Tribological Behavior of Whiteware with Different Transparent Glazes

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ABSTRACT

Tribological properties of whiteware with various transparent glazes, which have different composition and microstructure, were investigated. The wear resistance and friction behavior of the glazed whiteware are a very important aspect if the whiteware is used as tableware and for sanitation purposes. Generally, the wear property is influenced by the microstructure and surface morphology of the material. The whiteware specimens with two kinds of transparent glazes were fabricated by using the commercially available porcelain body. Furthermore, the commercial tableware, such as bone china, and traditional tableware were also examined as reference materials. All of the specimens showed that different pore structures might affect the mechanical and tribological properties. It seems that the wear resistance of whiteware is substantially related to the pore size and distribution of glaze rather than the hardness value of the specimen.

Key words : *Transparent glaze, Tribology, Hardness, Porcelain, Pores*

1. Introduction

Porcelain glaze is used to improve the surface properties of products and enhance their aesthetic textures, typically in a vitrified film condition onto material surfaces. Depending on the mixing ratios of the alkali elements, aluminosilicates (feldspar), for instance, within the glaze composition, glazes can be divided into low-fired through high-fired types and can be divided as well into transparent, opaque, and glossy types depending on the glaze surface and/or internal structural conditions.¹⁻³⁾ Furthermore, glazes can be divided into raw glaze (non-fritted glaze), frit glaze, and other types depending on the raw materials used in their manufacturing. Generally, raw glaze is manufactured with natural minerals as a raw material. On the other hand, frit glaze is fabricated using artificially treated mineral materials in the form of multi-composition powders through the melting and quenching of a mixture of minerals.^{1,4)} These types of frit glazes are provided as commercial glazes with diversified compositions and properties by the manufacturer. Apart from this, the type known as 'matte' glaze refers to a glaze without gloss, in contrast to a typical glossy glaze; it is known to be produced mainly via a surface treatment or a crystallization process.^{3,5)} As a typical industrial area in which glazes are used, there are the examples of the tableware and sanitary ware industries, where a variety of whiteware products is manufactured with porcelain materials and transparent glazes.^{6,7)} For such tableware or

sanitary ware, functionalities such as the mechanical strength, scratch resistance, and cleaning ease along with artistic aesthetics created through various patterns and shapes are becoming important criteria related to quality and purchasing competitiveness. Particularly, the transparent glaze used in tableware requires good mechanical strength and durability against damage due to frequent contact with metal materials and with each other during typical cleaning processes. Particularly with regard to wear resistance, impact or sliding wear which can occur during the cleaning process together with abrasive or adhesive wear which can commonly occur upon contact with metal materials such as knives, forks, spoons and sticks can appear in complex forms.^{8,9)}

In the present study, the mechanical characteristics and microstructures of whiteware samples with various transparent glazes having different compositions and pore structures were analyzed in a comparison with those of commercial bone china and traditional china, and the effects of the surface microstructural characteristics, including the glaze layer, on the tribology of the samples were analyzed by conducting wear tests against metal counterpart materials. Through these efforts, the effects of the structural rigidity of a material dependent on the pore distribution of material surfaces on the wear resistance were examined.

