SAKARYA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ

Sakarya University Journal of Science
SAUJS

ISSN 1301-4048 e-ISSN 2147-835X Period Bimonthly Founded 1997 Publisher Sakarya University
http://www.saujs.sakarya.edu.tr/

Title: Development of Cordierite Based Carrier Refractory Sagar Bodies for Bone Porcelain Firing Process

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Recieved: 2023-03-06 00:00:00

Accepted: 2023-05-03 00:00:00

Article Type: Research Article

Volume: 27
Issue: 4
Month: August
Year: 2023
Pages: 844-857

How to cite
Murat ISPALARLI, Zuhal KARAAĞAÇ; (2023), Development of Cordierite Based Carrier Refractory Sagar Bodies for Bone Porcelain Firing Process. Sakarya University Journal of Science, 27(4), 844-857, DOI: 10.16984/saufenbilder.1260673
Access link
https://dergipark.org.tr/en/pub/saufenbilder/issue/79486/1260673

Sakarya University Journal of Science 27(4), 844-857, 2023

Development of Cordierite Based Carrier Refractory Sagar Bodies for Bone Porcelain Firing Process

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Abstract

During the firing process of porcelain tableware; Biscuit firing takes place at low temperatures (980-1000°C), while glazed firing takes place at high temperatures (1250-1280°C for soft porcelain, 1350-1380°C for hard porcelain). Biscuit firing in bone porcelain products, which is in the soft porcelain class, is done at higher temperatures than glazed firings. Due to the presence of bone ash in the Bone China recipe formulation, it causes the bodies to undergo vitrification in a narrow range and thus the final product to deform during sintering. Bone porcelain products are fired on carrier refractories called sagar so that they do not deform during sintering. Sagars are designed to support that model for each product model and do not shrink or deform during firing thanks to its low thermal expansion coefficient. In this study, a refractory body with a porous structure with the code of "PS1-Std" was developed by performing the characterization analyzes of refractory products with different technical properties supplied from different companies. In order to improve the mechanical properties by changing the ratios of talc, alumina, quartz and zircon in the recipe composition; A refractory product containing 8.47% zircon in its recipe composition and containing indialite, corundum, mullite, quartz and zircon phases after sintering has been developed. The microstructure images of the developed refractory product were examined with the support of SEM analysis. It has been observed that refractory products obtained as a result of recipe development studies offer a 10% longer service life than equivalent refractory products.

Keywords: Biscuit, bone porcelain, cordierite, sagar, vitrification

1. INTRODUCTION

As a ceramic material, bone porcelain (Bone China) emerges as an extremely superior product in terms of its technical and aesthetic properties. In terms of aesthetic properties, they constitute the most attractive and expensive tableware in the world, mainly in terms of translucency, whiteness, glossy glazed surface and high mechanical properties (high strength). According to the definition of the American Society for Testing and Material (ASTM), bone china is a soft porcelain with high translucency, containing 25% bone ash. Bone ash is used as an ingredient in the bone china body, and this addition gives this product its unique properties. The traditional composition of the bone china body includes

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50% bone ash, 25% plastic clay (as plasticizer) and 25% cornish stone. The microstructures of bone porcelain are known as β-tricalcium phosphate (β-$Ca_3(PO_4)_2$) (β-TCP), anorthite ($CaAl_2SiO_8$), α-quartz (SiO_2) and calcium aluminosilicate glass. According to the BS EN 8654:2015 standard, it is defined as follows; Products that consist of a ceramic body containing at least 35% bone ash and defined as tricalcium phosphate are called bone china (Bone China) [1, 2].

The cornice stone mentioned in the bone porcelain body composition is basically a type of pegmatite. Mineralogically, it contains feldspar, quartz and mica and is used as a flux in the body. For this reason, feldspathic raw materials are preferred instead of this raw material. In general, potassium and sodium feldspars are used as a flux in porcelain. Anorthite is another mineral for white fired porcelain bodies [3, 4-7].

In bodies containing calcite, the anorthite phase is interesting because of the low temperature required for its formation and the properties it imparts to the final product. Anorthite; although lower temperatures are also mentioned in the literature, it generally begins to form as a result of the reaction of kaolin and wollastonite at temperatures of 1100°C and above. Two different crystallization structures are encountered in the formation of anorthite. If the primary crystallization structure of anorthite is encountered, anorthite also creates a high rate of vitrified phase and excessive shrinkage occurs. The use of anorthite is not appropriate, since a high rate of vitrified phase will occur in bodies with porous structure [8].

