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Bending strength of porcelains

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Abstract

Porcelains in the quartz–metahalloysite + kaolin–K-feldspar system with different quartz grain sizes were investigated to study the effect of firing temperature on the bending strength. The degree of vitrification of the fired bodies was determined measuring the bulk density, relative percentages of constituent minerals by XRD and their microstructures using SEM techniques. The maximum bending strength was obtained in the 10–20 μm particle size quartz containing porcelains at 1300 and 1350 °C interval. The distribution of closed pores, their geometric shapes and possible link with each other control the bending strength of the porcelain body. In addition, the presence of unmelted fine quartz grains in the porcelain body also increases the bending strength. It was found that the bending strength increases with both increasing bulk density of the porcelain bodies and the firing temperature, but upon further heating, after reaching the maximum level, the bending strength decreases due to bloating of isolated pores and the disappearance of quartz, which are also associated with a decrease in bulk density.

Keywords: Bending strength; Porcelain body; Particle size; Quartz content; Compression-prestress; Bloating

1. Introduction

The main phase of the porcelain body is made up from heterogeneous glassy matrix containing closed irregular shaped porosities due to gas bubbles and the melted residues of quartz grains, and numerous needle shaped mullite crystals <3 μm length. The bending strength of porcelain bodies have been experimentally studied by many researchers [1–6], because of its economic importance in ceramic industry. It is known fact that quartz grains in different sizes have significant effects on mechanical strength of porcelain bodies [1]. Especially, it is proposed that bending strength of the porcelains increases with an increase in inter planar spacing of quartz crystals, so the quartz is under the tensile stress, and consequently, the glassy matrix surrounding the quartz grains is a compressive stress which acts as pre-stress, improving mechanical strengthening [1]. The pre-stressing effect due to the residual compressive stress at the glassy phase around the grain is large [1,2], which is related to the quartz grain size and the firing temperature. A similar conclusion had been also reached that the mechanical strength of porcelain is influenced mainly by stresses set up in the glassy matrix rather than by the amount or size of mullite crystals formed [3].

In addition, it is also reported that with respect to the amount of quartz content of bodies, the pre-stress effect increases with an increase in the amount of residual quartz in bodies [3]. There are some other scientific arguments about the effects of quartz grains on mechanical strength of porcelain. It was experimentally documented that the presence of a higher amount of fine-grained quartz content increases to a higher strength [4]. In contrast, other studies claimed that the low quartz content provides high strength [5,6]. The purpose of this study is to investigate the differential changes of bending strengthening of porcelain bodies using various quartz grain sizes at different firing temperatures.

2. Experimental procedure

Size separation of quartz and feldspar grains were done according to Stoke's law after pulverizing the samples. Quartz and feldspar grains were dried in a

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drying oven, but a 50% ethanol and 50% water mixture were used in a glass baker to avoid adhesion of separated grains. Otherwise, some dissolved alkalis in water will act like water glass, causing the adhesion of grains again. The quality of particle size separation was checked using a Shimadzu SALD-2100 model laser diffraction particle size analyzer and the results are shown in Fig. 1. Standard composition of porcelain bodies is prepared with the mixture of 50% Katoh kaolin from Korea, 25% K-feldspar from India and 25% fine and pure quartzite. A total of 9 g mixture of raw materials is used during experiments.

