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研究課題名（和文）Material design to realize fine geometries porcelain with large, thin, and precise shape

研究課題名（英文）Material design to realize fine geometries porcelain with large, thin, and precise shape

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交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：In this study, we revealed the mechanism for suppressing pyroplastic deformation and liquid phase sintering shrinkage of alumina-strengthened porcelain. Both pyroplastic deformation and liquid phase sintering shrinkage could be controlled by adjusting the liquid viscosity at high temperatures.

研究成果の学術的意義や社会的意義
With our control strategies, high-precision porcelain with large, thin, and the precise shapes. can be developed. This is particularly significant for enhancing the value of Hizen ceramics and for developing new high-value-added ceramics through additive manufacturing.

研究成果の概要（英文）：In this study, we revealed the mechanism for suppressing pyroplastic deformation and liquid phase sintering shrinkage of alumina-strengthened porcelain. By adjusting the liquid viscosity at high temperatures, both pyroplastic deformation and liquid phase sintering shrinkage could be controlled using IA and IIA oxides or high-temperature crystal precursors. Based on these strategies, porcelain with both small pyroplastic deformation and low water absorption, or porcelain with near-zero sintering shrinkage, can be successfully fabricated. This allows for the creation of fine geometry porcelain with large, thin, and precise shapes. Additionally, to address the low strength and reliability of porcelain, we have improved its strength and toughness by controlling the macro- and micro-prestress introduced by the coating/glaze layer and the strengthening particles, respectively.

研究分野：セラミックス

キーワード：Strengthening porcelain　Pyroplastic deformation　Near zero shrinkage　Water absorption　Densification　Mullite　Anorthite　Arita-yaki

１．研究開始当初の背景

Porcelains are complex composite materials composed of a glass matrix, pores, quartz, mullite, and added alumina for strengthening. They are produced by firing a mixture of clay, feldspar, and quartz at high temperatures. Highly densified porcelain typically has a water absorption (WA) value of less than 0.5 mass%. This low WA, indicative of densification, is achieved through the formation of a liquid phase during the high-temperature firing of the green body.However, pyroplastic deformation (PD), caused by sintering shrinkage (SS) and/or the viscous flow of the liquid phase, is prone to occur at high temperatures【Mater. Construc., 65, e065(2015); J. Eur. Ceram. Soc., 39, 601-609(2019)】. SS occurs due to volume reduction when part of the raw materials transform into a liquid phase at high firing temperatures, which contributes to or increases PD. Essentially, SS always accompanies PD. Increasing the amount of liquid phase decreases the WA but accelerates PD due to increased SS. Conversely, decreasing the liquid phase increases WA but reduces PD. Therefore, there is always a trade-off between densification (low WA) and pyroplastic deformation (PD). Achieving high densification with low PD is a significant challenge.

The SS value changes with elevated temperatures until it reaches a maximum, about 10% for most porcelains. SS is crucial for controlling the final product size, which is closely related to WA and the technical characteristics of the products【J. Mater. Process., 209, 1240-1246(2009)】. However, controlling the SS rate in porcelains with large and precise shapes is difficult, as these are often fired in massive kilns with significant temperature variations. This leads to nonhomogeneous SS and inevitable PD. Overfiring can also cause bloating, resulting in further PD. Consequently, excessive PD can compromise the function or aesthetic properties of porcelain products, limiting the ability to produce finely shaped porcelains.

Previous studies have reported porcelains without SS, but these were porous ceramics lacking densification. Porcelains with both low WA and low PD across a wide firing temperature range have also been reported, but they still exhibited PD due to SS. Therefore, this research aims to design and develop porcelains with high densification and low PD from a materials design perspective, enabling the successful fabrication of finely shaped porcelains.

２．研究の目的

The main target of this research is to design and develop a novel porcelain with high densification and low PD to expand the application of Hizen wares.

Furthermore, the strength of the developed porcelain will be evaluated and optimized to achieve improved strength by controlling the addition amounts of raw materials. Finally, the feasibility of fabricating fine geometry porcelains with large, thin, and precise shapes will be explored.Recently, there have been new porcelain products and techniques developed in the Hizen area. However, most production relies on the experience of porcelain makers, and academic research remains limited, leading to inevitable production losses. Although non-shrinkage ceramic was developed in 2017, but it is not a true porcelain, and the mechanism for suppressing sintering shrinkage (SS) is not clear. We has developed densified porcelain with small WA and small PD over a wide firing temperature range, and we have clarified the mechanism for suppressing PD resulting from bloating. However, PD resulting from SS still exists and needs to be addressed. Therefore, this research aims to extend the understanding of the relationship among densification, SS, and PD, and to provide an integrated strategy for designing and developing fine geometry porcelains.

