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Journal of the European Ceramic Society 25 (2005) 1829–1834

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Crystallization behavior and mechanical properties of porcelain bodies containing zinc oxide additions

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Received 29 August 2003; received in revised form 9 June 2004; accepted 20 June 2004
Available online 25 August 2004

Abstract

The effects of ZnO addition on the crystallization behavior and mechanical properties of porcelain bodies have been investigated. When ZnO was incorporated, gahnite ($ZnAl_2O_4$) phase crystallized from 1130 °C, after feldspar had significantly melted and ZnO dissolved into the glass. Cristobalite formation was promoted with the addition of ZnO. However, alumina used as a raw material remained almost intact during sintering. An abundance of gahnite crystals with sizes of 50–400 nm were observed inside the glassy phase, which might contribute to the improved mechanical properties of the porcelain bodies. The flexural strength depended more considerably on the amount of ZnO, in comparison with water absorption and sintering temperature. Wear resistance was enhanced with the addition of ZnO.

Keywords: Crystallization; Gahnite; Porcelain; ZnO; Mechanical properties

1. Introduction

Zinc oxide is known to be a strong flux in whiteware industries and it is one of the major components in commercial glazes for sanitary ware and tiles.[1–3] It controls the thermal expansion coefficient, reduces glaze viscosity and enhances surface glossiness. If it is used more than 10 wt.% in a glaze, crystalline phases develop during cooling and the glaze shows a matte appearance.[4–6] When a much higher amount is employed and the appropriate cooling cycle is adopted, decorative willemite (Zn_2SiO_4) crystals as large as several millimeters appear on the glaze surface.[5,6] The crystallization depends on both the chemical composition of the glaze and heat treatment cycle during cooling from the sintering temperature.[7–10] Sometimes, coloring agents such as cobalt and copper oxide are introduced to impart color and to control crystallization.[9]

Even though there have been many investigations on the ZnO effects on the crystallization in glazes, studies concerning its effects on porcelain bodies are very rare. In general, all starting materials in glazes are completely melted and then crystallization occurs depending on their chemical compositions and the cooling process. However, porcelain bodies melt partially and their crystallization follows complicated routes during the entire firing process, leading to complex microstructures. The glassy phase in porcelain body is initially provided by raw materials of low melting temperature such as feldspar. Other raw materials dissolve into the glass while new crystalline phases develop. Therefore, the crystallization behavior of the porcelain body with the addition of ZnO must be different from that of a glaze.

In this study, the effects of ZnO addition on the crystallization behavior and mechanical properties of porcelain bodies were investigated. The phase development of porcelain body has been examined according to the increased additions of ZnO and the mechanism of the crystallization has been proposed. Water absorption and flexural strength of fired bodies were also measured according to ZnO content and sintering temperature. Finally, the potential applications of this material were discussed.

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doi:10.1016/j.jeurceramsoc.2004.06.009

Table 1
Chemical compositions of raw materials

Raw materials	Composition (wt.%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Ig. loss
Clay	47.12	34.39	1.36	0.21	0.23	1.2	0.41	0.45	14.63
Kaolin	44.64	37.1	1.77	0.6	0.48	0.64	0.45	0.23	14.09
Feldspar	75.6	14.0	0.1	0.35	0.02	3.87	5.32	–	0.74
Pyrophyllite	72.11	19.45	0.1	0.11	0.05	0.1	0.38	0.2	7.50
Alumina	0.02	99.7	0.01	–	–	–	0.26	–	–

Table 2
Proportioned ratio of materials for the reference specimens

Raw materials (wt.%)	
Clay	20.0
Kaolin	20.0
Feldspar	14.4
Pyrophyllite	28.1
Alumina	17.5