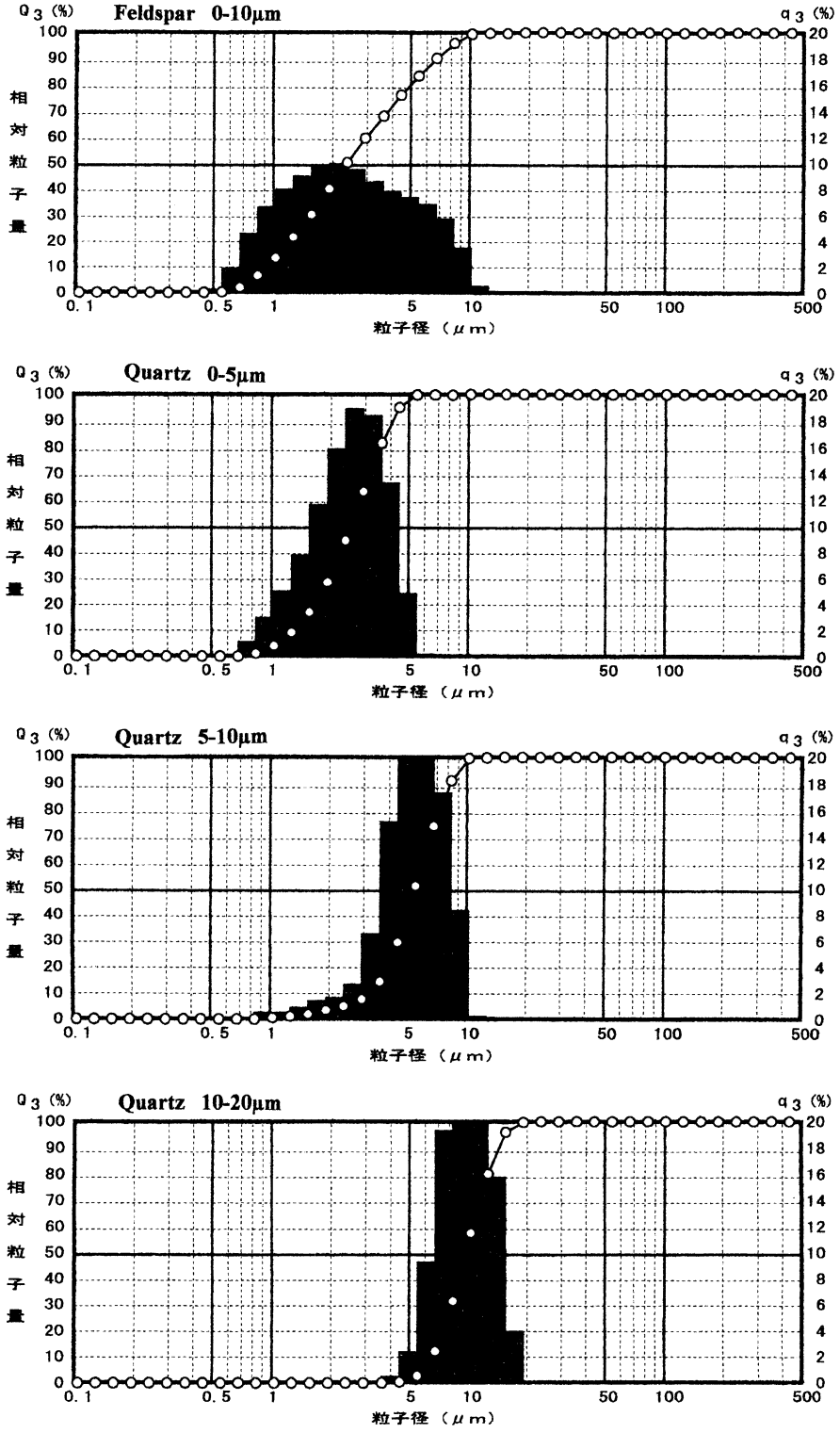

Fig. 1. Particle size distribution of raw materials.

Table 1
Composition of Specimens (wt.%)

	A	B	C
Quartz	<5 μm	5–10 μm	10–20 μm
Feldspar	<10 μm	<10 μm	<10 μm

The X-ray diffraction analysis showed that the Korean kaolin contains mostly metahalloysite, illite, small amount of quartz and traces of plagioclase. The Indian K-feldspar contains microcline with a little albite as a solid solution; quartz is the only mineral in quartzite. Table 1 shows the results of the chemical analysis of the raw materials. Table 2 shows the compositions of specimens used for the preparation of porcelain bodies in this study. Three groups of samples were prepared, each mixture was ground gently in an agate mortar, then mixed with distilled water while stirring and heated in a drying oven. Later, the mixtures were ground gently again in an agate mortar in order to obtain the best mixed powder samples; in this way, the quartz grain size is prevented from changing. To avoid lamination problem occurring during the pressing of samples, each powder mixture was moistured with ethanol, and then the sample was poured into $10\times10\times60$ mm bakelite lined molds under a pressure of 30 MPa, using a single-shaft hydraulic press. Samples waited at ambient temperature for 48 h for the evaporation of ethanol. Each pressed sample was put into a small rubber tube to vacuum the air and they were hydrostatically molded under a pressure of 98 MPa. The compacted samples were placed on a platinum folder in an electric furnace, heated at rate of 6 °C/min, and fired at temperatures of 1200, 1250, 1300, 1350 and 1400 °C for 1 h and then cooled in the furnace. An electric furnace was used for firing with silicon carbide heating elements. The bending strength was measured with an electronic universal tester (CATY20025 model) on 15 test pieces for each body by a three-point loading test with a span of 40 mm and a crosshead speed of 0.1 mm/min, and the results are listed in Table 3. A rubber plate is used between the porcelain bodies and supporting rolls during the three-point bending strength measurements. Bulk density of the specimens was determined by Archimedes's immersion technique, keeping the specimens in boiling water for 3 h.

The relative changes of quartz and mullite in porcelain bodies were determined by X-ray diffraction analysis. In order to determine the effects of stresses on crystal faces of the quartz and mullite, the peak intensities of the diffraction lines of quartz (100) and mullite (110) were measured. SEM observations were done to investigate the grain morphologies and microstructures on the broken surfaces using three groups of samples; (a) fresh surfaces, (b) polished surfaces with 0.5 μm diamond paste and (c) polished and etched surfaces with 1% HF at 0 °C for 24 h. In SEM samples, fresh and polished surfaces were prepared perpendicular to the test bars.

3. Test results

3.1. Bulk density

Fig. 2 clearly displays differential changes in bulk density through the firing temperature. The bulk densities continued to increase, reached a maximum value, and then decreased, like the general behaviors of almost all porcelain bodies. At higher firing temperature, containing the finer sized quartz grains, the higher bulk density of porcelain bodies should be obtained. However, at temperatures above 1300 °C, densities are lower for 0–5 μm sized quartz grains; at temperatures above 1350 °C for quartz grain sizes of 5–10 and 10–20 μm, the bulk densities are declined and upon further heating, more porosity developments begin (Fig. 2). At higher temperatures, the

