釉に作用するプリストレスによる強化磁器の強度向上

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Improving the Strength of Strengthened Arita Ware Based on Prestress in Glaze

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Enhancing the strength and reliability of porcelain remains a significant challenge. Unlike most of the porcelain strengthening strategies, this study focuses on improving the strength of porcelain by controlling the coefficient of thermal expansion (CTE) mismatch, thereby inducing compressive stress between the porcelain matrix and the surface coating or glaze. First, by adjusting the crystalline and glassy phases of the coating, a 64.6% increase in strength was achieved for ceramics coated on six sides with an anorthite-based coating. Second, the influence of the matrix with varying CTEs on the strengthening of the porcelain while maintaining a constant CTE for the glaze was investigated. Zirconia-strengthened porcelain, which exhibited the highest CTE, showed a 33.6% strength improvement with an optimized glaze design. Remarkably, this enhancement was achieved with only single-side coating. This study provides valuable insights into strategies for improving the strength of porcelain, paving the way for advancements in the development of more reliable and robust ceramic materials.

1. Introduction

Porcelain is widely used in tableware, sanitary ware, tiles, insulators, and crucibles worldwide. However, its brittleness and poor reliability significantly limit its application, particularly in hospitals, nursing homes, and airplanes. Therefore, strengthening porcelain remains a significant challenge in its production. Since Austin et al.[1] reported that the addition of alumina particles greatly improved the strength of porcelain, extensive research efforts have focused on enhancing porcelain strength through various methods, including mullite or needle-like mullite strengthening [2], fine particle strengthening [3] and prestress strengthening [4]. However, most studies have concentrated on strengthening the porcelain bodies themselves, with limited attention given to the prestress introduced by glazes or coatings and the potential for optimizing this prestress to enhance strength.

Residual stress is inherently present within the glaze due to the mismatch in sintering shrinkage between the porcelain body and the glaze layer. If the residual stress in the glaze layer is compressive, the bending strength of glazed porcelain can be enhanced by up to 1.4 times compared to that of unglazed porcelain [5]. Conversely, tensile residual stress in the glaze can lead to fractures within the glaze, thereby reducing the bending strength of the porcelain [6]. Therefore, it is important to design the glaze with the appropriate compressive stress so that the flexural strength of porcelain will be improved.

In this study, the coefficient thermal expansion (CTE) mismatch between the strengthened body and the coating or glaze was utilized to design prestressed coatings and glaze layers, thereby enhancing the strength of porcelain. Specifically, the application of six surface coatings increased the strength of the porcelain from 87.5 MPa to 144.0 MPa, representing an improvement of 64.6% compared to the uncoated porcelain. Furthermore, the use of a transparent glaze enhanced the strength of alumina- and zirconia-strengthened porcelain by 25.3% and 33.6%, respectively.

2. Experimental

The raw materials used in this research were Amakusa clay (Fuchino Ceramic Raw Materials Co., Japan), Masuda feldspar (Nishi-Nihon Kogyo Co., Japan), Alumina powder (A-34, Japan light Metal Co., Japan) with a mean diameter of approximately 4 μm and Zirconia powder (TMZ and HSY3.0, Daiichi Kigenso Kagaku Kogyo Co., Japan) with a mean particle diameter of approximately 1.12 and 0.65 μm. The transparent limestone glaze (Table 1), with the CTE of 5.63×10^{-6} K^{-1} was purchased from Saga Pottery Raw Materials Co., Japan.

Table 1. Chemical composition of limestone glaze

Mass%

	Lg. loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Total
Before firing	6.15	68.45	11.09	0.13	0.05	7.10	0.06	4.16	2.45	99.64
After firing	-	73.21	11.86	0.13	0.06	7.60	0.06	4.45	2.62	100

The amount of alumina and zirconia in the porcelain, which is used to control the flexural strength and densification, was set to 30 and 45 mass%, respectively. Raw materials composition of the porcelain substrate was listed in Table 2. The names STD, ASP, ZSP and YZSP correspond to standard, Alumina strengthened porcelain, zirconia strengthened porcelain and Yttrium Stabilized Zirconia strengthened porcelain, respectively. The procedure of making the ASP specimen using slip casting is described in details elsewhere [4, 7]. The specimens were fired at 900℃ in a biscuit-firing process. The glaze was coated using the dip-coating method. After dipping the entire specimen, only the surface

