Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi

Afyon Kocatepe University Journal of Science and Engineering

AKÜ FEMÜBİD **14** (2014) OZ5725 (159-163) AKU J. Sci. Eng. **14** (2014) OZ5725 (159-163)

Kuvarsın Spodumen Esaslı Porselen Karoların Lekelenme Direnci Üzerine Rolü

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Geliş Tarihi: 22.10.2012; Kabul Tarihi: 11.11.2013

Anahtar kelimeler
Lekelenme direnci; Porselen Karo; Spodumen; Kuvars içeriği; Mikroyapı

Özet

Yüksek miktardaki camsı faz ve düşük porozite gibi özellikleri ile karakterize edilen porselen karolar olarak kil, kaolen, feldspat ve kuvars kullanarak üretilirler. Kil ve kaolen plastiklik ve kuru mukavemet sağlarlar ayrıca sinterleme esnasında da camsı faz ve müllit oluşumuna katlı sağlarlar. Feldspat düşük sıcaklıkta camsı fazı oluştururken kuvars da refrakter özelliği sayesinde bünyenin termal ve boyutsal kararlılığını sağlar. Ancak kuvarsın bu özelliğinin yanında camsı faz ile arasındaki termal genleşme katsayısındaki farklılıktan dolayı camsı faz üzerinde kalıntı basma gerilimlerinin oluşmasına neden olur. Bu gerilimlerin büyüklüğü kuvars taneleri etrafında kritik çatlak boyutunu geçen böylece de gerilim rahatlamasına da neden olan çatlaklara neden olur. Aynı zamanda bu durum tane ayrışmasına da neden olarak mikroyapısal hatalar meydana getirir. Bu mikroyapısal hatalar ürünün mekanik özelliklerini ve lekelenme direncini olumsuz yönde etkiler. Bu çalışmada, sodyum feldspat yerine maksimum ağırlıkça % 2 spodumen kullanarak lekelenme dirençlerinin artırılması amaçlanmıştır. Ayrıca bu çalışmada kuvars içermeyen reçetelerde geliştirtmiştir. Elde edilen sonuçlara göre, kuvars içermeyen porselen karo bünyelerde pişirim esnasında düşük viskoziteli camsı faz oluşturularak kapalı porların ve ortalama por boyutlarının azalması sağlamış ve ayrıca bulk yoğunluklar ve mekanik özellikler artırılmıştır.

The Role of Quartz on Stain Resistance of Porcelain Tiles Based on Spodumene

Keywords
Stain resistance; Porcelain tile; Spodumene; Quartz content; Microstructure

Abstract

Porcelain tiles characterized by a large quantity of glassy phase, low porosity are basically produced from clays, kaolinite, feldspars, and quartz. Clays and kaolinites provide plasticity and dry mechanical strength and form mullite and glassy phase during firing; feldspars are low-temperature glassy phase formers; and quartz contributes to thermal and dimensional stability, due to its refractoriness property. However, quartz significantly affects triaxial porcelain properties. The difference between the coefficients of thermal expansion of the quartz and the glassy matrix has a strong effect by subjecting the glassy matrix to microscopic residual compressive stress. The magnitude of these stresses produces cracks around the quartz particles, which may exceed a critical size, thereby causing partial stress relaxation and increasing microstructural damage leading to particle detachment. This microstructural damage adversely affects the product's mechanical behaviour and stain resistance. In this study, in order to enhance the stain resistance of the porcelain tiles containing spodumene (max 2 wt %) substituted by Na feldspar it was prepared to compositions without quartz content. The results showed that it was obtained an increase in stain resistance of porcelain tiles without quartz by forming a low viscosity liquid phase during firing with a decrease in both closed porosity and average pore size, also increasing bulk density and mechanical properties.

1. Introduction

Porcelain tiles undergo a polishing process in order to modify their aesthetical appearance. However, this process results in amaterial removal in the form of surface defects and open pores formed by closed pores. There is an increase in stain sensitivity as a result of material removal. There is a relationship between stain resistance and the microstructure of the tile surface. (Dondi, 2004) Amount, size and morphology of defects (e.g. pores, cracks) are also important. In this study, it was focused on the effect of quartz on stain resistance of the porcelain tiles. Especially the difference between the coefficients of thermal expansion of the quartz and the glassy matrix has a strong effect by subjecting the glassy matrix to microscopic residual compressive stresses. The magnitude of these stresses produces cracks around the quartz particles, provided that it exceeds a critical size. These cracks result in a partial stress relaxation and leads to particle detachment and leads an increase in microstructural damages. Microstructural damages adversely affect the product's mechanical behaviour and stain resistance. The one of the aim of the study is to develop stain resistance of the porcelain stoneware tiles by using spodumene instead of Na Feldspar (max. 4% wt.)and the another aim of the study is to create easy-clean surfaces by consuming less energy and water without any chemical agent. (Tenorio, 2004, and Sanchez, 2006)