Table 3
Mechanical strength of 15 porcelain samples. Length (a) is 60 mm

Sample No.	Width b (mm)	Thickness c (mm)	Load P(N)	Strength (MPa)
1200 °C <5 μm	9.249	6.535	390.10	59.3
5–10 μm	9.580	6.691	338.65	47.4
10–20 μm	9.608	6.937	349.38	45.3
1250 °C <5 μm	9.195	6.219	377.91	63.8
5–10 μm	9.370	5.998	438.08	78.0
10–20 μm	9.487	6.474	379.06	57.2
1300 °C <5 μm	9.206	5.880	401.92	75.8
5–10 μm	9.265	5.068	270.78	68.3
10–20 μm	9.222	6.004	468.75	84.6
1350 °C <5 μm	9.283	6.310	396.94	64.4
5–10 μm	9.224	5.602	345.89	71.7
10–20 μm	9.172	6.365	514.29	83.0
1400 °C <5 μm	9.977	6.833	289.57	37.3
5–10 μm	9.498	6.586	326.92	47.6
10–20 μm	9.430	5.879	332.73	61.3

Table 2
Chemical composition of raw materials

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
Korean kaolin	46.37	0.16	37.42	0.93	0.42	0.26	0.73	0.42	13.0
Indian K-feldspar	65.66	0.01	18.69	0.08	0.10	0.01	12.32	2.89	0.2
Quartzite	99.74								

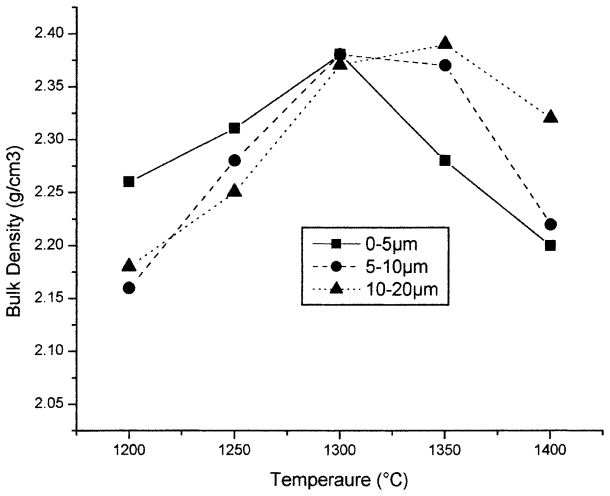

Fig. 2. Effect of firing temperature on bulk density as a function of grain size of quartz.

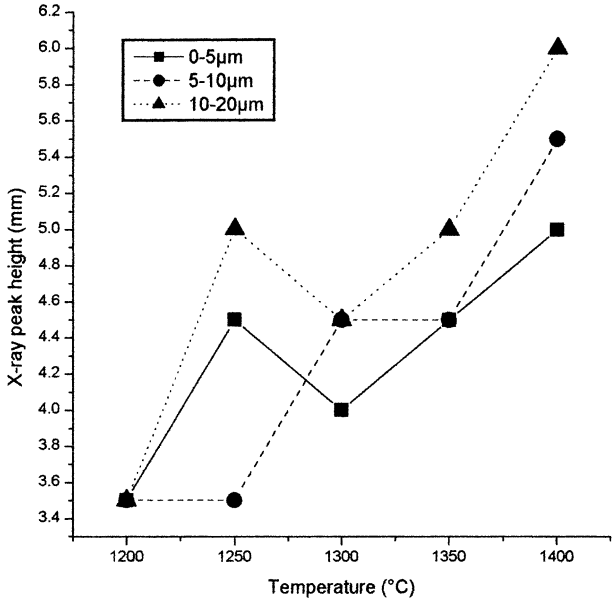

Fig. 3. Effect of firing temperature on mullite $d_{(110)}$ (5.39 Å) contents.

closed porosity tends to increase because of "bloating" and consequently the bulk density decreases rapidly. The source of "bloating" could be O_2 released from the reaction of Fe_2O_3 to Fe_3O_4 [7], the expansion of the air enclosed in the pores and dehydration of OH from the crystal structure of kaolinite started at 500 °C, but was trapped in the closed pores.

As a result, 0–5 μm sized quartz grains containing porcelain reached to a high bulk density at a lower sintering temperature. In contrast, 10–20 μm sized quartz grains containing porcelain has a higher sintering temperature and higher bulk density than the other porcelains, because of the formation of a more homogeneous vitreous matrix.

3.2. XRD studies

The microstructural changes in porcelain bodies were investigated by using X-ray diffraction analysis and SEM examinations. Based on peak heights, the content of quartz $d_{(100)}$ at 0.425 nm and mullite $d_{(110)}$ at 0.539 nm of the specimens are shown in Figs. 3 and 4. Residual quartz decreased with an increase in temperature, which caused an increase in bending strength. Figs. 3 and 4 show that quartz content decreases with increasing mullite content as a function of firing temperature and that a finer grain size has more of a tendency to be melted. As the quartz grain size increases, the occurrence of mullite increases, especially for a 10–20 μm grain size interval. Not enough data are available to present the exact relation between the strength and mullite content. Hamano et al. [1] reported that the strength increases with mullite content, which is affected by quartz grain size up to about 44 μm size limit, but after that, larger quartz grains have an inverse effect on the mullite content and the strength.