In Köseçavuş's thesis titled "Anorthite synthesis and characterization from volcanic tuff", anorthite was produced by powder metallurgy method using volcanic tuff and different proportions (2%, 4%, 6%) boron (boric acid). The samples obtained were sintered at different temperatures and it was observed that there was a stable change in temperature with the increase of boron ratio at 1100°C. Deformation was observed at 1200°C and 1300°C [9].

Bone porcelain production has always been a very difficult process; It requires strict control over a number of process parameters such as particle size distribution, temperature of the dryer, density of the mixture and biscuit baking temperature. One of the most important problems of bone porcelain production is the narrow firing range. Open pores that can be found in the structure are the most obvious parameters that restrict full permeability.

Permanent holes and damages may occur in the body due to its bad shape in firing applied below the optimum firing temperature. This is because bone ash contains carbonate, which acts as a powerful melter that can make the body quite malleable. When the pore relationship between a standard bone china and hard porcelain is examined; Parallel to the temperature increase, vitrification for hard porcelain takes place around 1200°C, which is well below the maximum firing temperature. In addition, bone porcelain has an apparent porosity of around 20% at this temperature. It is expected that the sintering of bone porcelain and the sintering of this product will be handled in two different stages.

Accordingly, in accordance with the remarkable changes in porosity and reduction in surface area, the existence of solid state sintering in the range of 700-800°C is mentioned, while the existence of liquid phase sintering, which is explained by the shrinkage and open pores that move away in parallel with the increase in bulk density, in the range of 1000-1150°C is mentioned. It is formed by the transformation of meta kaolin in clays into acicular-shaped mullite crystals and silica glass in the range of 950-1000ºC. As feldspars start to melt between 1010-1100ºC, the first interactions take place between the materials that make up the groups. Potassium feldspar melts at 1150ºC, sodium feldspar at 1050ºC. Potassium feldspar appears in the liquid phase below 1000 ºC in contact with the silicate and

if there is the effect of water vapor. The melting effects of feldspars with kaolin above 1050ºC cause the formation of a glassy phase and the formation of feldspar examination acicular (primary) mullite and row (secondary) mullite at the edges of the kaolin. Shrinkage occurs as a result of sintering of liquid phase components [1, 10, 11].

The first firing, called "Biscuit Firing", unlike the conventional porcelain production of bone china, is in the oxidizing atmosphere in the biscuit oven; Depending on the particle size distribution and final composition of the prepared bodies, they are fired at a temperature of approximately 1200-1300°C for an average of 15 hours. At this stage, a shrinkage of about 20% in the raw products tends to cause deformation and cracking. The product shrinks during firing and is very sensitive to overfiring. In order to prevent deformation during sintering, bone porcelain products are fired on a carrier refractory called sagar, which has a low thermal expansion coefficient and therefore does not cause shrinkage or deformation problems during firing. If the temperature rises slightly above the ripening point, it will cause the product to form bubbles and voids that cause a spongy body [12].

Playing a major role in the firing stage in the porcelain industry, refractories are defined as materials that are resistant to high temperatures and resistant to the effects of solid, liquid and gaseous substances at these temperatures. Of refractories; There are varieties based on magnesite or chrome magnesite, spinel, zircon, alumina and silica. Cordierite ceramics; It is used in the production of industrial ceramics due to its low coefficient of thermal expansion and excellent thermal shock resistance, high thermal and chemical stability. The stoichiometric formula of cordierite is $2MgO.2Al_2O_3.5SiO_2$ and its chemical composition is 13.7%MgO, 34.9% Al_2O_3 and 51.4% SiO_2. In a cordierite mixture consisting of clay, talc and alumina, at temperatures higher than 1250°C, clay and talc transform into mullite and protoenstatite ($MgO.SiO_2$). Then, cordierite phase is formed between 1250-1430°C from the alumina composition of mullite and protoenstatite. In the formation of cordierite phase, SiO_2 in the structure is released from both mullite and protoenstatite. However, while Al_2O_3 and MgO are only released from mullite and protoenstatite, here mullite plays the main role in the formation of cordierite. Because Al_2O_3 is the main component in cordierite formation compared to MgO. The coefficient of thermal expansion is more sensitive to MgO change than other ingredients [13, 14].

One of the negative features of cordierite ceramic is that it has low toughness properties. Different studies have been carried out by adding ZrO_2 to the formulation in order to improve its low toughness properties. It is a widely known phenomenon that the strength and toughness of ceramic materials increase with the transformation of zirconia from tetragonal to monoclinic. Although the toughening of zirconia has been applied to many ceramics, the most studied system is zirconia toughened alumina [15].

