Fabrication of New Porcelain Bodies in the System of Glass Microspheres-Quartz-Aluminous Cement

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1. Introduction

Glass microspheres named Shirasu-balloons or hollow glass microspheres are produced by heat treatments using volcanic glass or Shirasu glass, which is species of acidic volcanic ejecta. The manufacture process is continuously progressing to produce smaller hollow microspheres than the previous process. When glass microspheres are mixed with other materials by extrusion, the large glass microspheres are especially more easily broken under the low shear stress because they have very thin shell of glass microspheres. Glass microspheres possess low density, high heat resistance and low thermal conductivity. The glass microspheres have been mainly used as fillers for lightweight building materials, such as curtain walls in high-rise buildings and fillers for various materials, such as plastics, paper clay, paint and so forth. However, they are expected to be used in the new application fields that need more lightweight properties than the usual ceramics.

Up to now, porcelains are mainly fabricated using nonplastic raw materials, such as glass microspheres, quartz and alumino cement. Their mechanical properties were investigated. While the α-quartz and CaAl2O4 phases did not change with hydration time in the green body, the CaAl2O4 phase diminished and, finally, disappeared after 24h hydration. A new phase, CaAl4Si2O8. 4H2O formed but only at hydration times between 24 and 48h, which exhibits maximum green strength. Green strength decreased slightly with increasing the content of glass microspheres at a constant aluminous cement content of 20 mass%. This decrease of green strength is attributed to the decreased bulk density and the relative decrease of aluminous cement volume, due to the larger volume of glass microspheres. The phases formed in the fired body were α-quartz, α-cristobalite, anorthite, glass and a small amount of α-Al2O3. The addition of larger amount of glass microspheres (60 mass%) led to large pores in the fired body, due to low viscosity of glassy phase during the firing process. However, the addition of a small amount of glass microspheres, such as 20 mass%, hampered vitrification and sintering in the fired body. The increased flexural strength at an intermediate composition containing 40 mass% glass microspheres was attributed to a strong prestress induced by the mismatch in thermal expansion coefficient between the glass matrix and the α-quartz grains during the cooling process. Fewer fracture origins, a smaller water absorption and a higher density due to the appropriate vitrification process were also indicated as potential factors leading to the strengthening effect.

Key-words: Nonplastic raw materials, Porcelain bodies, Flexural strength, Prestress, Water absorption, Glass microspheres, Aluminous cement

2. Experimental procedure

2.1 Raw materials and sample preparation

The starting materials for the present study were glass microspheres of 20-60 mass%, silica stone (Ube Industries, Ltd., Japan) of 20-60 mass% and aluminous cement (Ube Industries, Ltd., Japan) of 20-50 mass%. However, the amount of aluminous cement in this study was fixed to 20 mass%. If more than 20 mass% aluminous cement are added, it is necessary to apply higher firing
temperatures due to higher refractoriness. Average particle sizes of glass microspheres, silica stone and aluminous cement used are 11.80, 4.63 and 14.51 μm, respectively. The chemical compositions of the raw materials are shown in Table 1.

Glass microspheres were fabricated by heat treatments at 1055°C using the aluminum hydrate-coated volcanic glass particles obtained by the method of directly dropping the precipitant (NH₄HCO₃) in laboratory. The glass microspheres consisted mainly of SiO₂ and contained small amounts of Al₂O₃, Na₂O and K₂O. The glass microspheres used for the present investigation are the sedimented parts in the water from the as-fabricated glass microspheres, as shown in Fig. 1 (b). Figure 1 (a) is as-fabricated glass microspheres and Fig. 1 (b) is partially hollow glass microspheres sedimented in the water. silica stone consisted of almost α-quartz, which is hereafter designated as quartz. Aluminous cement consisted of CaAl₂O₄ and CaAl₄O₇.