2. Experimental Procedure

2.1 Preparation of whiteware specimens with different transparent glazes

A commercially available porcelain body (Koryo Kaolin,

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Icheon, Korea) was used as a matrix material. The composition of this porcelain body was confirmed to be mainly 71.6 wt% SiO₂, 18.9 wt% Al₂O₃, 0.31 wt% CaO, 1.16 wt% Na₂O and 1.75 wt% K₂O according to the results of a compositional analysis using X-ray fluorescence (XRF, Rigaku ZSX Primus, Japan) and inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300DV, USA). To prepare specimens for the mechanical characterization and friction/wear tests, a slurry was prepared initially by mixing the porcelain body and water at a ratio of 3:1 with 0.2% of a deflocculant (Cerasperse, 44-CF). This was followed by agitation for 3 h. Subsequently, unglazed samples were prepared by casting the dried slurry in a gypsum mold that was dried at 50°C for more than 24 h with a subsequent drying step for 3 days followed by a heat treatment at 900°C (5°C/min, Air) for 30 min. The final sintered specimens were prepared through a heat treatment (1250°C (5°C/min) lasting for 1 hour under atmospheric conditions) after dip glazing of the as-prepared unglazed samples for 3 seconds. Two types of transparent glazes were used in this experiment, a commercial transparent glaze sourced from the Icheon area of Gyeonggi-do in Korea, and a transparent glaze directly prepared in a laboratory. The transparent glaze prepared in the laboratory was produced by mixing 56.12% feldspar, 13.44% silica, 19.6% limestone, and 10.84% kaolin with water at a 1 : 1 ratio followed by ball-milling (with high-purity alumina balls) for 24 h. For the commercial transparent glaze, it was confirmed to have a composition of 68.2% SiO₂, 21.6% Al₂O₃, 2.1% CaO, 5.8% Na₂O and 2.2% K₂O. Additionally, commercial bone china (a dish, Purewhite/Modern Square, Hankook Chinaware, Korea) and traditional porcelain (a whiteware dish, Sieun Ceramics, Korea) were selected as the comparison group. These were machined to the same size and shape as the prepared test specimens of whiteware bodies glazed with transparent glazes. The mechanical properties and friction/wear characteristics of all samples were then investigated. A summary of the analysis results of the matrix material and the major components of each glaze are given in Table 1.

2.2 Evaluation of microstructures and mechanical properties

Microstructural analyses of the sintered body and the surface structures after the friction/wear tests were conducted using a scanning electron microscope (SEM, JSM-6390, JEOL, Japan). The surface roughness levels of the samples

were measured under the initial condition without a special surface treatment such as mirror polishing using a surface profiler (Mitutoyo SJ-411, Japan) under a 0.75 mN load and a measurement distance of 25 mm. The initial surface roughness of each sample, which covered with a vitreous glaze, was relatively low. Also, with a Vickers hardness tester (Shimadzu HVM 2T, Japan), the surface hardness characteristics of each sample were measured. Due to the porous surfaces of the samples, preliminary hardness tests were conducted to determine the optimum load conditions within the range of 1 ~ 10 kgf. The specimens for the friction/wear tests were produced by machining them into a shape measuring 30φ by 3t (mm), while a type of steel (SUS304, 10φ, hardness: approximately 7.7 GPa) as a counterpart material was selected considering material of actual tableware. Because the counterpart material used in this experiment has a higher hardness value than the metal material used to manufacture actual commercial tableware (knife for metallic tableware hardness: approximately 2.5 GPa), the test conditions for the friction/wear experiments were more severe than the actual conditions. The friction/wear tests were conducted using a friction/wear tester (MPW110, Neopius Inc., Korea) with the ball-on-disk method based on the KS L1606 specifications, and an evaluation was done with a measurement distance of 0.5 km, an applied load of 20N, and a velocity of 0.1 m/s.

3. Results and Discussion

3.1 Microstructure analysis

The results of the microstructural analysis of the samples prepared in this experiment are shown in Figs. 1 and 2. The microstructures of the surfaces and cross-sectional views of the whiteware samples prepared with the glazes directly prepared in the laboratory and the commercial glaze are shown in Fig. 1. In Fig. 1(a), the surface morphology of the sintered matrix material is illustrated. The results of the sintering of particles with a particle size on the level of a few μm are shown inside the matrix of the whiteware body. A typical microstructure of the surfaces covered with the glaze is shown in Fig. 1(b), where no remarkably coarse pores are observed. Fig. 1(c) shows the cross-section of the microstructure of a specimen with KICET glaze, as prepared with the glaze produced with selected compositions in this experiment. The thickness of the glaze layer, which appears to be vitreous, is observed to be approximately 250 μm, with pores