2. Experimental procedures

The chemical compositions of the raw materials used in the present study and their proportioned ratios for the reference specimen are listed in Tables 1 and 2, respectively. To investigate the effects of ZnO addition, ZnO were added to batches as 1, 3, and 5 wt.% for the reference specimens. The proportioned mixtures were ball-milled for 2 h in porcelain jars with a purified water medium. The resultant slurries were passed through a 325-mesh sieve and dried in an oven at 90 °C for 24 h. The dried powders were then compacted and pressed into a form of pellet with the dimensions of 4 mm × 5 mm ×40 mm size with the application of 50 MPa pressure. The pressed specimens were sintered at temperatures between 1000 and 1300 °C and then furnace-cooled. The heating rate to the isothermal holding temperature and the cooling rate from the temperature were 7 and 10 °C/min, respectively. To check the possibility of crystallization during the cooling process, a specimen was water-quenched from 1300 °C and compared to the furnace-cooled ones.

The crystalline phases present in the specimens were identified via X-ray diffractometry (XRD) with Cu Kα target, and their contents were quantified by measuring the area of the strongest diffraction peak of each phase: d_{113} (alumina), d_{111} (cristobalite), and d_{311} (gahnite). The water absorption of each sintered specimen was measured according to the ASTM C373[11] after polishing the specimens to 3 μm. The flexural strengths were measured by means of a three-point bending test conducted with a crosshead speed of 0.5 mm/min and an outer span of 30 mm. For the strength measurements, the specimens were initially polished to 3 μm and chamfered with a diamond disk. For a few specimens, differential scanning calorimetric (DSC) analysis was performed from room temperature to 1300 °C. To observe the microstructure development through the scanning electron microscopy (SEM), the sintered specimens were polished to 3 μm and etched in a 10% HF solution for 1 min. The specimens were also analyzed through the transmission electron microscopy (TEM) and the energy dispersive X-ray spectrometer (EDX). To estimate the wear resistance, their weight losses of the specimens were measured after SiC particles of 10 kg with 20-mesh size were poured into the sintered specimen from the height of 1100 mm with an inclination angle of 45°.[12] Smaller weight loss refers to a higher wear resistance.

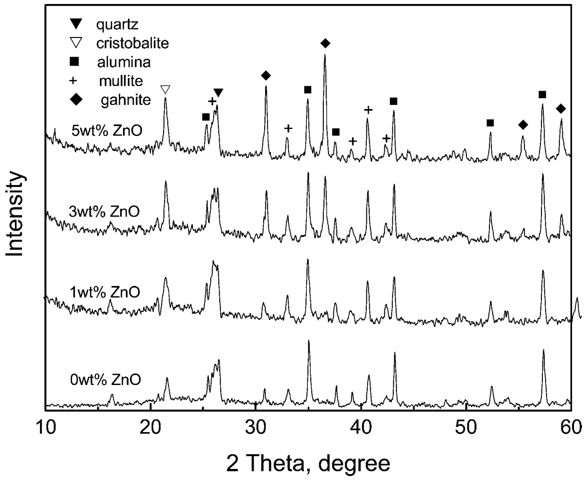

Fig. 1. XRD patterns of ZnO-added specimens sintered at 1300 °C for 30 min.

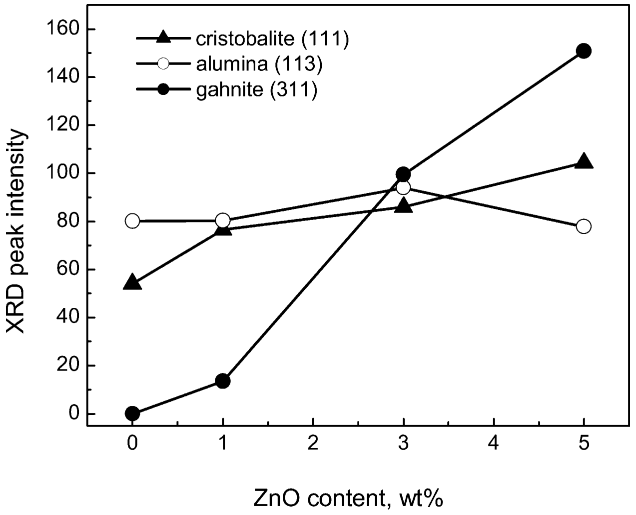

Fig. 2. Variations of crystalline phase content of specimens sintered at 1300 °C for 30 min with addition of ZnO.