The starting powders were mixed with various ratios in a planetary mixer for 40 min. The content of added water was 23 mass%. Table 2 shows the symbols of the respective mixing ratios. The symbol of 262 means that the mixing ratio of glass microspheres, quartz and aluminous cement is 20, 60 and 20 mass%, respectively. The addition of 20 mass% glass microspheres in the mixture ratios also means mixtures of 20 mass% glass microspheres, 60 mass% quartz and constant aluminous cement content (20 mass%). The mixed powders were pressed under a pressure of 10 MPa. Hydration time was kept for 6, 12, 24 and 48 h at room temperature in moist atmosphere and then the bodies were dried in oven at 50°C for 24 h. The firing was mainly performed in an electric furnace at 1300°C for 1 h. The firing was also partially performed at 1400°C for 1 h to investigate the extent of the vitrification and sintering with more aluminous cement addition. The raising rate was 10°C/min in temperature ranges 25–1000°C and 5°C/min in temperature ranges 1000–1300°C. The cooling rate was 10°C/min.

2.2 Evaluation of properties
Particle size and density of glass microspheres were measured by Microtrac (Leeds & Northrup Co., USA) and pycnometer (Quantas Chrome Co., USA). For the interplanar spacing analyses, the fired bodies were ground by a SiC abrasive paper, followed by polishing with diamond paste (1 and 3 μm) and lapping oil. X-ray diffraction (XRD, Philips, Holland) analyses were performed to determine the phases in the green and fired bodies. The samples were milled in an alumina mortar and then milled in a vibration mill for 30 s. The fracture surfaces were observed by scanning electron microscopy (SEM, ABT, Japan). Linear shrinkage was measured on the length direction before and after the firing. Water absorption was measured based on JIS-R2205. The flexural strengths of the specimens were measured by three-point bending test (Shimadzu, AGS–5KND, Japan) with a span of 25 mm under a crosshead speed of 0.5 mm/min, based on JIS–R1601. The dimension of the green body and fired body is approximate 3.0 mm × 5.0 mm × 40 mm and 3.0 mm × 4.2 mm × 34 mm, respectively. The surface conditions of measured samples in the green body and fired body are as-dried and as-fired conditions, respectively. Sample number used was more than five.

3. Results and discussion
3.1 Preparation and properties of green bodies
Figure 2 shows bulk density of 442 green body as a function of hydration time in the glass microspheres-quartz-aluminous cement system, in which plastic raw materials are not added. The bulk density increases gradually as the hydration time increases up to 48 h in moist atmosphere. Figure 3 shows flexural strength of green body (green strength) with hydration time in the 442 green body. The green strength increases with increasing hydration time and the strength attains to maximum value at hydration time of 24 h, then the value is almost constant in the hydration time range of 24 to 48 h.

X-ray diffraction analyses were performed on 442 green body to investigate the cause of the green strength increase with hydration time at room temperature in moist atmosphere, as shown in Fig. 4. The phases formed in the
green body are mainly glass, α-quartz, CaAl₂O₄ and CaAl₄O₇. α-quartz and CaAl₄O₇ phases do not change with the hydration time up to 48h. However, CaAl₂O₄ phase decreases with increasing the hydration time and disappears almost at the hydration time of 24h. On the other hand, a new phase, CaAl₂Si₂O₈·4H₂O begins to form at hydration time of 24h and the peak is almost constant with increasing hydration time up to 48h. The CaAl₂Si₂O₈·4H₂O formation means that aluminous cement undergoes a hydration reaction with SiO₂ in moist atmosphere. The increase of the green strength with hydration time thus is due to hardening by hydration reaction of aluminous cement in moist atmosphere, even though the body was formed under low pressure without using any binders and plastic raw materials. All the samples thereafter is kept for hydration time of 24h that exhibits maximum value in green strength.

Figure 5 shows changes of green strength and green specific strength as a function of composition in the green body of glass microspheres-quartz-aluminous cement system. The specific gravity of these samples is considered to be corresponding to the bulk density. Then, the unit of the green specific strength is defined as the flexural strength divided by the specific gravity. The green strength decreases as the glass microsphere content in increases under constant aluminous cement (20 mass%). The green specific strength decreases slightly with increasing glass microsphere content. The addition of a larger amount of glass microspheres leads to the relative decrease of aluminous cement volume by larger volume of glass microspheres, which results in the decrease in green strength. Glass microspheres and quartz react with aluminous cement. CaAl₂Si₂O₈·4H₂O was formed by the hydration reaction (24h) of aluminous cement with the glass microspheres and quartz in moist atmosphere. The hydration reaction for 24h in moist atmosphere has effect on the green strength.