３．研究の方法

This research developed a novel porcelain that consider following three aspects: ① One dimensional raw materials (e.g **Acicular wollastonite** and Al_2O_3 fiber) for suppressing the SS; ② High-temperature crystal precursor (e.g **Gairome clay** and talc or limestone): for suppressing the bloating and controlling the viscosity of liquid phase at high temperature; ③ Effective fluxing agent (e.g Petalite, spodumene, and wollastonite) for generating the liquid phase. The PD index (PI) is calculated by equation (1) , where s is the maximum deformation (mm), b is the thickness of the specimen (mm), and l the distance between two supports (mm).We reveal the mechanism of suppression of firing deformation and liquid phase firing shrinkage by comparing PD, WA and SS, in combination with other XRD, SEM and precise phase compositions, offering the possibility of developing high-precision ceramics.

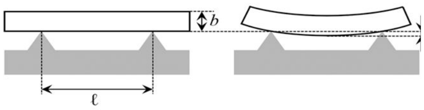

Fig.1 Schematic of PD test

$$PI = \frac{sb^2}{\ell^4} \qquad (1)$$

４．研究成果

4.1 Minimizing the water absorption and pyroplastic deformation of alumina-strengthened porcelain with wollastonite addition

We have identified the key strategies to realize both small water absorption (WA) and small PD in a wide firing temperature (MFT) range by optimizing the addition of talc (Mg^{2+}) and petalite (Li^{+}), but there is a possibility to decrease the thermal expansion/ shrinkage of ASP. To maintain or improve the thermal expansion/shrinkage, it is important to develop the Ca^{2+}-doping porcelain because there is no possibility to form any crystals with low thermal expansion/shrinkage. In this study, the densification and PD of ASPs were examined within a range of alumina and wollastonite contents. Both the alumina addition and anorthite crystallization not only prevent the liquid-phase sintering, which plays an important role in the densification of the porcelain during firing, but also the suppression of PD at high MFTs. The prevention of densification as well as the suppression of PD is basically described by the change in the amount of liquid phase at firing. As a result, the optimization between WA (<0.5%) and PI ($<1.5\times10^{-6}$ mm^{-1}) was found out in the relatively wide MFT range for porcelain with the addition of 30 mass% alumina and the addition of <10 mass% wollastonite. Consequently, WA and PD can be minimized in ASPs fired between 1290 and 1380 °C.

4.2 Near-zero sintering shrinkage (NZS) in pottery with wollastonite addition

In this study, NZS, with less than 2.0% sintering shrinkage (SS) and small pyroplastic deformation (Pyroplastic deformation index < $1.5\times10^{-6}\cdot mm^{-1}$), was developed by quantitative examination of the alumina and wollastonite addition. The anorthite was progressively crystallised above 1100 °C and remained stable after crystallisation, thereby suppressing sintering shrinkage. This was confirmed by the In-situ high-temperature X-ray diffraction, and the SEM image (Fig. 6)

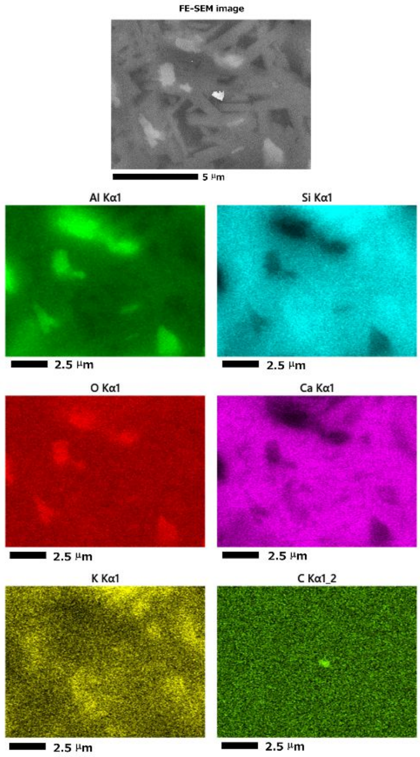

Fig. 6. FE-SEM image and EDX mapping of W20A30G20. In the SEM image, anorthite and alumina crystals are observed as grey rods and bright white particles, respectively, and the amorphous phases are shown as a dark area. Each crystal is assigned based on the EDX mapping. The brightest particle at the centre of the image was assigned to be diamond particles used for polishing the pottery.

