and its distribution can be regarded as important parameters since they affect the shrinkage of the product and allow the control of technical features during production process of porcelain tiles. In the consequence of this study, the amount, size distribution and morphology of porosity is determined through different methods. It is shown that the variation of total alkali amount affects the amount of glassy phase and concentration; hence the amount of porosity decreases in samples. According to size distribution of porosity investigated through image analysis, samples with a high amount of porosity have much more porosity than the standard at the interval of 5-15 μm. Furthermore, a porosity size higher than 30 μm is found in standard sample. Porosity analysis methods reveal more obviously how much even a small difference in the total alkali content and firing temperature affects the porosity morphology and amount. As an alternative to Archimedes and helium pycnometer, the facts that image analysis method provides determination of the amount of porosity, its size and morphology sooner Furthermore, the similarity between the results of the methods constitute an advantage.

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