3. Results and discussion

Fig. 1 shows the XRD patterns of the specimens sintered at 1300 °C for 30 min. The addition of ZnO resulted in the development of $ZnAl_2O_4$ (gahnite). In addition, cristobalite crystallization seems to be promoted by such an addition. On the contrary, the diffraction intensities of alumina remained almost constant, implying that the alumina added as a raw material may have not reacted with the other materials (Fig. 2). To check whether the crystalline phases developed during cooling from the sintering temperature, the specimen with 5 wt.% ZnO was water-quenched from the sintering temperature of 1250 °C after 1 h isothermal holding, and then compared to the ones furnace-cooled after 1 min and 1 h isothermal holding at the regarding temperature, respectively (Fig. 3). The diffraction pattern of the quenched specimen was the same as that of the furnace-cooled one, while an increase in sintering time resulted in stronger diffraction intensities of gahnite and cristobalite. Therefore, the crystallization must be occurring during the isothermal holding at the soaking temperature rather than during cooling.

Fig. 4 shows the diffraction patterns of specimens with 3 wt.% ZnO that were sintered for 30 min at temperatures from 1000 to 1250 °C. ZnO remained up to 1000 °C and then started to disappear as feldspar melted with an increase in the sintering temperature. When the temperature had reached to 1150 °C, the feldspar had almost melted, and gahnite and cristobalite phases started to develop. DSC curves shown in Fig. 5 comply well with the results of diffraction analysis. For the specimens with ZnO, a broad exothermal peak was observed from 1130 °C, in contrast to no such a peak for the reference specimen. On the other hand, mullite somewhat began to form at a lower temperature around 1100 °C and quartz gradually dissolved above 1150 °C. As seen in Fig. 1, diffraction intensities of alumina did not change (Fig. 4), strengthening the approach that the alumina did not participate in the reactions and remained mostly intact during sintering. Contrary to the previous studies,[7–9] willemite (Zn_2SiO_4) was not observed in this study, which might be due to higher amount of alumina containing raw materials than usual glazes rich in silica.

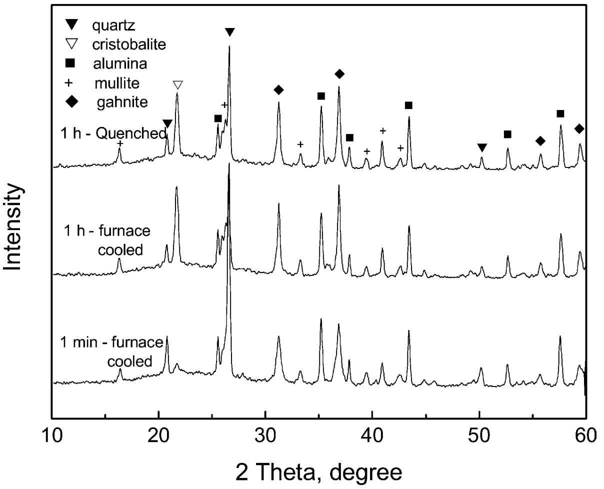

Fig. 3. XRD patterns of specimens with 5 wt.% ZnO, water-quenched after 1 h isothermal holding, and furnace-cooled after 1 min and 1 h isothermal holding at 1250 °C.

