PREPARATION AND PROPERTIES OF NEW PORCELAIN BODIES WITH LIGHTWEIGHT AND HIGH-STRENGTH

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1. Introduction

Porcelains are mainly made from feldspar, quartz, and clay minerals including plastic raw materials,[1] but high-grade plastic raw materials have recently started to deplete. It is required high-cost to refine low-grade plastic raw materials. Thus, a new approach to the development of porcelain body without using plastic raw materials is necessary for the future of porcelain industry. Aluminous cement improves the green strength by a hydration reaction in moist atmosphere[2] and it is crystallized to anorthite with glass microspheres and quartz during the firing process.[3] The glass microspheres play the role of a flux such as feldspar. To develop a new porcelain body which meets lightweight and high-strength, the quartz skeleton and glass microspheres in the fired body should be kept under an appropriate vitrification. Moreover, the prestress for increasing the strength of the fired body should be generated by a large difference in the thermal expansion coefficient between the glassy phase and the quartz grains.[4,5] In the present study, new porcelain bodies are fabricated using only nonplastic raw materials without using a binder. The effect of quartz particle size on their properties was investigated.

2. Experimental procedure

The starting materials were glass microspheres, silica stone (quartz) and aluminous cement. Average particle sizes of glass microspheres and aluminous cement are 11.80μm and 14.51μm, respectively. Quartz particle was separated to small(S) size of 4-10μm, medium(M) size of 6-20μm, and large(L) size of 10-32μm. Average particle size at respective quartz particles was 6.6μm(S), 10.6μm (M), and 18.2μm(L). The chemical compositions of the raw materials are shown in Table 1. The starting materials were mixed with various ratios in a planetary mixer for 40min. The content of added water was 23wt%. Hydration was performed for 24h in a moist atmosphere and then the bodies were dried for 24h at 50°C. The firing was performed for 1h at 1300°C.

For the interplanar spacing analyses, the fired bodies were ground and then followed by polishing. XRD analyses were conducted to determine interplanar spacing of quartz (112) plane in the fired bodies, and (112) plane of quartz powder as a standard. XRD analyses were also conducted to determine the phases. Water absorption was measured based on JIS-R2205. The flexural strength was measured by three-point bending test with a lower span of 30mm.

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

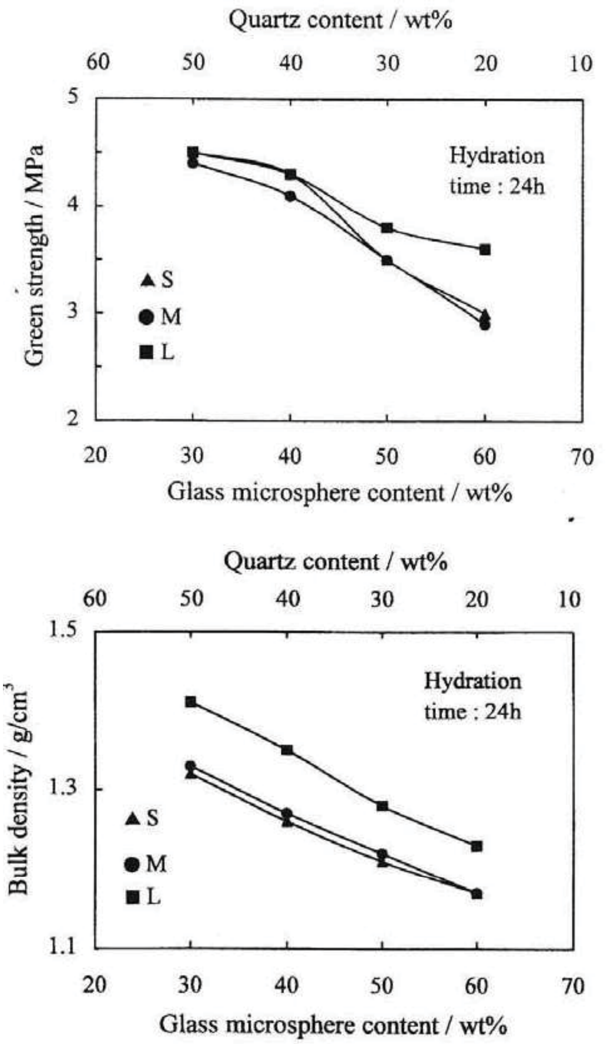
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Ig.loss
Glass microspheres	76.5	12.8	1.6	1.0	0.3	3.1	3.0	1.7
Silica stone(Quartz)	98.1	1.0	0.2					
Aluminous cement	0.6	70.4	0.1	28.1	0.2			

3. Results and Discussion

3. 1 Preparation and properties of green bodies

Green strength attained to maximum value at hydration time of 24h due to hardening by a hydration reaction of aluminous cement with glass microspheres and quartz in a moist atmosphere.[2] Hydration time in all the samples was kept for 24h in a moist atmosphere. The phases formed in the green body are α-quartz, $CaAl_2O_4$, and $CaAl_4O_7$, and $CaAl_2Si_2O_8 \cdot 4H_2O$ formed with the hydration time of 24h.