Figure 6 shows changes of bulk density with various compositions in the green body. The density decreases with increasing glass microsphere content at a constant amount of aluminous cement. In general, large size of glass microspheres compared with small size of ones exhibit weaker shear stress because they exist as hollow glasses with thin thickness, and hence the large size of glass microspheres in the mixtures with quartz and aluminous cement seem to be easily broken during forming. The glass microspheres used in the present study are collected into the sedimented parts in the water from the as-fabricated...
glass microspheres and possess relatively low particle density (1.99 g/cm³), even though they exhibit higher particle density compared with as-fabricated glass microspheres (1.08 g/cm³) as shown in Fig. 1. Such low density of glass microspheres makes the bulk density decrease in the mixing with quartz (particle density, 2.60 g/cm³) and aluminous cement (particle density, 2.93 g/cm³). The bulk density is proportional to the green strength. The decrease of green strength with increasing glass microsphere content is attributed to the decreased bulk density and the relative decrease of aluminous cement volume due to the larger volume of glass microspheres.

3.2 Fabrication of fired bodies

The green bodies with various mixture ratios were fired at 1300°C for 1h. Figure 7 shows X-ray diffraction patterns with various compositions in the fired bodies. The symbol of 622 in the Fig. 7 means that the mixing ratio of glass microspheres, quartz and aluminous cement is 60, 20 and 20 mass%, respectively. The phases formed at all the batch compositions are α-quartz, α-cristobalite, anorthite, glass and a small amount of α-Al₂O₃. The peaks of α-quartz and α-cristobalite decrease with increasing glass microsphere amount, i.e., less quartz content. Anorthite peak decreases slightly with increasing glass microsphere content up to 40 mass% glass microsphere addition, then the peak increases slightly with the addition of any more glass microspheres. Anorthite might be formed by the reaction of aluminous cement and the SiO₂ in the glassy phase. Imanaka et al. showed that cristobalite was formed when borosilicate glass powders themselves were sintered at around 900°C. They also demonstrated that cristobalite was formed as the stable phase in the glass matrix when the alumina content and firing temperature were low. Lundin suggested that the amorphous silica liberated during the metakaolin decomposition transformed directly to cristobalite at about 1050°C. Carty and Senapati have explained that α-cristobalite in the fired body is crystallized either from the glass phase or by the direct conversion of quartz. In the present study, α-cristobalite peak decreases notably with increasing glass microsphere content and the α-cristobalite does not form almost at addition of much more glass microspheres (622 body), as shown in Fig. 7. Furthermore, SiO₂ amount in the glass phase is rich in 622 compared with 262 mixture ratio and the SiO₂ is easy to crystallize to cristobalite because the SiO₂ rich-glassy phase in the respective mixture ratios is melted from a larger amount of quartz. Anorthite is attributed to be formed from the SiO₂ rich-glassy phase with the addition of a larger amount of quartz.

3.3 Properties of fired bodies

Figure 8 shows bulk density with various compositions in the fired bodies at 1300°C for 1h. The bulk density increases with increasing glass microsphere content at a constant amount of aluminous cement, and then attains to a maximum value at a glass microsphere addition of 40 mass% and the value decreases with the addition of any more glass microspheres. The viscosity of volcanic glass microspheres is quite rapidly decreased at about 1100°C and the decreased viscosity of glassy phase makes smaller quartz particles melt easily. In the glass of E composition (ER-348), the viscosity of a glass melt decreased with increasing temperature in the range around 1200 to 1500 °C. The viscosity of alkali silicates decreased with increased alkali content. In the feldspar-quartz-aluminous cement system, the higher feldspar content results in the lower vitrification temperature by the low viscosity due to a larger amount of glass phase and then lowered the density due to the formation of large pores in the fired body.
diation of a larger amount of glass microspheres makes the viscosity of liquid phase (glassy phase) lower during the firing process. In addition, the small amount of SiO2 which melted from low quartz content, lowers the viscosity of the glassy phase, as compared to SiO2 which melted from high quartz content. As a result, the low viscosity of glassy phase makes the body vitrify easily, which leads to lower firing temperature for vitrification. However, the addition of too much glass microspheres can induce the expansion of pores due to lower viscosity of glassy phase during the firing process.