2. Materialsand Methods

Porcelain stoneware samples were prepared under the industrial conditions (Seranit Granit Seramik A.Ş.,Bilecik) with different ratios of spodumen (up to. 4 wt. %). All compositions consist of clay, kaolin, quartz, and albite. The raw materials and their chemical compositions were given in Table 1. After grinding process all compositions were dried at 100 °C, 1 h. And then dried powders containing about 5 % moisture were pressed under 147 kg/cm^2 by using uniaxial pressing in order to obtain 5 mm x 11mm tile samples. After drying tiles were sintered at 1210°C, 60 min. in anindustrial roller kiln.

Bulk density (D_b) and open porosity (P_o) was analyzed by water saturation and Archimedes' principle, the specific weight of the body was measured by Helium pycnometry (Quantachrome He pycnometry). X ray fluorescence chemical analyses were conducted with a Rigaku ZSX Pirumus spectrometer. Mineralogical qualitative phase analysis of powder has been performed using data collected with a RigakuRint 2200 diffractometer. Surface and bulk of bodies was investigated by SEM, (Zeiss Evo 50 Ep). Image analyses of tile bodies were obtained by using the ImageJ, Fiji Win32 and Scandium software's, on SEM photomicrographs was previously investigated in order to the textural elements. The following parameters were measured: pore area *P*area, mean size of macropores*P*av, pore aspect ratio (*P*ar) and pore roundness (*P*ro), total surface area of samples and total pore area on the samples. The resistance to stain of the tile surface were determined according to the TS EN ISO 10545-14 standard, using the green staining agent (i.e. a 40%, w/w, of chrome oxide in light oil), olive oil as a staining agent creating film and iodine as a powerful chemical and oxidant staining agent. The amount of staining was quantified after each cleaning step. Step 1 is to wash gently with warm water; Step 2 is to wash together with warm water and neutral detergent; Step 3 is mechanical cleaning by using rotary brushing equipment also with alkaline detergent.

Class 1: Stain cannot be removed by using Step 1, 2 or 3

Class 2: Stain can be removed after dipping in a powerful solvent up to 2 hour.

Class 3: Stain can be removed by using a powerful chemical and using rotary brushing

Class 4: Stain can be removed by using a weak cleaning material.

Class 5: Stain can be removed only by using a wet cloth after cleaning a hot water

3. Results and Discussion

The chemical compositions of raw materials, seger oxide ratios and technical properties of porcelain tile samples were reported in Table 1, Table 2 and Table 3.

As seen in Table 3 closed and open porosity of the samples were decreased with the addition of spodumene (D1-D2). Shrinkages were also decreased. Through spodumen addition bending strengths were increased in comparison with standard porcelain tile. Although there was a decreasing in porosity with the addition of spodumene, stain resistance of D1 and D2 bodies has not been improved as seen on Table 4. As mentioned in previous study (Aydin, 2012) amount of porosity is not only one parameter to affect stain resistance. A previous study by the authors showed that the most important parameter affecting to stain resistance is pore aspect ratio. The lower aspect ratio the easier the surface cleans. According to Kozeny-Carman equation (equ. 3.1) while there is a direct proportion among penetration of a liquid, capillary pressure and permeability, there is an inverse relationship between liquid penetrationand liquid viscosity. (Tamsü, 2010) Therefore when spherical pores showed a change towards capillarity, capillary pressure of the liquid increases and accordingly an increase in the penetration rate of liquid is. Thus as the aspect ratio of pores increases, penetration towards tile surface becomes faster and dirt from the irregular capillary pores is more difficult to clean. Due to the formation of pores with high aspect ratio are quartz particles. A lower liquid phase viscosity was obtained with only %1 and % 2 spodumene addition compared with bodies not to contain quartz. As a result of lower viscosity there was an increase in strength together with increase in amount and size of mullite crystals and also there was a decrease in amount of porosity compared with STD body. But decrease in porosity has not positively affected stain resistance (pore aspect ratio is 4 for D1 and D2). In this study,quartz which is a most important parameter affecting to pore aspect ratio was removed from receipts. D1A, D2A, D1AK and D2AK bodies was improved in order to investigate on stain resistance

$$q = \frac{\Delta P k_{kc}}{L\mu} \quad (3.1)$$

q: absorption rate, k_{kc}: permeability, P: pressure, L: height of porous support, µ: liquid viscosity

Table1. The chemical composition of the raw materials (wt., %)