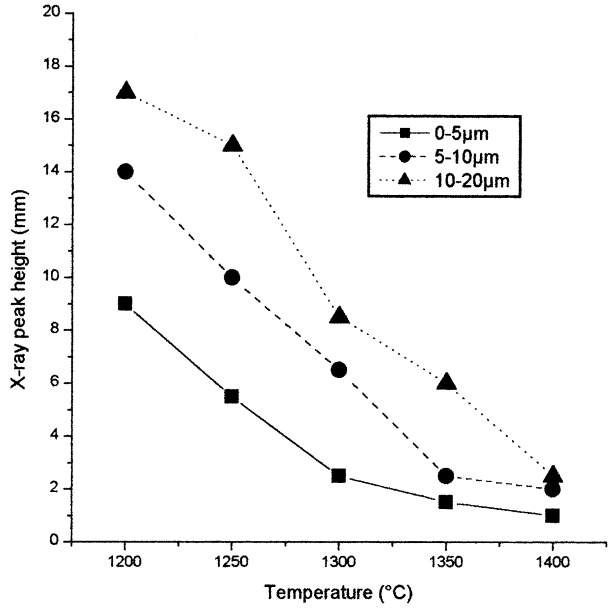

Fig. 4. Effect of firing temperature on quartz $d_{(100)}$ (4.25 Å) contents.

The relation between $d_{(211)}$-values of quartz grains and the firing temperature is shown in Fig. 5, which indicates a slight increase in $d_{(211)}$-values with increasing firing temperature. This increase is more apparent for coarse quartz grain (10–20 μm) specimens.

3.3. Bending strength

Figs. 6 and 7 show the bending strength of three groups fired in the range of 1200–1400 °C. The bending strength of porcelain bodies increased with an increase in firing temperature and reached maximum values of about 85 MPa at 1300–1350 °C interval in coarse quartz grains

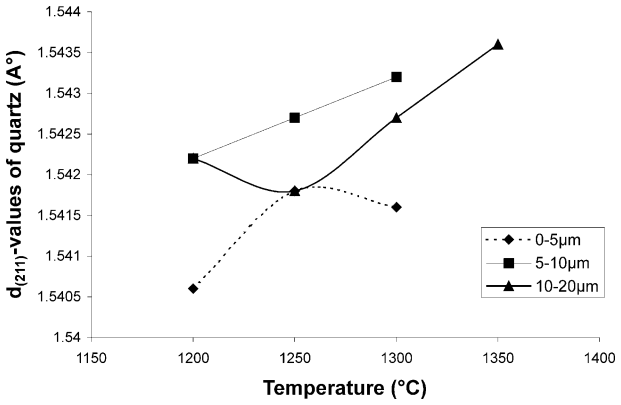

Fig. 5. The distribution of $d_{(211)}$-values of quartz vs. firing temperature.

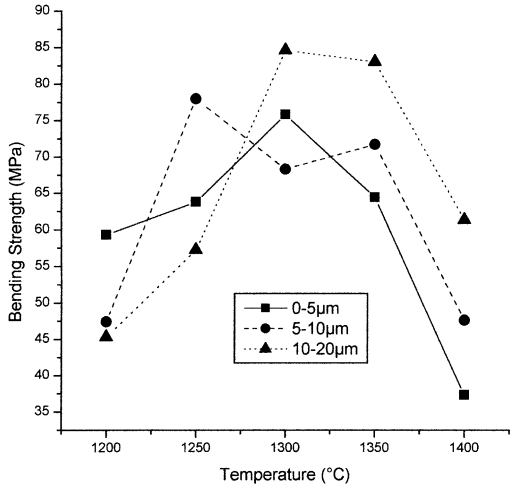

Fig. 6. Effect of firing temperature on bending strength as a function of grain size of quartz.

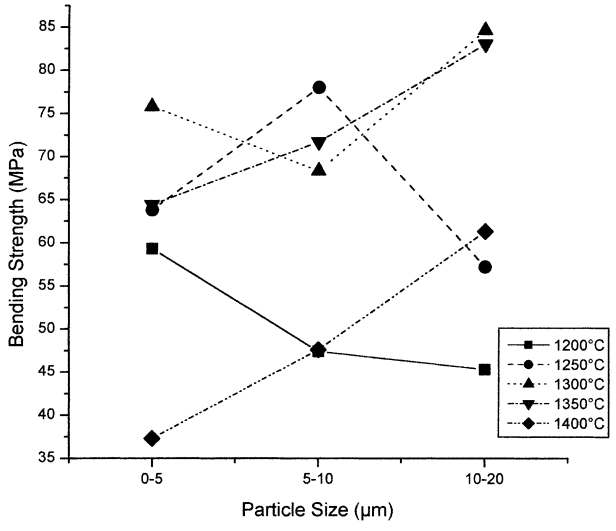

Fig. 7. Bending strength of fired bodies vs. grain size of quartz.

(10–20 μm) containing porcelain bodies. After continuing the heating, the bending strength values (Fig. 6) decreased with both corresponding microstructural changes, mainly caused by porosity developments, as examined in SEM studies and decrease in bulk density (Fig. 2). As a general rule, at the higher firing temperature, the higher bending strength should be attained. However, quartz grain sizes decrease as firing temperature continues to increase and after reaching the maximum temperature, the bending strength begins to decrease together with a decrease in bulk density due to closed porosity development.

The bending strength of 5–10 μm sized quartz grains containing porcelain at 1200 °C was 47.4 MPa, which is almost the same bending strength of 47.6 MPa at 1400 °C. It increased rapidly with an increase in firing temperature from 1200 to 1250 °C. After reaching the maximum bending strength of 78 MPa at 1250 °C, it almost stays on the same level of strength up to 1350 °C, and then decreases rapidly on further heating.