Figure 9 shows SEM micrographs of fracture surface with glass microsphere content at a constant amount of aluminous cement. The pore size is larger with increasing glass microsphere content at fracture surface of the fired body. It can be considered as two types of pores that are either expanded from the glass hollow microspheres or formed by the release of gases due to a large amount of lowly viscous glass phase during the firing process. The large pores compared with small ones seem to be formed from the glass microspheres. The glass microspheres also seem to keep almost the same shapes and the addition of a larger amount of glass microspheres makes pore size larger in the fired body, as shown in Fig. 9. Large pores form with the addition of more than 50 mass% glass microspheres. In the 622 fired body that adds 60 mass% glass microspheres, the pores form even at the surface of the fired body. Moreover, the flexural strength of the fired body decreases because the pores formed at the surface act as a fracture origin. The decreased density with increasing glass microsphere content is attributed to formation of large pores in the fired bodies by the expansion of glass microspheres themselves and the release of gases as the viscosity of glassy phase is lowered by the increased glass microsphere amount during the firing process. However, the low density at small amount of glass microspheres (262 body) is attributed to less sintering and vitrification during firing (Fig. 9(a)). This can be demonstrated by comparing with the water absorption values because the water absorption of 262 body exhibits larger value compared with the other bodies, as mentioned later. The highest density at glass microsphere addition of 40 mass% (442 body) is caused by higher densification due to an appropriate vitrification.

Figure 10 shows changes in flexural strength with various compositions in the fired bodies at 1300°C for 1h. The flexural strength increases with increasing glass microsphere content at a constant amount of aluminous cement, then the strength attains to a maximum value at 40 mass% glass microsphere addition and the strength decreases with the addition of any more glass microsphere content. The firing temperature was fixed at 1300°C.
because nowadays porcelain body has been usually fired at around 1300°C. The addition of much more aluminous cement amount is also necessary for higher flexural strength to firing at higher temperature, as shown in Table 3. In the 325 body which includes more aluminous cement content compared to 244 body, the flexural strength is lowered by firing at 1300 and 1400°C for 1h, respectively. The flexural strength in both bodies increases prominently by firing at higher temperature, 1400°C compared to 1300°C. The flexural strength is closely related to the water absorption. The 244 body fired at 1400°C exhibits low water absorption. The 244 body having small water absorption that well vitrifies at 1400°C compared with 325 body exhibits higher flexural strength.

Quartz grains generally play a skeleton role in fired body. The addition of lower quartz, i.e., addition of higher glass microsphere content decreases quartz skeleton in the fired body, as shown in Fig. 7 and hence the decrease of the skeleton can lead to the decrease of flexural strength. On the other hand, less glass microsphere amount, i.e., addition of a larger amount of quartz makes quartz skeleton increase in the glass matrix, but too much amount of quartz produces less sintering and vitrification during the firing process (Fig. 9(a)) because quartz increases the viscosity of the molten phase at high temperature as stated by Villegas-Palacio and Dinger. Moreover, α-cristobalite forms in all the mixing ratios and the peak increases with decreasing glass microsphere content. Carty and Senapati indicated strength increase in cristobalite porcelain: the cristobalite grains are much smaller than the quartz grain; the quartz content is reduced by the cristobalite that formed at the expense of quartz; and the cristobalite produces lower strain during the cooling process because of lower inversion temperature (225–250°C) of cristobalite compared to that (573°C) of quartz. In present study, the flexural strength seems to be not affected by the cristobalite despite the formation of a large amount of cristobalite in the 262 and 352 fired bodies.

Figure 11 shows interplanar spacing of quartz (112) plane in the fired body. For comparison, the interplanar spacing of (112) plane of standard quartz is also shown in Fig. 11. The large interplanar spacing in the fired body compared with that of (112) plane of a standard quartz means large residual tensile strain of the quartz grain in the fired body. Hence, a strong compressive stress is produced on the glassy phase surrounding the quartz grains in the fired body by the mismatch of the thermal expansion coefficient between the glass matrix and the α-quartz grains during the cooling process. The addition of 40 mass% glass microspheres (442 body) exhibits a maximum value in the interplanar spacing. The maximum strain of quartz grain thus occurs at the 442 body, which exhibited a maximum flexural strength. The 442 fired body that exhibits larger interplanar spacing compared with the other bodies thus produces stronger compressive stress on the glassy phase surrounding quartz grains, i.e., prestress effect in the fired body, by larger difference in the thermal expansion coefficient between the glass matrix and the α-quartz grains during the cooling process and hence the 442 body leads to a maximum flexural strength.