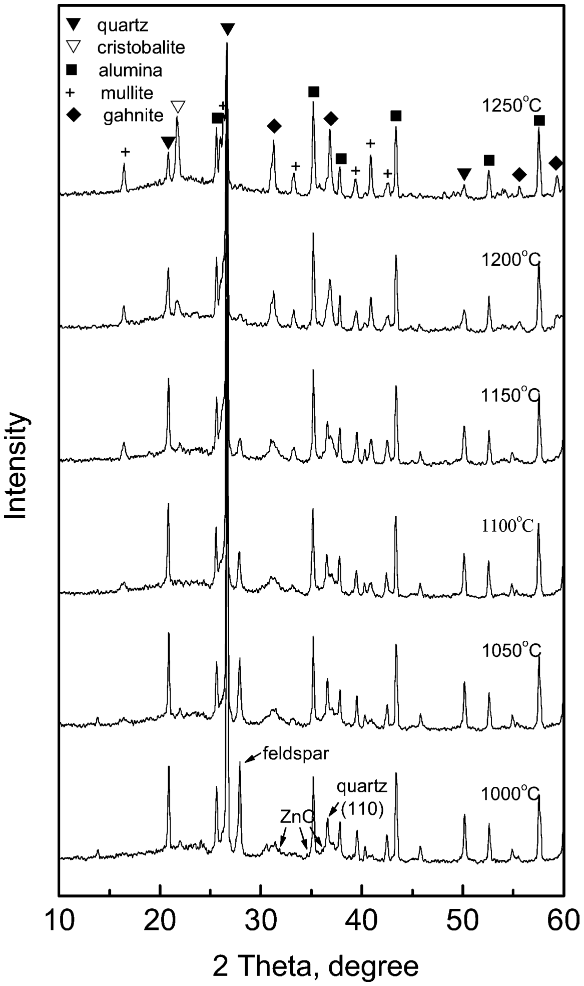

Fig. 4. X-ray diffraction patterns of specimens with 3 wt.% ZnO sintered at various temperatures for 30 min.

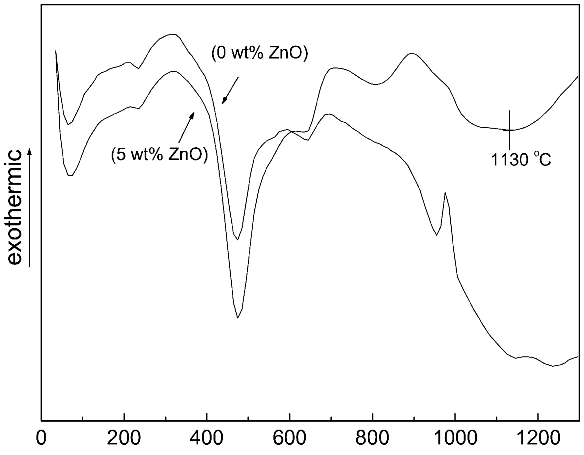

Fig. 5. DSC curves for specimens with and without added ZnO.