The bending strength of 0–5 μm sized quartz grains containing porcelain tended to behave differently from other porcelain groups. It started from 59.3 MPa at 1200 °C, increased to its maximum value of 75.8 MPa at 1300 °C and then gradually decreased down to 37.3 MPa at 1400 °C, which is lower than the starting value at 1200 °C. The sintering and bending strength behaviors of 5–10 and 10–20 μm sized quartz grains containing porcelain bodies differed from those of 0–5 μm sized quartz grains containing porcelain. The bending strength of 0–5 μm sized quartz grains containing porcelain at 1200 °C is higher than the other two porcelains, but it reached the lowest value at 1400 °C. It is obvious that these changes in bending strength are related to total porosity developments in bodies. Porcelain specimens of 0–5 μm size fractions at 1200 °C showed higher bending strength and bulk density values than at 1400 °C.

Norris et al. [8] described a range-curves method for vitreous pottery bodies to determine both maximum vitrification temperature and bulk density. Theoretically, a maximum bending strength developed when the apparent porosity decreased to zero. Temperature of maximum bulk density is about 40 °C above the maximum vitrification temperature for siliceous- and aluminous-porcelains, and about 20 °C above bone china. However, using the Norris's approach, we found that this idea may be applicable for 10–20 μm sized quartz fractions, but definitely it is not applicable for the other quartz grain sizes. Of course, the reliability of this method depends on the collection of the best representative samples.

3.4. SEM studies

The surface morphologies of fired specimens are carefully examined using broken fresh (Fig. 8), polished

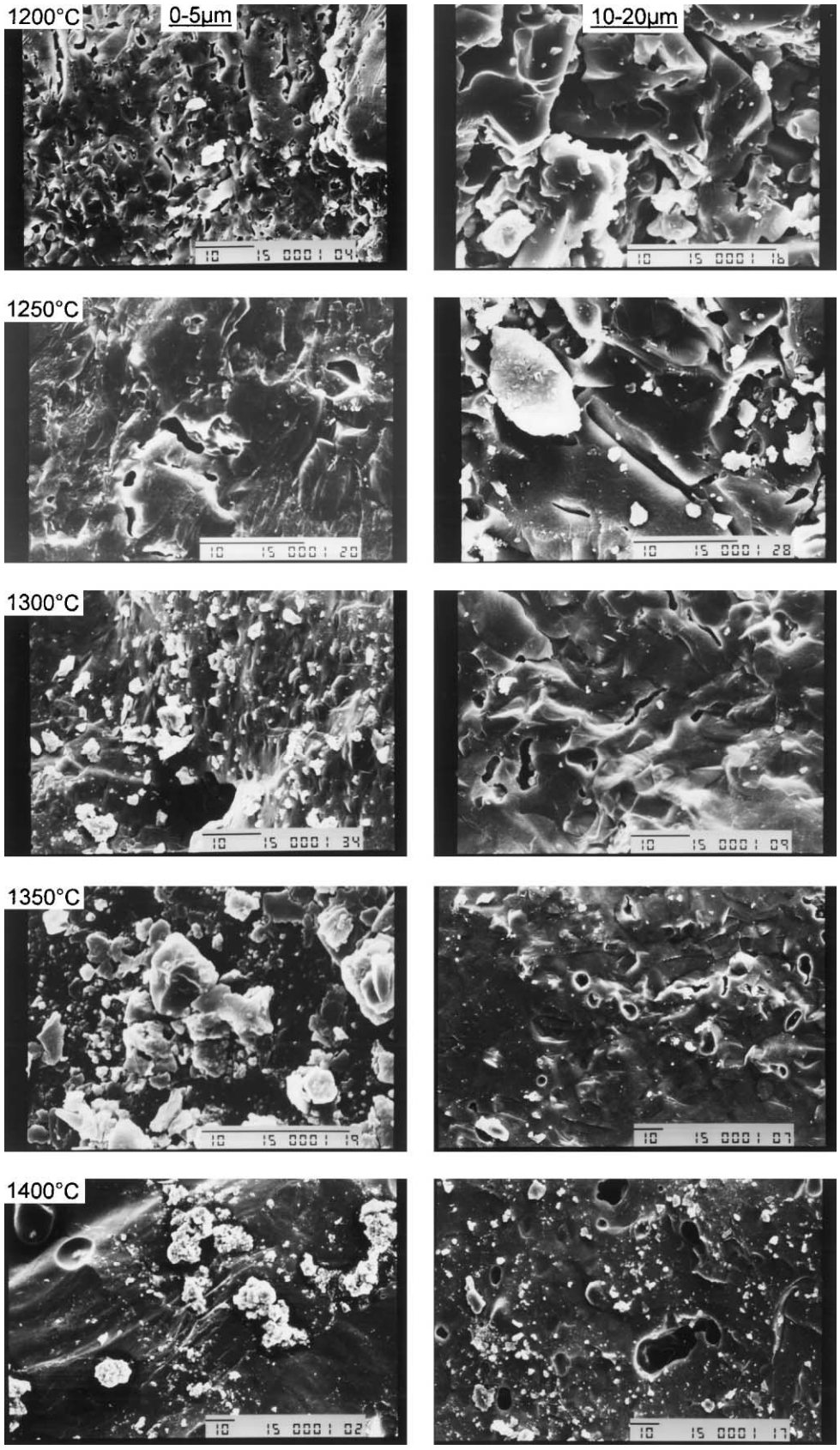

Fig. 8. SEM photomicrographs of broken fresh surfaces at elevated temperature.