Table 1. Compositions of the Substrate and Glazes

Element (wt%)	Substrate (Porcelain)	KICET (Glaze)	Commercial (Glaze)	Traditional Whiteware	Bone china
SiO ₂	71.6	67.5	68.2	72.1	61.8
Al ₂ O ₃	18.9	18.7	21.6	10.8	10.9
CaO	0.3	6.9	2.1	10.8	14
Na ₂ O	1.2	3.4	5.8	2.1	6.4
K ₂ O	1.7	3.5	2.2	4.2	6.9

Fig. 1. Microstructures of whiteware with different glazes: (a) substrate, (b) substrate with glaze, (c) glaze (KICET), and (d) glaze (Commercial).

Fig. 2. Microstructures of commercial tableware specimens: (a) traditional whiteware specimen with (b) glaze, and (c) bone china specimen with (d) glaze.

of about 10 ~ 100 μm in diameter found. Also in Fig. 1(d), the cross-section of the microstructure of a whiteware body specimen prepared using a commercial glaze is shown. The thickness of the glaze layer is about 200 μm , and pores with a diameter of a few ten μm of diameter can be observed. When compared to the case shown in Fig. 1(c), the structure is similar but with a relatively small amount of pore size deviation. In Figs. 2(a) and 2(b), the matrix and glaze layer structure for the traditional ceramic ware specimens and the bone china specimens (Figs. 2(c) and 2(d)), respectively, are shown for a comparison. Fig. 2(a) depicts the internal structure of the traditional ceramic product, where the structures inside the body are composed of a mixture of relatively large particles, with the presence of pores having a diameter of less than 10 μm . For the glaze layer (Fig. 2(b)),

Fig. 3. Hardness values of the specimens.

pores of a relatively smaller size are shown to be distributed as compared to the glaze layer of the specimens shown in Fig. 1. The internal structure of the bone china product shown in Fig. 2(c) is shown to consist of particles of a relatively small size as compared with those of the traditional whiteware products, with presence of pores of a few tens of μm in size. However, the structure of the glaze layer shows pores of a markedly smaller size and with a lower distribution in comparison with the three other types of samples.

3.2 Evaluation of the mechanical and friction/wear properties

In Fig. 3, the results of the surface hardness tests of each sample are shown. Prior to the hardness measurements of each sample, to secure optimum conditions for the hardness measurement of the whiteware body samples with the glaze layer having numerous pores, indentation tests were performed while changing the applied load of the Vickers hardness tester used from 1 to 10 kgf for whiteware body specimens with the glaze prepared in the laboratory (the KICET glaze). Consequently, the formation of optimum indentations at 2 kgf was confirmed, and the hardness measurement was conducted under the same condition for individual samples. As shown in Fig. 3, the hardness values of all of the samples did not differ greatly, with all at approximately Hv 550 ~ 600 despite the mutually different glazes and pore distribution structures. Despite the use of different contents of CaO , Na_2O and K_2O , for instance, which existed in relatively small amounts, the typical hardness characteristics of a whiteware body with vitreous glaze with similar amounts of SiO_2 and Al_2O_3 as major components were observed. Although it was by a small margin, it can be confirmed that the highest hardness value was observed in the whiteware specimen prepared using the commercial glaze with the highest content of Al_2O_3 .