Raw materials	%	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Li_2O	L.o.I
Kaolinite	5.5	65	23.0	0.5	0.50	0.20	0.15	0.20	0.30	-	10.0
Kaolin2	9	78.78	13.34	0.02	0.16	4.78	0.01	2.1	0.04	-	0.51
Clay 1	6	59	26.0	1.20	1.50	0.60	0.10	0.10	2.00	-	10.0
Clay 2	18	59	25.0	1.00	1.50	0.60	0.70	0.60	2.70	-	8.50
Clay 3	6.5	65	21.5	2.50	1.30	-	-	0.10	2.00	-	7.50
Quartz	8	97.6	0.730	0.18	0.03	0.10	0.01	0.01	0.47	-	0.43
Na Feldspar	47	71.1	17.40	0.05	0.24	0.60	0.10	9.36	0.34	-	0.50
Spodumene	0	65.2	25.12	0.15	0.05	0.21	0.1	0.34	0.57	7..5	0.36

*L.o.I loss of ignition

Table 2. Seger oxide ratio, S: SiO_2, A: Al_2O_3, K: K_2O, L: Li_2O, C: CaO, M: MgO, N: Na_2O

	S+A	S/A	RO+R_2O/S+A	N/K	N+K	N+K+L
STD	11,90	6,57	0,084	7,50	0,71	0,761
D1	11,79	6,54	0,085	7,34	0,74	0,764
D2	11,67	6,51	0,086	7,18	0,72	0,767
D1A	12,49	5,14	0,08	6,77	0,79	0,820
D2A	12,35	5,11	0,081	6,62	0,77	0,822
D1A-K	11,25	5.12	0,089	5,10	0,75	0,781
D2A-K	11,14	5,09	0,090	4,99	0,73	0,783

Table3. Technological properties of the investigated bodies

	Bulk density (g/cm^3)	Shrinkage (%)	Porosity			Bending strength (N/mm^2)	Water Abs. (%)	Chromatic coordinates		
			Open por. (%) P_O	Closed por. (%) P_C	Total por. (%) P_T			L*	a*	b*
STD	2.38	8.36	0.43	5.50	5.94	51	0.13	76.4	1.56	10.4
D1	2.39	8.31	0.00	3.61	3.61	54	0.00	75.4	1.6	10.3
D2	2.37	8.11	0.00	4.48	4.48	66	0.00	75.2	1.61	10.2
D1A	2.43	7.26	0.00	2.87	2.87	68	0.00	79.4	0.85	10
D2A	2.41	6.97	0.00	4.53	4.53	73	0.00	78.6	0.94	10
D2A1	2,40	7,27	0,00	4,08	4,08	67	0,00	79,63	1,02	10,07
D2A2	2,40	6,80	0,35	4,38	4,73	66	0,15	80,04	0,96	9,82
D2A3-50'	2,40	7,91	0,00	4,28	4,28	67	0,00	80,06	1,06	9,54
D1AK	2.42	6.75	0.00	3.17	3.17	68	0.00	76.6	0.92	12.1
D2AK	2.42	6.99	0.00	3.12	3.12	72	0.00	76.6	0.88	11.8

Table 4. Stain resistances class of the polished tiles

	Green staining agent (Cr_2O_3)	Olive oil	Iodine
STD	1	1	1
D1	1	1	1
D2	2	2	2
D1A	5	5	1
D2A	5	5	5
D2A1	5	5	2
D2A2	1	1	1
D2A3-50′	5	5	1
D1AK	5	5	5
D2AK	5	5	5

3.1. Effect of composition

In traditional ceramics maximum densification rate and temperature shows differences depending on feldspar ratio and type. Viscosity of liquid phase and melting point is related with kind of feldspar thereby depending on alkaline ratio (Tamsü, 2010 and Fluegel, 2007). Viscosity of liquid phase determines the quartz dissolution rate and mullite formation. Quartz dissolution was considered as one of the parameters effecting stain resistance of porcelain tile bodies. Also type of fluxing agent has an important effect on quartz dissolution and mullite formation. In this study, it was required to eliminate microcracks formation in order to increase stain resistance by using different kinds and ratios of fluxing agents such as spodumene. Using potassium feldspar increases viscosity of liquid phase than sodium feldspar in spite of larger sintering interval. Higher viscosity adversely effects quartz dissolution (Fluegel, 2007). In this study it was aimed to obtain larger sintering interval and also aimed to obtain stable liquid phase viscosity without pyroplastic deformation by adjusting NaO/K_2O ratio (Table 2).

As show in Table 2, while normally expected to decrease in stain resistance with a decreasing in the rate of N/K, in accordance with the concept of the study stain resistance of bodies has shown an increase because of the fact that spodumene addition and with the removal of quartz provided a low viscosity liquid phase at the beginning of sintering and increased quartz dissolution. As result of quartz dissolution, it was detected an increase in the viscosity of liquid phase at the flex temperature. Increase or in other words stability in the viscosity provided a decrease in high temperature deformation trend (PI) so that it was obtained bodies more resistant to deformation at the high temperature.