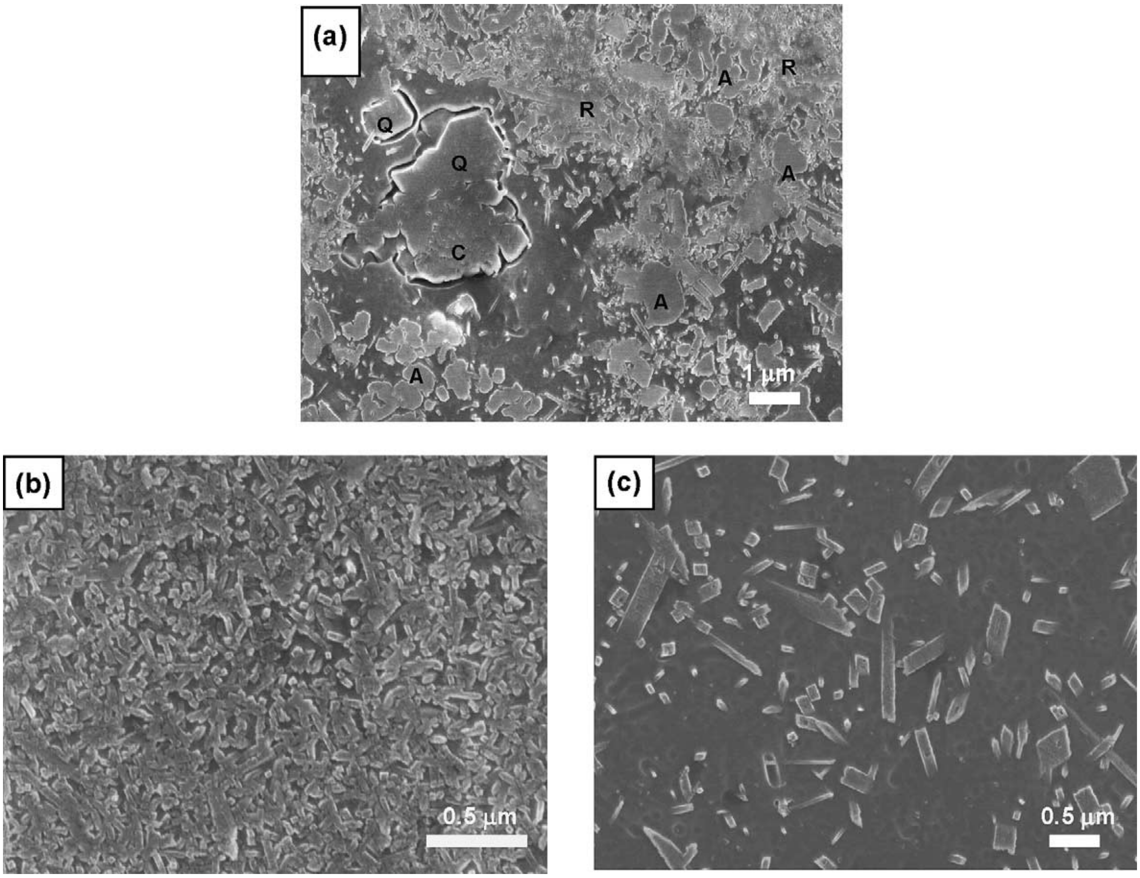

Fig. 6. SEM microstructures of the specimen with 5 wt.% ZnO sintered at 1300 °C for 30 min (a) at low magnification, (b) in clay relict, and (c) in glass region (Q: quartz, C: cristobalite, A: alumina, R: clay relict).

From X-ray diffraction analyses, gahnite formation is assumed to be related to the ZnO dissolution and its consequent crystallization inside the glass as gahnite phase, instead of a direct solid-state reaction between ZnO and Al_2O_3 containing raw materials. To verify this assumption, the specimen with 5 wt.% ZnO, sintered at 1300 °C for 30 min, was analyzed through SEM and TEM. Fig. 6 shows the SEM images of the specimen, which was etched in a HF solution for the observation. The microstructure consisted of glass and crystalline phases. Through the EDX analyses, crystalline phases such as quartz, alumina and mullite could be identified as shown in Fig. 6. A quartz grain seems to be under transformation from quartz to cristobalite and very small mullite crystals were observed in clay relict. On the other hand, inside glassy phase, an abundant number of fine crystals were revealed. When the specimen was observed through the TEM, the fine crystals with the size of 50–400 nm were composed of ZnO and Al_2O_3 without any other elements (Fig. 7). Since the gahnite is the only binary compound in the ZnO–Al_2O_3 phase diagram,[13] the analyzed crystal must be gahnite. These results also support our assumption that the gahnite crystallized inside the glassy phase formed from feldspar melting and ZnO dissolution during heating to the sintering temperature.

The gahnite crystallization temperature of 1130 °C in the present study is much higher than those of investigations on glass and glass ceramics.[7–10,14–16] It was reported that gahnite crystallization starts from 950 °C in a SiO_2–Al_2O_3–ZnO–CaO system, which is preceded by anorthite formation and assumed to occur by decomposition of anorthite.[16] In the present study, however, anorthite was not observed. Considering the chemical compositions of the feldspar used in this experiment (Table 1), the glass viscosity under 1130 °C may be so high for allowing the crystallization.