Table 2. Raw materials composition of the porcelain substrate

Mass%

	Amakusa clay	Masuda Feldspar	Alumina	Zirconia	Stabilized Zirconia
STD	85.7	14.3	0	0	0
ASP	60	10	30	0	0
ZSP	47.1	7.9	0	45	0
YSZSP	47.1	7.9	0	0	45

with specified length and width dimensions retained the glaze layer, while the glaze on other surfaces was wiped off using a wet sponge. Finally, the specimens with a single glazed surface were refired at a specific to get the test bars temperature, at which we get the highest bending strength for the unglazed specimens.

The flexural strength of the ASPs and the ASPs with glaze were measured using a three-point bending test according to standard JCRS 203 at room temperature. The span L of the bending test was 30 mm, and the loading rate was 5 mm/min. The flexural strength σ of the specimen was calculated using the following equations.

$$\sigma = \frac{3PL}{2bh^2} \qquad (1)$$

Where P is the maximum load at fracture and b and h are the width and thickness of the specimen, respectively.

Other detailed characterization information could be found elsewhere [7-9]. The anorthite prestress coating work was co-conducted with Jingdezhen Ceramic University. The details can be found in the literature [10].

3. Result and discussions

3.1 Design the anorthite coatings for improving the flexural strength of porcelain by residual stress

The anorthite coating was prepared using calcite, silica, and alumina as raw materials. The coatings consist of anorthite and amorphous phase, and the compressive stresses introduced by the coating were changed with the change of anorthite amount in the coating. The maximum compressive stress was obtained when with the coating formula of 20% alumina content, at which the coating shows the lowest CTE of 4.34×10^{-6} K^{-1}. As a result, the matrix with a 20% alumina coating on all six sides exhibited the highest bending strength of 144 MPa (Fig. 1). The thickness of the coating is 50 μm, which was obtained in a Single brushing process. The residual stress was analyzed according to Kingery's calculation model [6]. The results show that the compressive stress between the matrix and coating is related to Young's modulus, CTE, and the thickness of both coating and matrix.

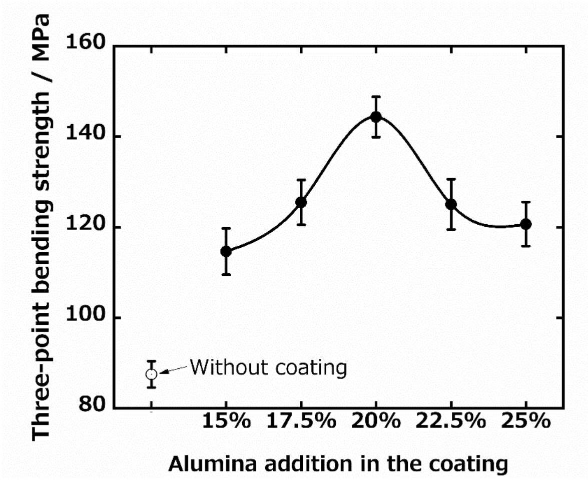

Fig. 1. The flexural strength of the specimens with different alumina additions in the coating

3.2 Optimization of the glaze layer to obtain a high flexural strength

STD is the commonly used formula for making Arita-ware in the Hizen area (Saga and Nagasaki Prefecture). In our research, 30% alumina or 45% zirconia was added to strengthen the Arita ware. As shown in Fig. 2, both alumina and zirconia-reinforced porcelain matrices exhibited an improved bending strength compared to the STD, due to the presence of internal prestress generated between the glass phase and alumina or zirconia particles. At the same, the CTE of the ceramic matrix also changed obviously due to the addition of alumina and zirconia particles (Fig.3).