Resistance to stain for polished porcelain tile bodies without quartz were increased with the addition of the spodumene (D1A-D2A and D1AK-D2AK, Table 4) that’s why there was a decrease in magnitude of cracks around the quartz (Figure 1) and filled by lithium alumina silicate phases (LAS). Also studies on formation of the LAS phases and effects on stain resistance in progress. Another reason for an increase in the stain resistance is lower aspect ratio for D1A, D2A, D1AK and D2AK (A.R: 3).

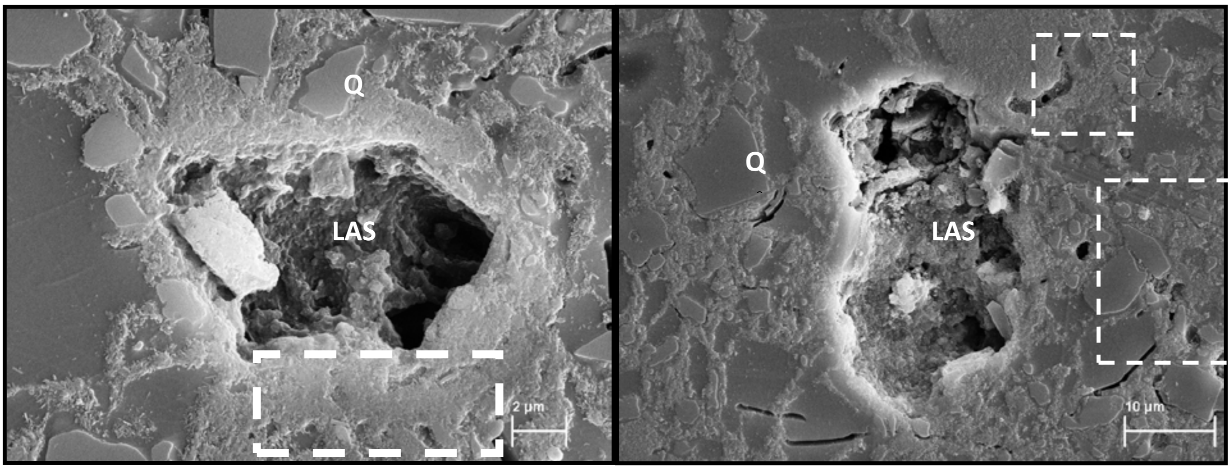

Figure 1. SEM micrographs of D1A and D2A bodies fired at 1210^{o}C, 60 min

Figure 2 shows that there was a relationship between pore fraction and pore aspect ratio. Especially it was determined that an increase in stain resistance of bodies having aspect ratio smaller than 3 (D1A, D2A, D1AK and D2AK). The densification appears to be rate-controlled by the strong dependence of melt viscosity on temperature and by the solubility of solids in the liquid phase. Nevertheless, in the final stage, coarsening and solubility of gases filling the closed pores become the most important phenomena affecting the microstructure and stain resistance (Tulyaganov 2006). Therefore one of the important point of the study is to control viscosity as mentioned before that in lower limit was determined to consider pyroplastic deformation of the tile, upper limit of viscosity was determined to consider stain resistance of the bodyTable 6 and Table 7 show changes in viscosities and pyroplastic deformations of tile bodies. It was determined an increase in viscosity and a decrease in pyroplastic deformation index by adding spodumen and by emerging quartz. Pyroplastic deformation index shows deformation trend at high temperature. As pyroplastic deformation index decreases, deformation trend decreases (Aydin, 2012). Spodumene addition provided a low viscosity liquid phase at the beginning of sintering and increased quartz dissolution.

As shown in Table 6 and Table 7 it was identified an increase in viscosity at the flex point together with the increase in quartz dissolution and it was also determined an decrease in pyroplastic deformation index. (Raimondo, 2008, Bernardi, 2006). For D1A, D2A and D1AK, D2AK bodies with spodumene addition and decreasing in N/K ratio have provided a larger sintering interval and emerging pores without pyroplastic deformation. Pores and cracks were also filled easily by LAS phases and /or molten phase. (Oberzan, 2009) Filling of cracks and pores with these phases has been provided easy-clean surfaces. All surfaces have been cleaned by using only water