In this study, the development of an alternative formulation to carrier saggars for the imported bone porcelain process in bone porcelain production and the characterization analyses of the developed body were investigated by supporting it with (XRF, XRD, XRD, SEM, EDX).

2. MATERIALS AND METHOD

2.1. Analysis of Equivalent Products

Physical tests of equivalent products called cordierite, mullite-cordierite and sagar in the market were carried out in the Porland Porcelain R&D Center Laboratory. CIEL*a*b* color measurements of the products were made with the "Konica - CMA145" brand device and the results are given in Table 1.

Table 1 Color chromatic coordination measurements of alternative commercial products (CP)

Firm	*Product*	*L**	*a**	*b**
CP1	Sagar	93.94	-0.41	4.33
CP2	Cordierite	95.98	-0.31	3.86
CP3	Cordierite	83.07	3.03	18.36
CP4	Mullite Cordierite	93.44	-1.14	3.82

Table 2 Alternative commercial products; Water absorption, apparent porosity, apparent relative density, bulk mass measurements

Analysis	*CP1*	*CP2*	*CP3*	*CP4*
Water Absorption (%)	16.53	14.36	10.82	11.23
Apparent porosity (%)	30.34	28.16	22.05	26.73
Apperent Relative Density (gr/cm^3)	02.63	02.73	02.61	03.25
Bulk Mass (gr/cm^3)	01.84	01.96	02.04	02.38

Table 3 Chemical analysis of commercial products

Oxide %	*CP1*	*CP2*	*CP3*	*CP4*
SiO_2	48.56	44.27	50.03	16.82
Al_2O_3	41.24	51.52	40.41	81.45
Fe_2O_3	01.12	00.45	01.19	00.43
TiO_2	00.24	00.49	00.54	00.25
CaO	00.18	00.15	00.24	00.11
MgO	07.28	02.49	06.73	00.10
Na_2O	00.00	00,00	00.00	00.29
K_2O	01.00	00.63	00.86	00.30
K.K.	00.38	00.00	00.00	00.25

Water absorption measurements and bulk densities of the products under vacuum were measured with the "Ceramic" device. Device - VSVD/60" brand device and results are given in Table 2. Characterization analysis of equivalent products were also made by the Ceramics Research Center (SAM). chemical compositions (XRF) are given in Table 3 and phase analysis results (XRD) are given in Table 4.

Table 4 Phase analysis of selected commercial products

(%)	*CP1*	*CP2*	*CP3*	*CP4*
İndialite	54.47 ±0	26.13 ±0	55.17 ±0	-
Corundum	-	8.26 ±0.4	-	-
Mullite	26.77 ±0.9	40.18 ±0.9	24.78 ±0.9	67.23 ±0.9
Amorf	18.76 ±1.6	20.39 ±1.6	15.61 ±1.9	32.77 ±1.9
Cristobalite	-	0.05 ±0.2	4.45 ±0.2	-

2.2. Experimental Studies

According to the results of the literature review and the analysis of equivalent products, considering the availability and costs of raw materials; The raw materials to be used in the study were determined by evaluating their chemical properties, physical properties, availability and cost.

In the study, the raw materials used to create the refractory body recipe and the raw materials whose chemical analyses were determined according to Table 5 were mixed in the ratios determined according to Table 6. “PS1-Std.” PS2, PS3, PS4, PS5, PS6, PS7 and PS8 trial recipes were prepared in order to increase the thermal-mechanical activity of this standard recipe.

Table 5 Chemical analysis of raw materials (XRF) used in recipe preparation

%	Kaolin1	Kaolin2	Clay	Calcined Alumina	Talc	Zircon	Quartz	K-Feldspar
SiO_2	45.13	44.72	53.14	00.56	64.41	31.96	99.13	67.46
Al_2O_3	38.85	39.34	29.68	98.24	00.69	09.47	00.41	17.73
Fe_2O_3	00.78	00.49	02.40	00.02	00.34	00.15	00.03	00.09
TiO_2	00.09	00.08	01.33	00.03	00.08	00.35	00.04	00.03
CaO	00.12	00.09	00.66	00.06	01.26	01.45	00.02	00.10
MgO	00.60	00.38	00.67	00.26	24.84	07.99	00.00	00.00
Na_2O	00.56	00.55	00.53	00.68	00.49	04.52	00.04	02.72
K_2O	01.79	00.66	02.16	00.04	00.23	01.58	00.06	11.32
ZrO_2	00.00	00.00	00.00	00.00	00.00	41.85	00.00	00.00
K.K.	12.08	12.69	09.43	00.10	07.66	00.68	00.27	00.55