After coating with the limestone transparent glaze, an increase in bending strength was observed in porcelain STD, ASP, and YSZSP. The bending strength increased from 95, 173.6, and 203 MPa to 112.2, 217.5, and 270.3 MPa, respectively. In contrast, the bending strength of ZSP decreased from 185 to 95.1 MPa. The bending strength of glazed porcelain is closely related to the CTE of the matrix and the glaze layer. When the CTE of the glaze layer is lower than that of the porcelain matrix, compressive prestress is formed at the interface. This prestress enhances the bending strength of the porcelain, as shown in 3.1. Therefore, the improved bending strength of glazed STD, ASP, and YSZSP is due to their CTE being greater than that of the glaze layer (Fig.3). However, for ZSP, the CTE is lower than that of the glaze layer, resulting in a decrease in strength after glazing and the formation of cracks on the surface of the glaze layer. The variation in the density of the glaze slurry was aimed at achieving different glaze layer thicknesses, which in turn influenced the bending strength. In this study, the thickness of the glaze layer was kept below 100 microns. In conclusion, the bending strength of glazed YSZSP is 1.4 times higher than that of STD. Therefore, if the entire ceramic matrix is glazed, ceramics with a strength exceeding 300 MPa could potentially be achieved.

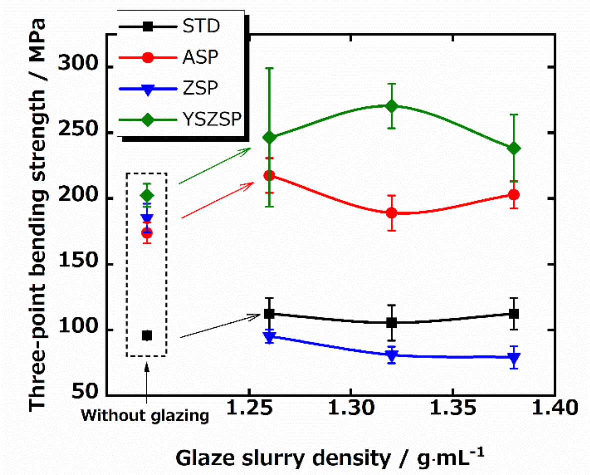

Fig.2. Three-point bending strength of porcelain matrix with one-sided glaze fired at～1290℃ as a function of glaze slurry density

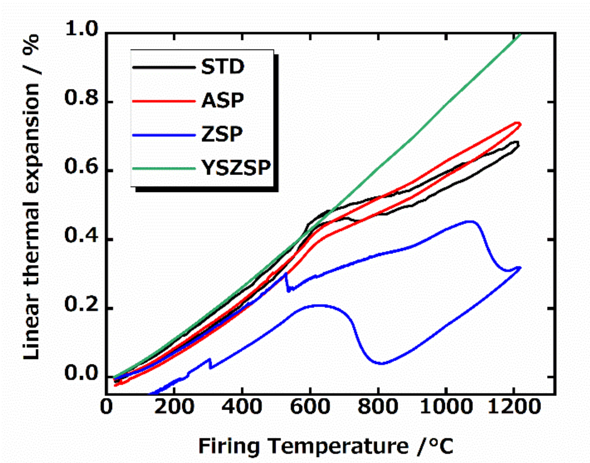

Fig.3. Linear thermal expansion and shrinkage of porcelain matrix fired at～1290℃

4. Conclusions

The bending strength of porcelains can be improved by adjusting the CTE mismatch between the ceramic matrix and the glaze layer. This can be achieved by modifying the chemical composition of either the ceramic matrix or the glaze. In the first part of this study, the compressive stress in the glaze layer was tailored by adjusting the content of anorthite and amorphous phases. As a result, the flexural strength of ceramics with six glazed surfaces increased by 64.7% compared to unglazed samples. In the second part, the same glaze coating applied to different ceramic substrates resulted in significant differences in flexural strength, primarily due to variations in the CTE. Among the tested materials, the 45% zirconia porcelain, with the highest thermal expansion coefficient, exhibited the maximum bending strength. When glazed on only one surface, its flexural strength increased by 33.6% compared to the unglazed sample, reaching 270.3 MPa, significantly higher than that of traditional Arita ware. This study provides valuable insights for the design and development of high-strength ceramic products and opens new possibilities for expanding the applications of Arita ware in broader fields.

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