In summary, we have revealed the mechanism for suppressing pyroplastic deformation and liquid phase sintering shrinkage of alumina-strengthened porcelain. By adjusting the liquid viscosity at high temperatures, both pyroplastic deformation and liquid phase sintering shrinkage could be controlled using IA and IIA oxides or high-temperature crystal precursors. The progress of porcelain research allows for the creation of fine geometry porcelain with large, thin, and precise shapes. With our control strategies, high-precision porcelain with large, thin, and the precise shapes can be developed. This is particularly significant for enhancing the value of Hizen ceramics and for developing new high-value-added ceramics through additive manufacturing.

５．主な発表論文等

〔雑誌論文〕　計4件（うち査読付論文　4件／うち国際共著　2件／うちオープンアクセス　1件）

１．著者名 Dong Hao, Takashi Akatsu, Nobuaki Kamochi, Miki Inada, Atsunori Shiraishi	４．巻 43(2)
２．論文標題 Near-zero sintering shrinkage in pottery with wollastonite addition	５．発行年 2023年
３．雑誌名 Journal of the European Ceramic Society	６．最初と最後の頁 700-707
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jeurceramsoc.2022.10.037	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Hao Dong、Akatsu Takashi、Kamochi Nobuaki、Shiwa Yuzo	４．巻 9
２．論文標題 Minimization of water absorption and pyroplastic deformation of wollastonite-containing alumina-strengthened porcelain	５．発行年 2021年
３．雑誌名 Journal of Asian Ceramic Societies	６．最初と最後の頁 1481～1488
掲載論文のDOI（デジタルオブジェクト識別子） 10.1080/21870764.2021.1996865	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Xu Wei、Li Kai、Li Yueming、Sun Yi、Bao Yiwang、Wan Detian、Tan Xiang、Hao Dong	４．巻 19
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1111/ijac.14003	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Zhang Xiaona、Li Yueming、Sun Yi、Hao Dong、Li Kai、Wan Detian、Bao Yiwang	４．巻 -
２．論文標題 Improving the flexural strength of porcelain by residual stress in anorthite coating	５．発行年 2022年
３．雑誌名 International Journal of Applied Ceramic Technology	６．最初と最後の頁 -
掲載論文のDOI（デジタルオブジェクト識別子） 10.1111/ijac.14076	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計6件（うち招待講演　2件／うち国際学会　2件）

1．発表者名 Dong HAO,　Takashi AKATSU, Nobuaki KAMOCHI
2．発表標題 Near-zero sintering shrinkage in porous porcelain with wollastonite addition
3．学会等名 Spring Meeting of the Japan Society of Powder and Powder Metallurgy, 2022（招待講演）
4．発表年 2022年～2023年

1．発表者名 Dong Hao, Takashi Akatsu, Nobuaki Kamochi, Miki Inada, Atsunori Shiraishi
2．発表標題 Suppression of the sintering shrinkage of porcelain with wollastonite addition
3．学会等名 The 35th Fall Meeting of the Ceramic Society of Japan
4．発表年 2022年～2023年

1．発表者名 Dong Hao, Takashi Akatsu, Nobuaki Kamochi
2．発表標題 Materials design to Minimize the water absorption and pyroplastic deformation of alumina-strengthened porcelain
3．学会等名 47th International Conference and Expo on Advanced Ceramics and Composites (ICACC2023)（国際学会）
4．発表年 2022年～2023年

1．発表者名 Dong Hao, Takashi Akatsu, Nobuaki Kamochi,Asami Ohtake, Atsunori Shiraishi
2．発表標題 Realizing both small water absorption and small pyroplastic deformation in alumina-strengthened porcelain through Materials design
3．学会等名 International Cermaic Federation, The Korean Ceramic Society（招待講演）（国際学会）
4．発表年 2021年～2022年

1．発表者名 Dong Hao, Takashi Akatsu, Nobuaki Kamochi
2．発表標題 The 12th International Conference on the Science and Technology for Advanced Ceramics
3．学会等名 Institute of Innovative Research, Tokyo University of Technology; The Ceramic Society of Japan
4．発表年 2021年～2022年

1．発表者名 Dong Hao, Takashi Akatsu, Nobuaki Kamochi
2．発表標題 Minimization of water absorption and pyroplastic deformation of wollastonite-containing alumina-strengthened porcelain
3．学会等名 The Ceramic Society of Japan
4．発表年 2021年～2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関