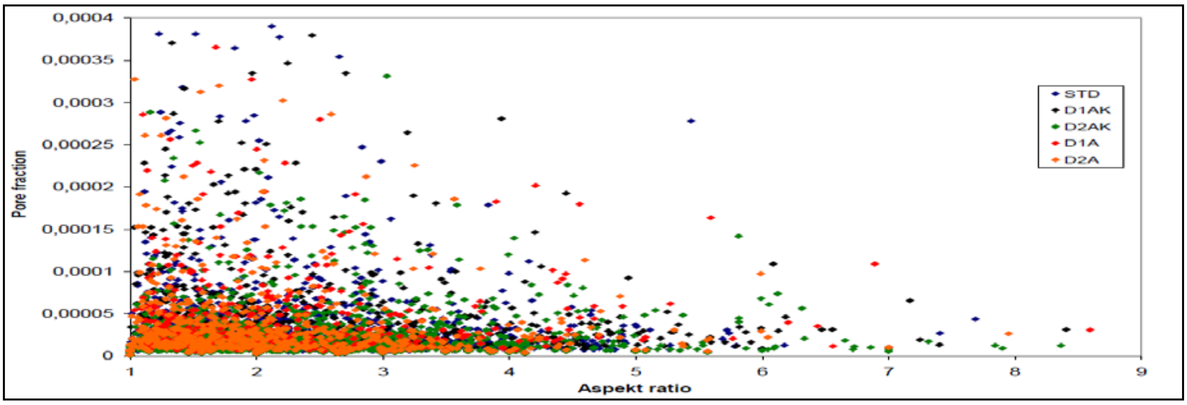

Figure 2. Relationships between (%) pore aspect ratio and pore fraction

Tablo6. Viscosity and deformation rate at theflex and soaking temperature

Sample	Flex Temp. (°C)	Soaking Temp. (°C)	Flex Def. (cm)	Soaking Def. (cm)	Def. rate (dy/dT) $.10^{-3}$	η_{Flex} (GPa.s)	η_{soakig} (GPa.s)	$\log\eta_{flex}$ (Pa.s.)	$\mathrm{Log}\eta_{soaking}$ (Pa. s.)
STD	1217	1217	0.1708	0.3634	9.15	1.251	0.784	9.097	8.894
D1	1210	1217	0.0867	0.3609	8.09	1.991	0.824	9.299	8.916
D2	1215	1217	0.1169	0.3006	8.40	1.459	0.873	9.164	8.941
D1A	1207	1217	0.0448	0.1634	4.15	2.992	1.342	9.476	9.127
D2A	1207	1217	0.0861	0.3003	10.49	1.697	0.924	9.229	8.965
D2A-1	1192	1202	0,0632	0,1793	5.83	2.235	1.360	9.349	9.133
D2A-2	1195	1202	0,0539	0,1584	4.28	1.858	1.343	9.269	9.128
D2A-3-50’	1197	1212	0,732	0,2405		2.988	1.421	9.475	9.152
D1A-K	1199	1217	0.0653	0.184	7.89	2.217	1.430	9.345	9.155
D2A-K	1197	1217	0.0518	0.1719	6.25	2.471	1.414	9.392	9.150

Tablo7. Pyroplastic deformation indexes of bodies

Sample	PI $_{fleks}$.	PI$_{soaking}$	PI (cm^{-1})	S$_{MAX}$ (cm)
STD	3.14586.10^{-5}	6.69323.10^{-5}	7.49.10^{-5}	*0.4068*
D1	1.54721.10^{-5}	5.87158.10^{-5}	6.22.10^{-5}	*0.3824*
D2	1.94472.10^{-5}	5.0007.10^{-5}	5.6.10^{-5}	*0.3365*
D1A	8.22663.10^{-6}	3.00052.10^{-5}	2.61.10^{-5}	*0.1422*
D2A	1.3039.10^{-5}	4.54776.10^{-5}	4.74.10^{-5}	*0.3127*
D2A1	1.0883.10^{-5}	3.08752.10^{-5}	3.34.10^{-5}	*0.1942*
D2A2	9.48469.10^{-6}	2.78734.10^{-5}	2.92.10^{-5}	*0.1659*
D2A3-50'	1.1795.10^{-5}	3.87529.10^{-5}	4.05.10^{-5}	*0.2511*
D1A-K	1.10357.10^{-5}	0.000031096	3.19.10^{-5}	*0.1888*
D2A-K	9.00332.10^{-6}	2.98778.10^{-5}	3.06.10^{-5}	*0.1762*

As it can be seen in Figure 3 D1AK and D2AK were determined to have a lower thermal expansion at the quartz transformation temperature than the other bodies. As mentioned before it should have been an increase in thermal expansions with a decrease in N/K ratio vice versa has been obtained through spodumene addition. This data is one of the signs for quartz-spodumene reaction in order to form LAS phases and quartz dissolution. Spodumene addition provides a stable viscosity range without pyroplastic deformation. As shown in Figure 1 microcracks around quartz particles, which is most important effect on stain resistance have been largely eliminated