The water absorption and flexural strength of the sintered specimens were measured. Water absorption decreased with increasing sintering temperature and ZnO content (Fig. 8). Compared to typical porcelain body, whose water absorption is lower than 0.3%, these specimens show high water absorptions like 1.4–7.3% but quite high mechanical strengths around 100 MPa, as shown in Fig. 9. For the specimens sintered at 1300 °C, as ZnO content increased to 5 wt.%, flexural strengths were improved from 87 to 105 MPa, an increase of roughly 20%. As the sintering temperature was lowered to 1250 °C, water absorption increased considerably (from 1.4 to 3.8%) for the specimen with 5 wt.% ZnO, yet strength reduction was moderate, from 106 to 100 MPa. These strength improvement seems to be related to gahnite crystallization because the other crystalline phases such as alumina, mullite

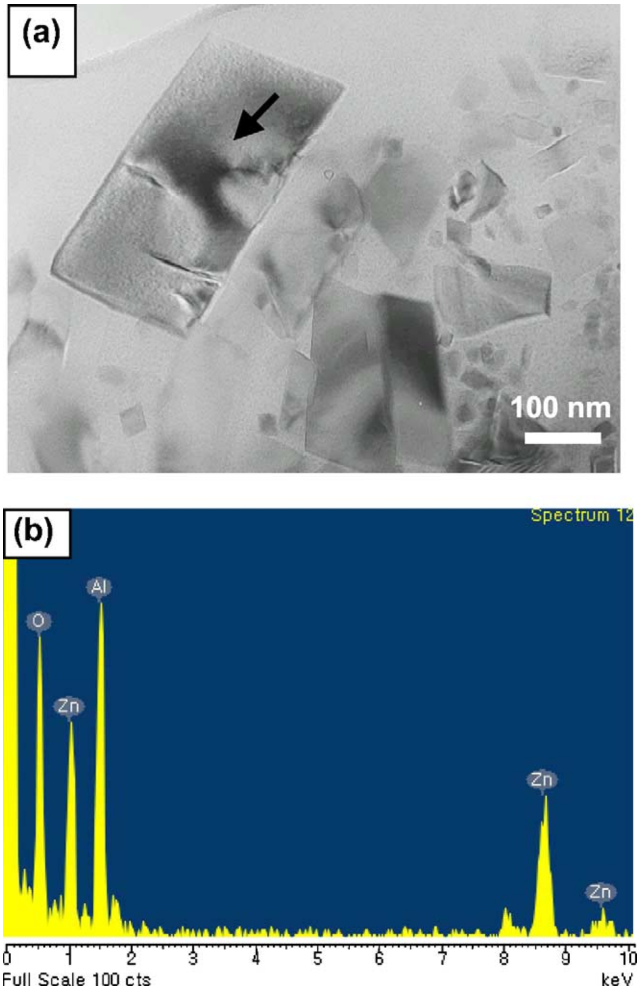

Fig. 7. TEM microstructure and composition analysis of the specimen with 5 wt.% ZnO sintered at 1300 °C for 30 min: (a) micrograph of glass region and (b) EDX pattern taken from the crystal indicated by the arrow in (a).

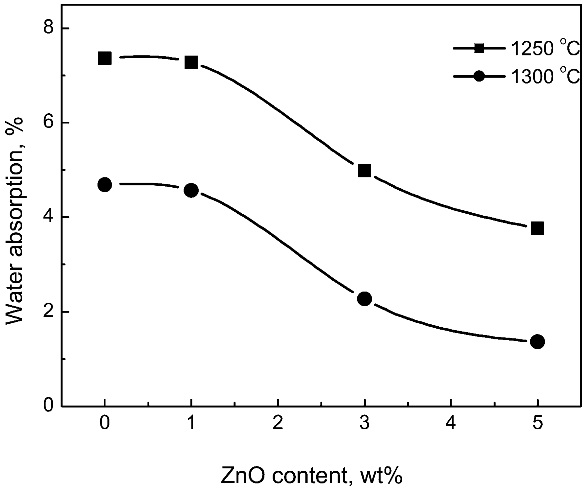

Fig. 8. Water absorptions of specimens with addition of ZnO sintered at 1250 and 1300 °C for 30 min.