Figure 1 shows change in the green strength of green body as function of composition and quartz particle size in the glass microspheres-quartz-aluminous cement system. The green strength decreases with increasing glass microsphere content at constant aluminous cement content (20wt%). The green strength is relatively higher at L quartz particle addition than at S and M quartz particles. Figure 2 shows change of bulk density in the green body. The bulk density decreases linearly with increasing glass microsphere content. The bulk density at the S and M quartz particle addition is lower than that at the L quartz particle addition. The glass microspheres are the sedimented parts in the water from the as-fabricated glass microspheres (1.08g/cm^3) and possess relatively low particle density (1.99g/cm^3). Such low density of glass microspheres make bulk density decrease in the mixing with quartz (particle density, 2.60g/cm^3) and aluminous cement (particle density, 2.93g/cm^3). The decrease of bulk density with increasing glass microsphere content is due to the relative increase of glass microsphere volume in the mixtures. The decreased green strength with increasing glass microsphere content is attributed to the decrease of bulk density and the relative decrease of aluminous cement volume.



Figs. 1 and 2. Variation of green strength and bulk density as function of composition and quartz particle size in green bodies.

3. 2 Preparation of porcelain bodies

Figure 3 shows XRD patterns with glass microsphere content at M quartz particle addition in the fired bodies at 1300°C for 1h. The phases formed are glass, α-quartz, α-cristobalite, anorthite and a small amount of α-Al_2O_3. The peaks of α-quartz and α-cristobalite decrease with increasing glass microsphere content. The α-cristobalite peak disappeared with 60wt% glass microsphere addition except S quartz particle. Anorthite peak increases with increasing glass microsphere content. A larger amount of anorthite forms with the addition of smaller quartz particles at a larger glass microsphere content. These mean that anorthite is formed by the crystallization from the glassy phase melted from smaller quartz particles, larger amount of glass microspheres and aluminous cement.[3] The decreased viscosity of glassy phase with a larger amount of glass microspheres makes smaller quartz particles melt easily. However, the low viscosity of the glassy phase melts less larger sized quartz particles. α-cristobalite peak decreases notably with increasing glass microsphere content and the addition of larger