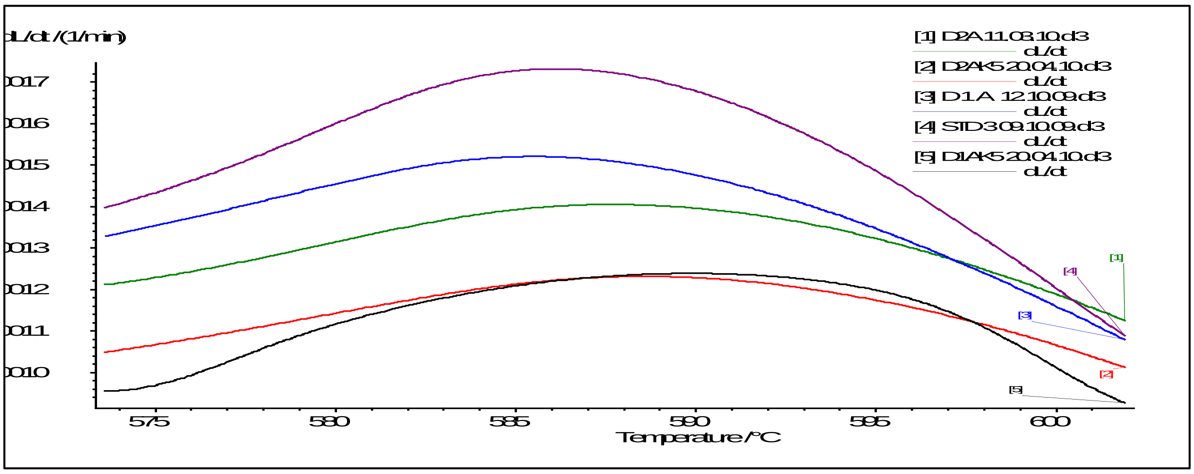

Figure 3. Thermal expansion curves at 600 ^{0}C for STD, D1A, D2A,D1AK and D2AK

3.2. Effect of particle size distribution and soaking time

The study has been conducted on a D2A porcelain tile composition, in which the particle size distribution was varied. In order to evaluate the influence of the particle size distribution and soaking time on mechanical behaviour and stain resistance the samples were subjected to two different grinding time and peak temperature. Firstly, it was analysed grain size and grain distribution of D2A body depending on grinding time. The data obtained have shown in Figure 4. As a result of different grinding time more coarse grains were detected in D2A1 and D2A2 bodies. As can be seen from Table 4 and Table 5, the more coarse grain the less resistance to stain obtained. Porosity in a polished porcelain tile surface directly affects porcelain tile aesthetic characteristics, such as gloss and cleanability (Junior, 2008, Sanchez, 2006 and Amoros, 2000).

The graph in Figure 5 presents the amount distribution of the surface pores as percentage for the samples D2A, D2A1 and D2A2 and the pore aspect ratio (A.R). The plots show that as the particle size increases (Table 5), pore aspect ratio also increases. For the samples, D2A contains pores that pore aspect ratio is 1, which is about 40 per cent of the total pore amount and D2A1 contains pores that pore aspect ratio is 1, which is about 36 per cent of the total pore amount and also D2A2 contains pores that pore aspect ratio is 1, which is about 33 per cent of the total pore amount. Therefore as the pore size distribution increases pore aspect ratio increases. Thus pore size is directly related to the coarsest fraction of the particle size distribution. Results in this section indicate that peripheral cracks around the quartz particles determine the surface characteristics of polished porcelain. As mention before that the most important parameter for stain resistance is pore aspect ratio, so the coarser grain microstructure has the bigger pore aspect ratio is. Consequently, stain resistance of the porcelain tiles decreased.

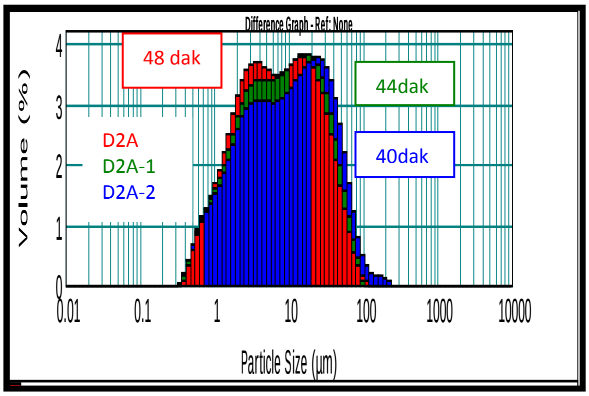

Figure 4. Grain Size Distribution of D2A, D2A1, D2A2

Tablo 5. Grain Size Distribution of D2A, D2A1, D2A2

	Grain Size (µm)		
	d_{10}	d_{50}	d_{90}
D2A	1.336	7,033	33,630
D2A-1	1.320	7.941	36.711
D2A-2	1.362	9.523	45.804