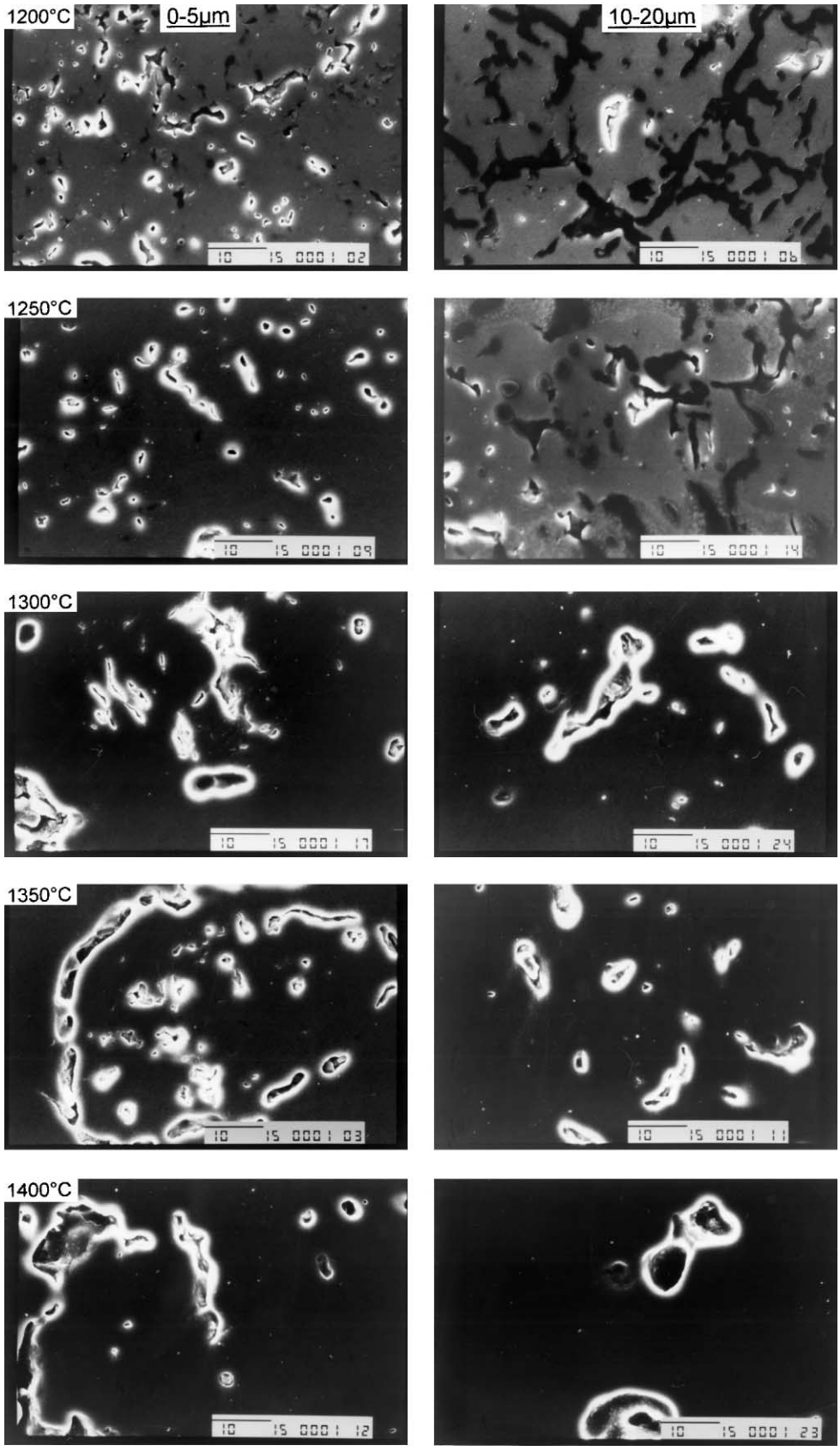

Fig. 9. SEM photomicrographs of polished specimens, showing the effects of firing temperature on microstructures.