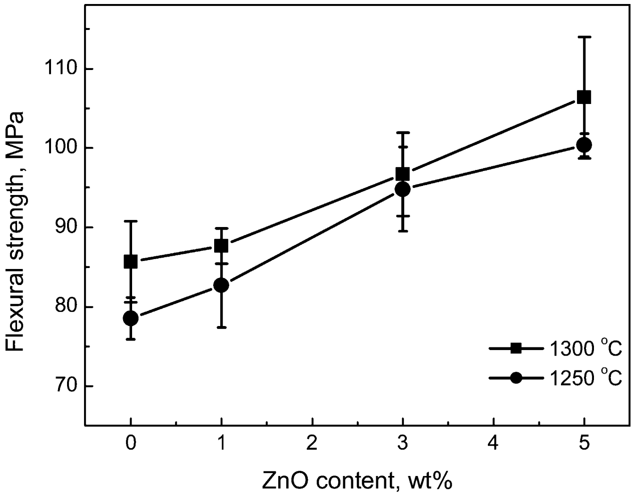

Fig. 9. Flexural strengths of specimens with addition of ZnO sintered at 1250 and 1300 °C for 30 min.

Table 3

Weight losses determined in the abrasion test of the specimens containing 1–5 wt.% ZnO sintered at 1250 °C for 30 min

ZnO content (wt.%)	Weight loss (g)
1	0.0159
3	0.013
5	0.0102

and quartz did not change considerably with ZnO addition as shown in Fig. 1. Wear resistance of the porcelain developed in the present investigation was also measured. Table 3 shows the weight losses after abrasion test on the sintered specimens. ZnO addition improved wear resistance, which might be also due to the gahnite crystals of high scratch hardness (8.5 on Mohs' scale).

This study was conducted under the motivation to impart moderate open porosity yet high wear resistance and high flexural strength to porcelain bodies for their potential applications as abrasive parts in food crushing equipment. Though ceramics have been promising candidate materials for these abrasive parts because of superior wear resistance and biosafety compared to cast iron, the low crushing efficiency of dense ceramics due to their low friction coefficient impeded their practicality. Since the porcelain bodies developed in the present investigation showed high water absorption, they might have high adherence to crushed materials, resulting in greater crushing efficiency. In addition, since the raw materials used in this study are mostly supplied from natural resources, the abrasive parts could be manufactured at low cost.

4. Conclusion

As ZnO content increased, the gahnite ($ZnAl_2O_4$) phase was crystallized and cristobalite formation was promoted in the sintered bodies. However, alumina added as a raw material remained mostly intact during the sintering process and mullite formation was not affected by the addition of ZnO. The ZnO survived until 1000 °C and disappeared with glass formation due to the melting of feldspar. The gahnite crystals started to form inside the glassy phase from 1130 °C when glass was significantly formed and its viscosity was low enough for the gahnite crystallization. Gahnite crystals with sizes of 50–400 nm were homogeneously distributed throughout the glassy phase after sintering. These experimental results suggest that the gahnite crystallization occurs after glass formation. With increases in ZnO content and sintering temperature, water absorption decreased and flexural strength improved. The strength depended on ZnO content rather than water absorption. Wear resistance was also significantly improved with ZnO. These variations in strength and wear resistance appear to be closely related to the formation of gahnite crystals of high hardness. The porcelain developed in this study might be one of the candidate materials for the abrasive parts of food crushing equipment, which require moderate porosity and high strength with low manufacturing cost.

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