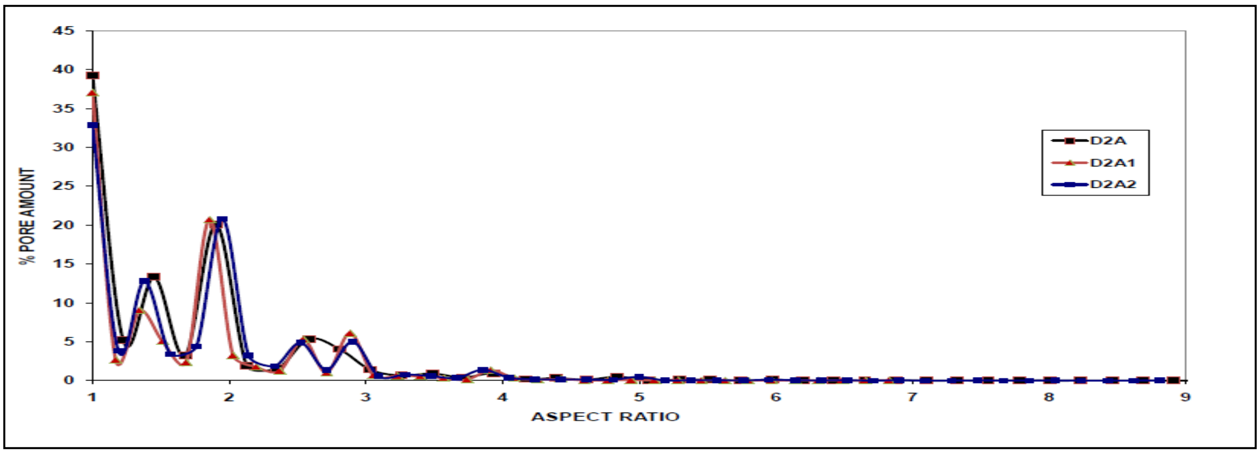

Figure 5. The graph of pore aspect ratio vs. % pore amount

D2A body was sintered at 1210 ^{0}C, 50' under the industrial conditions in order to investigate the effect of soaking time on stain resistance. As seen in Table 3 there was a slightly decrease in bulk density due to the decrease in soaking time. And also it was determined a decrease in bending strength. Decrease in soaking time results in an increase in viscosity at flex temperature. As it can be seen in Table6it was detected that dissolution of quartz has decreased as a result of increase in viscosity at flex temperature and inefficient soaking time. Due to lower quartz dissolution it was detected more quartz crystals than D2A. Also, decrease in quartz dissolution can be explained with decrease in amount of glassy phase (Table 6).

Table 6. Quantitative phase analyses

	Müllit %	Petalit	Albit %	Kuvars %	CamsıFaz %
STD	5.44		1.42	17.13	75.99
D1	5.086		0.73	14.57	79.60
D2	4.01		0.38	14.62	80.97
D1A	6.07	2.27	4.74	14.2	72.72
D2A	6.26	-	-	12.86	80.87
D2A-1	7.41	1.21	4.56	14.65	72.15
D2A-2	7.65	-	1.42	15.03	75.88
D2A-3	7.69	-	2.76	13.47	76.06
D1A-K	10.01	-	-	12.06	77.92
D2A-K	9.18	-	-	12.51	78.29

As a result of decrease in quartz dissolution, there was an increase in cracks around the quartz particles. Deterioration in the microstructure had an adversely effects on stain resistance and bending strength (Table 3, and Table 4). Especially, because of the increase in capillary pressure caused by cracks iodine stain could not be removed from D2A3 body (Figure 6).

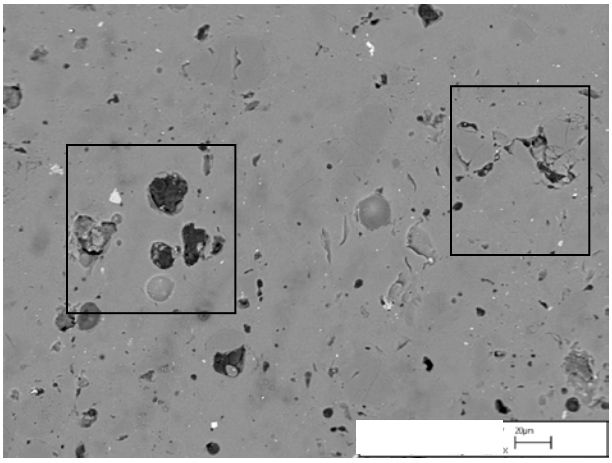

Figure 6.SEM micrographs of D2A3 bodies fired at 1210^{0}C, 50 min.