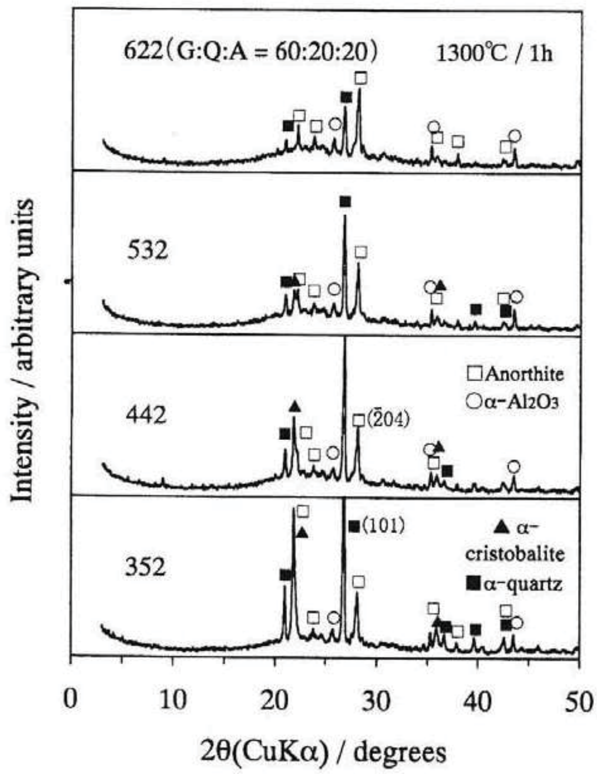


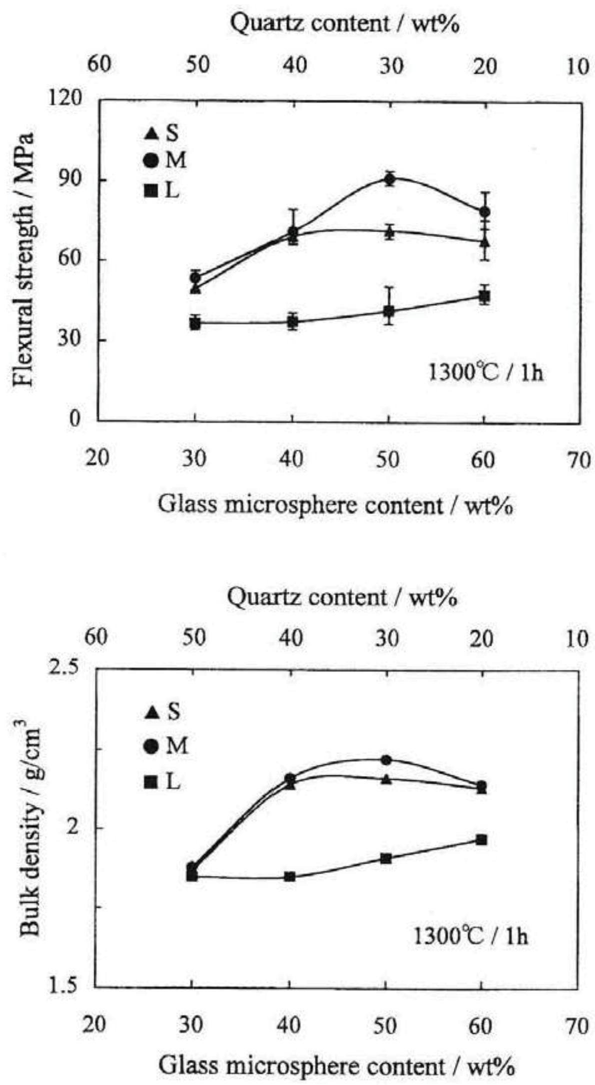
Fig. 3. XRD patterns with various compositions and M quartz particle size in the fired bodies. G, Glass microsphere; Q, Quartz; A, Aluminous cement.

quartz particle. The α-cristobalite does not form at addition of 60wt% glass microspheres except S quartz particle. Hence, the SiO_2 content in the glass phase is higher in the 352 body than 622 body because the highly siliceous glass phase is melted from a larger amount of quartz and smaller quartz particle.

3. 3 Properties of porcelain bodies

Figure 4 shows change in flexural strength with quartz particle size and various compositions in the fired bodies. The flexural strength of the fired body at L quartz particle addition increases slightly with increasing glass microsphere content. At the S quartz particle, the flexural strength increases with the addition of up to 50wt% glass microspheres, and then the strength decreases slightly with more glass microsphere addition. The maximum flexural strength exhibits at M quartz particle addition in the 532 body. Figure 5 shows bulk density with various compositions and quartz particle size in the fired bodies. The bulk density at M quartz particle addition exhibits a maximum value with the addition of 50wt% glass microspheres. At S and M quartz particle addition, the bulk density increases slightly with increasing glass microsphere content up to 50wt% glass microsphere addition, then the density decreases slightly with more glass microspheres content. The bulk density at L quartz particle increases slightly with increasing glass microsphere content. The bulk density at L quartz particle addition is lower than that at the S and M quartz particles except the 352 fired body. The addition of appropriate glass microspheres makes the viscosity of glass phase lower during the firing process and the glass phase vitrifies the body well, which leads to higher bulk density. However, the addition of too much glass microspheres lowers the density by the formation of large pores in the fired body due to larger amount of lowly viscous glass phase. On the other hand, small amount of glass microspheres make the body become less sintered and vitrified, which leads to the low bulk density.

The flexural strength is also closely related to the water absorption. It means that smaller water absorption generates lower stress concentration at the surface of the fired body because the body with small



Figs. 4 and 5. Change of flexural strength and bulk density with various compositions and quartz particle size in fired bodies.

water absorption does not have almost surface defect. Figure 6 shows change of water absorption. Water absorption at the respective quartz particle sizes decreases as the glass microsphere content increases, and then the value is very small in the range of 40-60wt% glass microspheres at the S and M quartz particle addition. The small water absorption is attributed to the increase of glass bond amount in the body caused by easy vitrification due to a large amount of lowly viscous glass phase. The large water absorption at less glass microsphere content (352 body) with the S and M quartz particle and at all with the L quartz particle is due to less sintering and vitrification during firing process.