Table 6 The percentage (%) components of the raw materials that make up the cordierite-based bodies recipes

Raw Material (%)	PS1-Std.	PS2	PS3	PS4	PS5	PS6	PS7	PS8
Clay	07.92	09.75	09.66	09.30	08.88	08.85	08.47	08.47
Kaolin 1	19.80	23.90	23.67	22.79	21.77	21.68	20.76	20.76
Calcined Alumina	25.74	25.36	25.12	24.18	23.11	23.00	22.03	22.03
Kaolin 2	09.90	09.75	16.42	15.81	15.11	15.04	14.40	14.40
Talc	20.79	20.48	20.28	23.25	22.25	22.15	25.42	21.18
Quartz	10.89	10.73	04.85	04.65	04.44	04.42	04.23	04.23
K-Feldspar	04.96	00.00	00.00	00.00	00.00	00.00	00.00	00.00
Zircon	00.00	00.00	00.00	00.00	04.44	04.44	04.23	08.47
Bentonite	00.00	00.00	00.00	00.00	00.00	00.42	00.42	00.42

Raw materials were weighed according to the ratios determined in the recipe in Table 6 and loaded into the ball mill. In order to increase the thixotropy property of the mud, 0.42% bentonite was added to the recipe and the mud rheology was brought to the desired values. Standard production steps are as follows; By adding water to the raw material mixture, the liter weight of which will be adjusted in the range of 1350-1420 gr/lt in the mill and the desired TDA; D (90): ground to 15-20 μm range. After obtaining the particle size distribution approval according to Table 7 for the sludge suspension, it is filtered through a 100 DIN sieve and turned into KEK with a Filter Press. Then, the sludge (KEK) coming out of the Filter Press is opened with a mixer and filtered through a 60 DIN sieve with the help of electrolyte by adjusting its liter weight in the range of 1730-1800 gr/lt. The reason why sludge is grinded in a low liter mill first is to turn it into a KEK after the Filter Press and open it again, making the mud more plastic and increasing the shaping performance in the pressure casting method in mass production. However, since the trial stages of the study were carried out in the laboratory, the sludge was not made into cake with a filter press. However, in order to increase the plasticity of the mud and to analyze its rheological properties, the mud that was ground in the mill and reached the desired particle size distribution range was turned into sausage with the help of plaster molds. After turning the mud into sausage, it was opened again in the mixer. In order to determine the rheological values of the recipe suspensions, casting mud 1710-1720 gr/lt liter weigh was prepared.

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The firing of the prepared carrier refractory bodies was carried out in FORNO CERAMICA brand furnaces in the R&D Center laboratory of Porland Porcelain. Furnace regimes PS1-Std. determined on the basis of the coded prescription. The initial firing temperature for the sintering of the developed carrier refractory bodies was carried out for 18-20 hours at the same temperature (980°C-1000°C) with the biscuit firing applied in standard porcelain production. If the firing range of cordierite is too narrow and the sintering range is exceeded, the formation of a high amount of liquid phase makes it difficult to bake these products. For the sintering of the recipes prepared within the scope of the study for the second firing; The oven regime with a peak temperature of 1300°C and a peak residence time of 60 minutes was chosen.

Table 7 Grain sizes after grinding of prescription suspensions

Grain size (μm)	*D(10)*	*D(50)*	*D(90)*
PS1-Std.	0.891	6.207	17.628
PS2	0.568	6.103	17.021
PS3	0.680	6.190	17.498
PS4	0.498	5.921	16.213
PS5	1.037	5.879	16.186
PS6	0.464	5.715	15.247
PS7	1.622	5.962	17.863
PS8	0.166	5.671	18.702

In order to determine the physical properties of the prepared bodies, Porland Porselen A.Ş. In the R&D Center laboratory; The drying and firing shrinkage of the samples were measured from the shrinkage rods after sintering and calculations were made according to the formulas in ASTM C-236 standard.

$$Sd = \frac{Lp-Ld}{Lp} x\ 100 \quad (1)$$

It's here; Sd represents the dry shrinkage percentage (%), Lp represents the length of the wet test product (mm), and Ld represents the length of the test specimen after drying (mm).

$$St = \frac{Lp-Lf}{Lp} x\ 100 \quad (2)$$

It's here; St firing shrinkage percentage (%) and Lf firing test sample length (mm). Strength measurements of sintered samples were calculated by three-point bending test. Rectangular bending strength formula in ASTM C 974 standard was used to calculate the strength values [16].