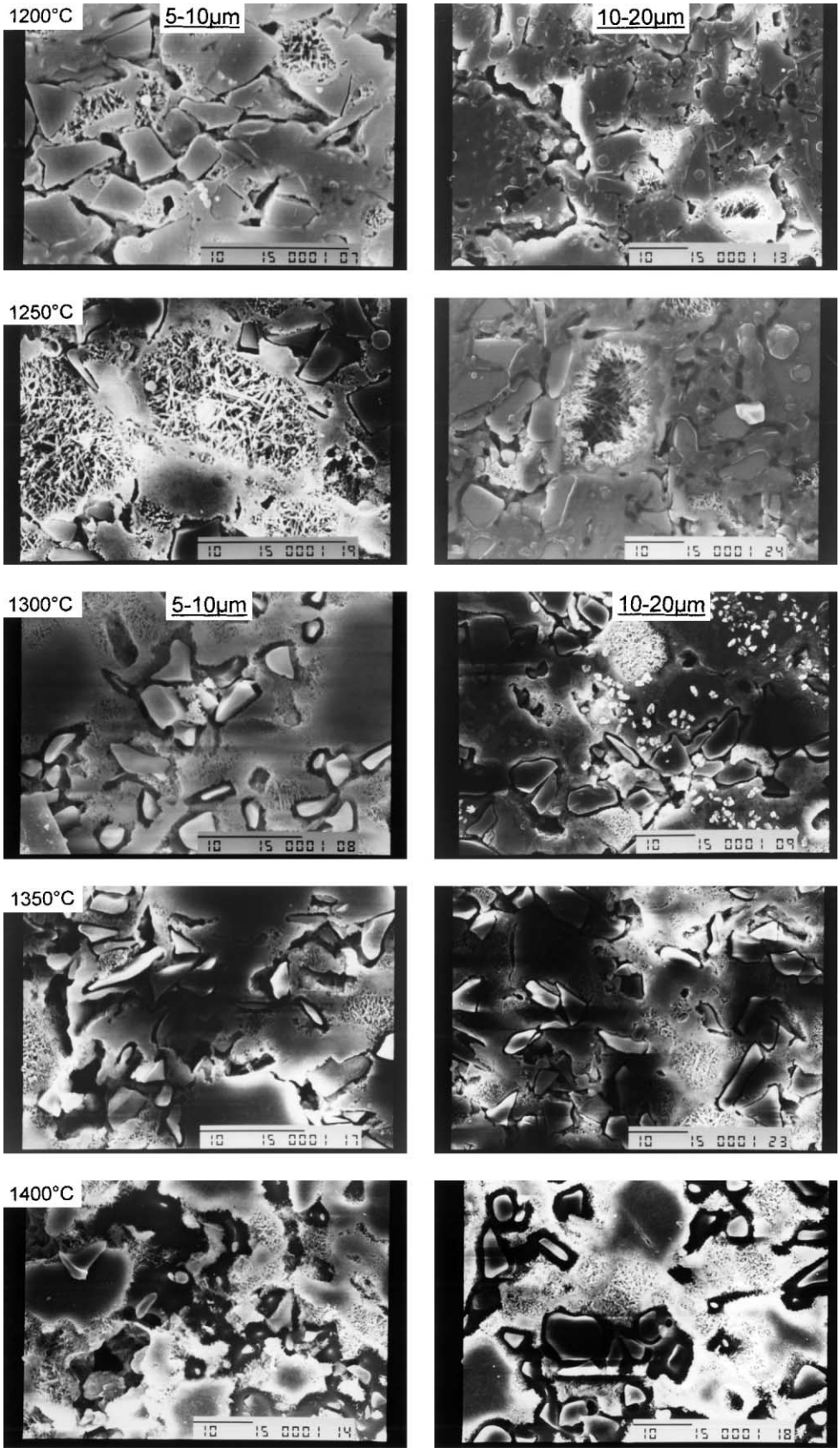

Fig. 10. SEM photomicrographs of polished and etched specimens at different firing temperatures.

(Fig. 9) and polished + etched (Fig. 10) surfaces by SEM techniques. SEM examinations revealed the effects of closed porosity developments due to the melting of quartz grains and trapped gases in pores. In order to better understand microstructural developments and how the crackings initiated during the bending strength test, three sets of SEM specimens were examined. The content and the size of the pores in 0–5 μm sized quartz fractions showed that pores are very abundant at 1200 °C and 2–8 μm long with an elongated shape. Fig. 8 also revealed that the broken surface followed the cracking around quartz grains, but these crackings were also linked to isolated pores. The number of pores diminished and the size of pores increased at elevated temperatures. In addition, for the 10–20 μm size quartz grains, the shape of pores changed from irregular elongated shape less than 0.1 μm wide and about 5 μm long at 1200 °C to more spherical and ellipsoidal shapes from 5 to 15 μm at 1400 °C (Fig. 8).

Fig. 9 shows that dense glassy matrix is not observed on the specimens at 1200 °C for 0–5 μm size quartz grains, indicating that the sintering temperature was not high enough. The dense glassy matrix is observed at 1250 °C, especially above 1300 °C, denser matrix is formed and the bending strength reached a maximum level. Fig. 9 also shows connection of isolated pores with each other, especially observed at 1350 °C for 0–5 μm size quartz grains, which initiate large scale fracture flaws, causing low bending strength and low bulk density.

The comparison of 0–5 and 10–20 μm quartz grains at elevated temperature revealed that 0–5 μm sized quartz grains have more of a tendency to create elongated pores, but 10–20 μm sized quartz grains exhibit more spherical shaped pores at above 1350 °C (Figs. 8 and 9). The shape, size and linkage trend of pores with each other played an important role in the bending strength. These irregular shaped elongated pores decrease the bending strength, in contrast, spherical pores formed after melting of quartz, show relatively higher strength. Kobayashi et al. [9] also noticed changes in shape and size of pores with elevated temperature, and between the core and rim of porcelain. At 1300 °C, feldspar grains are completely melted and spherical shape closed porosity increased clearly because of bloating pores (Figs. 8 and 9). Above this temperature, bending strength decreased abruptly for 0–5 μm quartz grains. But, for 10–20 μm size fractions, advancing the temperature above 1350 °C, it decreased abruptly with increasing in pore sizes and porosity due to enhancing of the bloating effect (Figs. 8 and 9). The comparison of two different quartz grain sizes at the same temperature revealed that larger quartz grains remained undissolved; at 1200 and 1250 °C, pores are small and isolated, but beginning at 1300 °C, a glassy dense matrix began to form and pore sizes increased. In Fig. 10, the needle shaped mullite crystals are common and generally 0–2 μm in size.