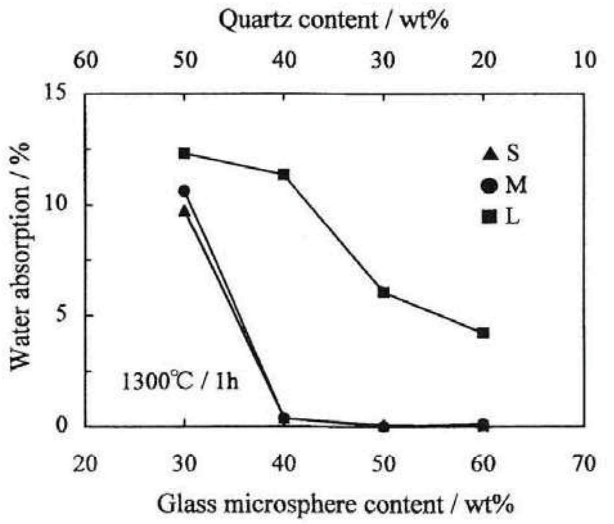


Fig. 6. Change of water absorption in fired bodies.

Quartz grains play a skeleton role in fired body. The addition of less quartz amount decreases quartz skeleton in the fired body as shown in Fig. 3 and, hence, the large decrease of the skeleton can lead to the decrease of flexural strength. On the other hand, addition of a larger amount of quartz makes quartz skeleton increase in the glass matrix, but a larger amount of quartz and large quartz particles produce less sintering and vitrification during firing at the same temperature. Figure 7 shows interplanar spacing of quartz (112) plane in the 532 fired bodies and all the bodies with M quartz particles. A dotted line is the interplanar spacing of (112) plane of a standard quartz.

The larger interplanar spacing in the fired body

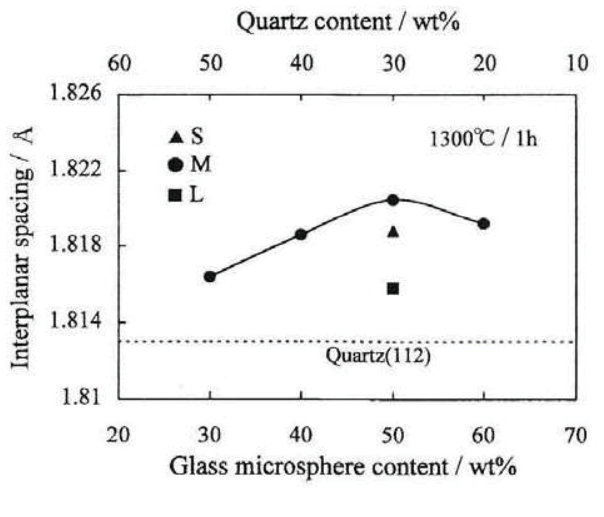


Fig. 7. Interplanar spacing of quartz (112) plane with various compositions and quartz particle size in fired bodies. --- Quartz (112) standard.

compared to that of a standard quartz means larger residual tensile strain of the quartz grain in the fired body.[5] Hence, a strong compressive stress is produced on the glassy phase surrounding the quartz grain in the fired body. The addition of 50wt% glass microspheres at M quartz particle exhibits a maximum value in the interplanar spacing, which presents the maximum strain of quartz grain. The 532 fired body that exhibits maximum interplanar spacing produces a strong compressive stress, i.e., prestress effect,[4,5] on the dense glass phase surrounding the quartz grains by larger difference in the thermal expansion coefficient between the glass matrix and the quartz grains during the cooling process. Thus, high flexural strength in the 532 body with M quartz particle is attributed to fewer fracture origins and higher density by an appropriate vitrification and to a strong prestress effect.

4. Conclusions

New porcelain bodies which possess lightweight and high-strength from glass microspheres-quartz-aluminous cement system were fabricated and the effect of quartz particle size on their properties was investigated. The green strength decreases with increasing glass microsphere content and the decrease is attributed to the relative decrease of aluminous cement volume due to the increase of glass microsphere content. The phases formed in the fired body are glass, α-quartz, α-cristobalite, anorthite and a small amount of α-Al_2O_3. High flexural strength in the 532 fired body with M quartz particle is attributed to a strong prestress and to higher density and fewer fracture origins by an appropriate vitrification.

References

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