Furthermore, the addition of more glass microspheres makes the density lower due to the formation of large pores in the fired body, which exhibits porous and light body as shown in Figs. 8 and 9. At glass microsphere content of 60 mass% (622 body), however, the pores form even at the surface of the fired body, which lead to a decrease in the flexural strength as a fracture origins. On the other hand, small amount of glass microspheres make the body become less sintered and vitrified during firing at the same temperature (Fig. 9(a)), which results in the low bulk density and large water absorption value. The flexural strength is almost proportional to the bulk density, as shown in Figs. 8 and 10. The flexural strength is also closely related to the water absorption, as explains latter. It means that smaller water absorption generates lower stress concentration at the surface of the fired body because the body with small water absorption that is well vitrified does not have almost surface defect. However, the fired body such as the 622 body forms pores even at surface by too much vitrification due to lower viscosity of glassy phase, then the stress concentration acts largely at the pores on the surface. Higher flexural strength at addition of 40 mass% glass microspheres (442 body) compared with the other bodies is attributed to fewer fracture origins and higher density by appropriate vitrification, and to stronger prestress induced by the mismatch of the thermal expansion coefficient between the glass matrix and the α-quartz grains during the cooling process.

Figure 12 shows linear shrinkage with glass microsphere content at constant aluminous cement content. The linear shrinkage increases as the glass microsphere content increases, and then the shrinkage is almost constant in the range of 40 to 60 mass% glass microspheres. If only glass particles are fired, a larger shrinkage will occur. However, almost the same shrinkage occurs in the range from 442 to 622 fired bodies. This shrinkage seems to be attributable to the formation of pores that are foamed or expanded either from glass microspheres or by the low viscosity due to a large amount of glassy phase. It also means that the fired bodies at addition of more than 40 mass% glass microspheres are well vitrified, even though the 622 body occurs too much vitrification. The large linear shrinkage...
glass microspheres are attributed to the less vitrification of small amount of glass microspheres and large amount of \(\alpha\)-Al\(_2\)O\(_3\). The low bulk density with the addition of \(\alpha\)-quartz, \(\alpha\)-cristobalite, anorthite, glass and a small amount of plastic raw materials. The phases formed in the fired body in moist atmosphere without using any binders and hardened mechanical by hydration reaction of aluminous cement and their properties were investigated. The green body is prepared in the range of 40-60 mass% of aluminous cement. Water absorption with glass microsphere content at a constant amount of aluminous cement (20 mass%) corresponds closely to water absorption. Figure 13 shows water absorption with glass microsphere content at a constant amount of aluminous cement. Water absorption decreases as the glass microsphere content increases, then the value becomes almost 0 in the range of 40-60 mass% of glass microspheres. The small water absorption is attributed to the increase of glass bond amount by easy vitrification. The addition of more glass microspheres (622 body) forms large pores in the fired body and also forms pores even at surface of the fired body by too much vitrification which leads to smaller water absorption, higher bulk density and fewer fracture origins. The new porcelain body that exhibits the lightweight and relatively high-strength can be produced by using only nonplastic raw materials without using a binder, and it will contribute to the future of porcelain industry.

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4. Conclusions

Fabrication of new porcelain bodies from glass microspheres-\(\alpha\)-quartz-aluminous cement system was tried and their properties were investigated. The green body is hardened mechanical by hydration reaction of aluminous cement in moist atmosphere without using any binders and plastic raw materials. The phases formed in the fired body are \(\alpha\)-quartz, \(\alpha\)-cristobalite, anorthite, glass and a small amount of \(\alpha\)-Al\(_2\)O\(_3\). The low bulk density with the addition of small amount of glass microspheres and large amount of glass microspheres are attributed to the less vitrification and the formation of large pores due to a large amount of lowly viscous glass phase during the firing process, respectively. Higher flexural strength in the 442 fired body (40 glass microsphere-40 quartz-20 aluminous cement) compared with the other fired bodies is due to stronger prestress in the fired body and to an appropriate vitrification which leads to smaller water absorption, higher bulk density and fewer fracture origins. The new porcelain body that exhibits the lightweight and relatively high-strength can be produced by using only nonplastic raw materials without using a binder, and it will contribute to the future of porcelain industry.

References