4. Discussion

The relationship between the bending strength and bulk density of specimens are shown in Fig. 11. Due to relatively lower strength values, very clear correlation among the different particle size fractions was not observed. However, both the highest bulk density and strength were obtained in the 10–20 μm fractions. Generally, the quartz grain size has a greater effect on bending strength up to a certain threshold level. In coarse grains, glassy matrix displays some cracks surrounding the quartz particles causing moderate strength in the porcelain body.

Figs. 12 and 13 show the relationship between the bending strength, the relative residual quartz and mullite contents with the indication of firing temperature. Fig. 12 presents the changes in strength with quartz grain sizes, but no regular relationship is found between these two parameters. Generally, the strength decreases with the development of melting related cracks, and even these cracks increase when the presence of coarse quartz grains are more common, as examined in SEM studies. Fig. 12 shows that the melting of quartz contributes to the formation of vitreous matrix and consequently, the strength increases with firing temperature; a more homogeneous matrix will provide a higher strength. Also, Fig. 13 clearly shows that there is no relation between the strength and mullite content. But, the

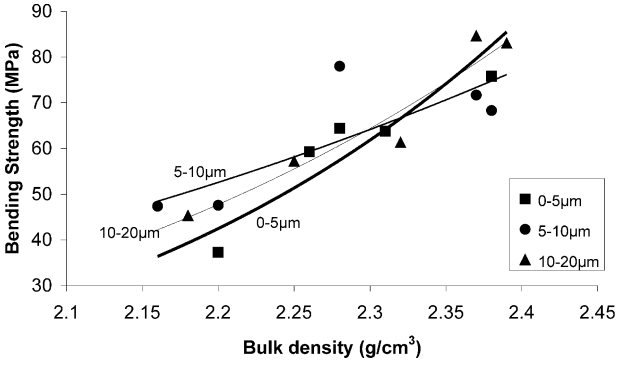

Fig. 11. Relation between bending strength and bulk density of porcelain body.

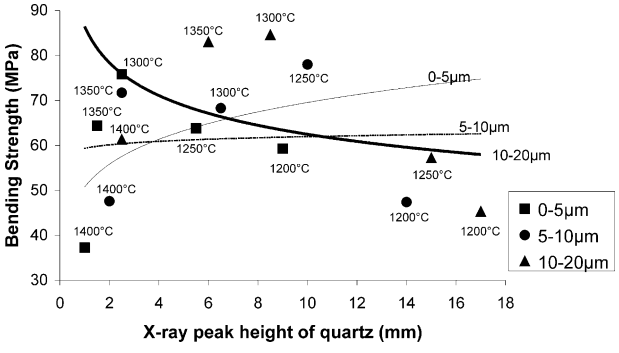

Fig. 12. Relation between bending strength and amount of residual quartz in porcelain body.

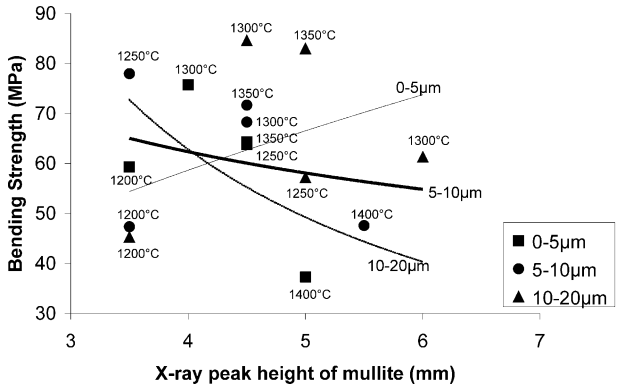

Fig. 13. Relation between bending strength and mullite content in porcelain body.

general firing temperature trend shows that mullite content increases with temperature and also quartz grain size. Large grains are subject to cause cracks in the vitreous phase and, in contrast, fine quartz grains melt very easily and in both cases, they reduce the bending strength of specimens. Therefore, there is no one single solution to this problem. The larger quartz grain sizes and mixture of different quartz sizes in different percentages versus the firing temperature relation should be determined separately in order to attain the best porcelain body with maximum strength and bulk density. It was reported that the uniformly sized quartz grains between 15 and 30 μm would be the best to withstand tensile stress [3]. This concept should be examined in detail in the future studies. Because, fine quartz grains dissolve on firing they cannot contribute to favorable pre-stressing of the matrix.

5. Conclusion

The development of melting is caused by closed pores that increase the heterogeneity and decrease the bending strength of porcelain. The strength is dependent on the homogeneous glassy matrix and no effect of the mullite content on bending strength is observed. Our experiments showed that the porcelain above the sintering temperature would lose its strength. Also, the smaller the quartz grain sizes the more the tendency to lose relative weight, so bulk density, by over firing.

The pre-stress of the matrix is related to the amount of quartz residue in the fired specimens. Therefore, maximum bending strength is found in 10–20 μm quartz grain sizes at the 1300–1350 °C interval. During the bending test, the fracture-initiating flaws were the micro cracks around the quartz grains acting linked together with other closed pores, like a chain reaction, reducing the strength and specimens break down along these unpreventable flaws. It is more likely that homogeneous distribution of 10–20 μm sized quartz grains in glassy matrix can better tolerate the negative effects of flaws. SEM studies also revealed that small spherical shaped pores are the effects of bloating and more irregular shape, size and sharp edges of pores are due to melting effects.

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