4. Conclusion

Li_2O was added in amounts of 1 and 2 wt.% in porcelain tile bodies with spodumene. The phase composition and the microstructure evolution of the standard composition and the Li_2O-containingcompositions were studied at 1210 °C. Compositions (D1A, D2A and D1AK, D2AK) reached a higher degree of densification at same peak temperatures in comparison to the standard composition. The influence on the densification is greater, with the amount of Li_2O increasing. During heat treatment the phase composition of the bodies is influenced by the amount of added Li_2O. It is evident that the reduction of quartz in the presence of Li_2O is because of the quartz's reaction with spodumene, forming $LiAlSi_3O_8$ (LAS). The reaction of quartz is promoted by the increased amount of Li_2O. Studies about formation of LAS are still in progress.

Homogeneity of the microstructure, a high bulk density and an improved flexural strength are exhibited by compositions without quartz and with 1 and 2 wt. % of Li_2O fired at 1210 °C (D1A, D2A and D1AK, D2AK). When fired compositions containing quartz, all the compositions containing Li_2O (D1 and D2) attain a noticeably lower flexural strength, mainly due to the bloating phenomena related with lower viscosity, which increases with the increasing amount of Li_2O, as is obvious from the decreasing pyroplastic deformation index and bulk density.

The increasing amount of Li_2O for D1 and D2 bodies which contain quartz greatly affects the deformation during firing in the industrial kiln, which considerably increases with decreasing viscosity related with the increasing amount of Li_2O (Tulyaganov, 2006) However, removal of pores was easily provided from microstructure with the removal of quartz and studied with larger sintering interval by decreasing Na_2O/K_2O (D1A, D2A and D1AK, D2AK). In previous study authors shows that shape of residual pores (especially, aspect ratio) in the microstructure is responsible for stain resistance of porcelain tiles. It was detected that Li_2O-bearing (D1 and D2) compositions contained larger aspect ratio related with cracks around the quartz particles than the Li_2O-bearing compositions without quartz. Because of the larger aspect ratio in the Li_2O-bearing compositions, capillary pressure increased. Increase in capillary pressure results in lower stain resistance than the compositions without quartz. Capillary cracks around the quartz particles were largely eliminated with the removal of quartz from receipt. In this way it was obtained an increase in stain resistance of the porcelain tile bodies. In the Li_2O bearing compositions without quartz under the existing firing schedule in the industrial kiln the most favourable characteristics from an industrial perspective are attained by the compositions with 2 wt.% Li2O (D2A and D2AK). Consequently, for the specified purpose it was obtained easily clean surfaces by consuming less energy and water without any chemical agent.

Kaynaklar

Aydin, T. 2012, Critical parameters on stain resistance of porcelain tiles, *Ecers 2012 proceedings/**245.pdf***

Amoros, J.L., 2007, Effect of the green porous texture on porcelain tile properties, *Journal of European Ceramic Society*, **27**, 2295–2301

Amoros, J.L., 2000, Effect of quartz particle size on the thermal expansion of porous whiteware bodies, *Qualicer 2000*, 35-37

Bernardi, A.M., 2006, Pyroplasticity in porcelain tiles, *Material Science and Engineering*, A, **427**, 316-319

Dondi, M., 2004, Stain resistance of porcelain stoneware tiles: the influence of microstructure *Key Engineering Materials*, **264-268**, 1511-1514

Fluegel, A., 2007, Glass viscosity calculation based on a global statistical modeling approach, *Glass Technology: European Journal of Glass Science and Technology A*, **48 (1)**, 13–30.

Junior, A.D.N., 2008, Analysis of the development of microscopic residual stresses on quartz particles in porcelain tile, *Journal of European Ceramic Society*, **28**, 2629–2637.

Junior, A.D.N, 2009, Effect of quartz particle size on the mechanical behaviour of porcelain tile subjected to different cooling rates, *Journal of European Ceramic Society,* **29**, 1039–1046

Oberzan, M., 2009, High-alumina porcelain with the addition of a Li_2O-bearing fluxing agent, *Journal of European Ceramic Society*, **29,** 2143-2152

Raimondo, M., 2008, Process of Pyroplastic shaping for special purpose porcelain stoneware tiles, *Ceramic International*, **35,** 1975-1984

Sanchez, E., 2006, Porcelain tile microstructure: Implications for polished tile properties, *Journal of European. Ceramic Society,* **26**, 2533–2540.

Tenorio, P.M., 2004, The influence of microstructure on performance of white porcelain stoneware, *Ceramic International*, **30**, 953–963.

Tamsü, N., 2010, Enhancing the stain resistance of the polished porcelain tile, PhD Dissertation, Anadolu University, Graduate School of Sciences, Eskisehir, 208

Tulyaganov, D.U., 2006, Influence of lithium oxide as auxiliary flux on the properties of triaxial porcelain bodies, *Journal of European Ceramic Society*, **26**, 1131–1139.

Tulyaganov, D.U., 2006, Influence of Li_2O doping on non-isothermal evolution of phases in K–Na-containing aluminosilicate matrix, *Journal of American Ceramic Soc*iety, **89 [1]**, 292–297