In Fig. 4, by measuring the friction coefficients and wear volumes of each sample after the friction/wear tests, the relationship between roughness level and the pore size of

Fig. 4. Wear and friction trends of whiteware specimens with different surface structures.

each sample was considered. In the view of the wear volume, much higher values by more than fourfold were observed in the samples with the laboratory-prepared glaze (the KICET glaze) and the commercial glaze (the Commercial glaze) compared to the traditional whiteware and bone china products. Also, while the commercial product group shows relatively low friction coefficient values as compared with the samples prepared in the laboratory in a manner similar to the wear volume, the difference was shown to be minor in comparison with the wear volume. The pore sizes of the samples as examined through a microstructure analysis were shown to be nearly double for the laboratory-prepared sample group in comparison with the commercial product group, showing a trend similar to that of the wear volumes for each sample. Specifically, lower wear resistance is presumed to arise in the laboratory-prepared sample group, which showed larger pores with higher fractions as compared to the commercial product group, having relatively small pores and lower fractions. These assumptions can be inferred from the model with regard to the effect of pores on the increase in the wear volume, as shown in Fig. 5. As shown in the schematic diagram presented in Fig. 5, when internal pores exist beneath the surfaces, if the edges of the internal pores are exposed to the surface by continuous wear against the counterpart material, the formation of wear debris by the dropout of edge parts can occur. As a result, the wear of the surface can accelerate.^{10,11)} In the roughness measurement results, typical results are indicated, where relatively low friction coefficients are exhibited in the samples showing low roughness, such as bone china and traditional whiteware, in the commercial product group.

Figure 6 shows the surface microstructures after the wear test of each sample. Observable inside the wear tracks of all sample groups is a mechanically compacted alloying layer, presumably a hydration reaction layer from the friction/wear test conditions in the atmosphere with 80% humidity.¹²⁾ For the laboratory-prepared sample group (Figs. 6(a) and 6(b)), the aspect of sliding wear is conspicuous, while only a trace of wear debris is observed inside wear tracks,

Fig. 5. Modeling of the wear behavior dependence with pore structure¹⁰⁾.

Fig. 6. Surface morphologies of the specimens after the wear test: (a) KICET (glaze), (b) Commercial (glaze), (c) traditional whiteware, and (d) bone china.

along with the areas exposing internal pores, which existed underneath the surfaces. On the other hand, as shown in Figs. 6(c) and 6(d)), for the samples in the commercial product group, periodic local cracking sections (Hertzian-type cracks), among other types, are observed along with the mechanically compacted alloying layer.¹³⁾ These types cracks formed inside the wear tracks are presumably attrib-

Fig. 7. Cross-sectional view of glazed whiteware including large pores after the wear test: (a) KICET (glaze) and (b) Commercial (glaze).

utable to the role of CaO, which exists at a relatively high content compared to that in the laboratory-prepared specimen group as a network modifier within the structure of the vitreous glaze layer.¹⁴⁾

In Fig. 7, which shows the cross-section of the microstructure of the laboratory-prepared sample group after the wear test, a higher wear volume is noted compared to that in the commercial product group. In both cases, flake-like delamination, microcracks and subsurface cracks are observed on the sample surfaces and subsurface area.¹⁵⁾ Such phenomena represent wear phenomena with which cracks can propagate after being generated more easily around the pores. This can be explained in connection with the phenomenon of the increased wear volume of the laboratory-prepared sample group, with larger pores of higher fractions.^{10,12,13)}

4. Conclusions

The mechanical properties and friction/wear characteristics of whiteware body specimens prepared using two types of glaze were compared with those of commercially available traditional whiteware and bone china. Considering the typical structure of the type of glaze used with these products, including the substantial pore distribution, the wear volume was shown to be increased in the structures with relatively large sizes and a greater distribution of pores. These results were presumed that the additionally formed wear debris due to the exposure of the pore edge by the continuous contact movement contribute to the acceleration of wear. From the results of the experiments conducted here, the wear resistance of the samples can be affected relatively more by the pore structure of the subsurface with its sizes and by the distribution status of glazed porcelain than by the hardness levels of the sample itself. Therefore, considering transparent glazes, optimization of the surface struc-

tures, including their pore sizes and distributions, by the appropriate selection of the glaze composition and control of the heat treatment conditions is required to obtain improved tribological properties with transparency. These achievements will contribute to satisfy the functionality and appearance of whiteware.

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