$$M = \frac{3PL}{2bd^2} \quad (3)$$

It's here; M represents the bending strength (MPa), P is the applied load (N), L is the

distance between supports (mm), b is the sample width (mm), and d is the sample thickness (m). Deformation is the bending of the bar during sintering depending on temperature and time. After sintering, deformation bars are placed on millimetric paper and the amount of deformation is calculated. Water absorption test was performed according to BS EN 1217 standard method A and calculations were made. Here; The m^2 shows the weight of the sample after the water absorption test (gr) and the m1 shows the weight of the sample before the water absorption test [2, 17, 18].

$$Water\ Abs.(\%) = \left(\frac{(m_2 - m_1)}{m_1}\right) * 100 \qquad (4)$$

"PS1-Std. and PS8" coded samples; XRF (Rigaku brand, ZSX Primus Model X-Ray Fluorescent device with semi-quantitative chemical analysis) and XRD (Minifleks-600 model, Rigaku brand, X-Ray Diffraction device (2Θ=5°-70°)) analysis were performed. Electron microscope (SEM) analysis was performed on samples coded as "PS1-Std. and PS8" by the Ceramics Research Center (SAM). For analysis, the surface of the samples was coated with gold (Au) and palladium (Pd), ensuring conductivity, and BSE images were taken and analyzed with elemental distribution (EDX).

3. FINDINGS AND DISCUSSION

Within the scope of the study, a total of 8 carrier refractory bodies recipes with the codes PS1-Std., PS2, PS3, PS4, PS5, PS6, PS7 and PS8 were prepared. The data on the rheological results of the suspensions are given in Table 8. The plasticity water, kneading water, water absorption percentages under vacuum and mechanical properties of dry, biscuit (after the 1st firing) and firing (after the second firing) of the prepared bodies are given in Table 9. Refractory bodies; The thermal expansion coefficients were measured at α300x10^{-7} °C, α400x10^{-7} °C and α500x10-7 °C values after sintering in the furnace regime with a peak temperature of 1300 °C and a peak residence time of 60 minutes and are given in Table 10.

Table 8 Rheological values and molding processes of prescription suspensions

Values	*PS1-Std.*	*PS2*	*PS3*	*PS4*	*PS5*	*PS6*	*PS7*	*PS8*
Electrolyte amount (%)	0.1	0.1	0.12	0.12	0.12	0.15	0.15	0.15
Liter weight (gr/lt)	1720	1729	1710	1711	1711	1721	1724	1718
Viscosity (sn)	18	17	18	19	19	24	26	26
Thixotropy (sn)	1	1	1	1	1	2	2	2
5 min. flesh thickness (mm)	1.5	1.91	1.93	1.97	1.83	2.09	2.17	2.14

Table 9 Mechanical properties of the developed support refractory bodies

Test Methods	*PS1-*	*PS2*	*PS3*	*PS4*	*PS5*	*PS6*	*PS7*	*PS8*
Dry shrinkage (%)	3.1	1.95	2.1	2.5	2.65	2.13	2.4	2.31
Biscuit shrinkage (%)	3.78	2.92	3.2	3.27	3.13	3.64	3.42	3.65
Firing Shrinkage (%)	7.8	3.4	5.6	4.5	6.53	6.7	7.25	6.05
Dry Strength (kg/cm^2)	11.2	12.6	12.5	13.4	12.1	14.75	14.85	15.74
Biscuit Strength (kg/cm^2)	35.7	43.8	47.36	50.7	55.7	66.2	65.87	68.89
Firing Strength (kg/cm^2)	205	227	245	265	365	395	370	415
Deformation (mm)	4	1	1	2	2.5	2	3	2
Plasticity water (%)	25	26	28	27	29	38	37	38
Kneading water (%)	28	30	31	29	32	40	39	39
Water Absorption Vacuum	13	20	18	12	14	15	13	17

Table 10 Thermal expansion coefficients of refractory body samples

Samples	*α 300x10^{-7} (°C)*	*α 400x10^{-7} (°C)*	*α 500x10^{-7} (°C)*
PS1-Std.	34.2	37.6	37.7
PS2	30.5	31.2	33.6
PS3	27.5	28.2	29.3
PS4	27.8	29.2	30.2
PS5	27.5	28.2	29.2
PS6	26.6	27.3	28.2
PS7	26.4	27.3	28.0
PS8	26.7	27.7	28.8

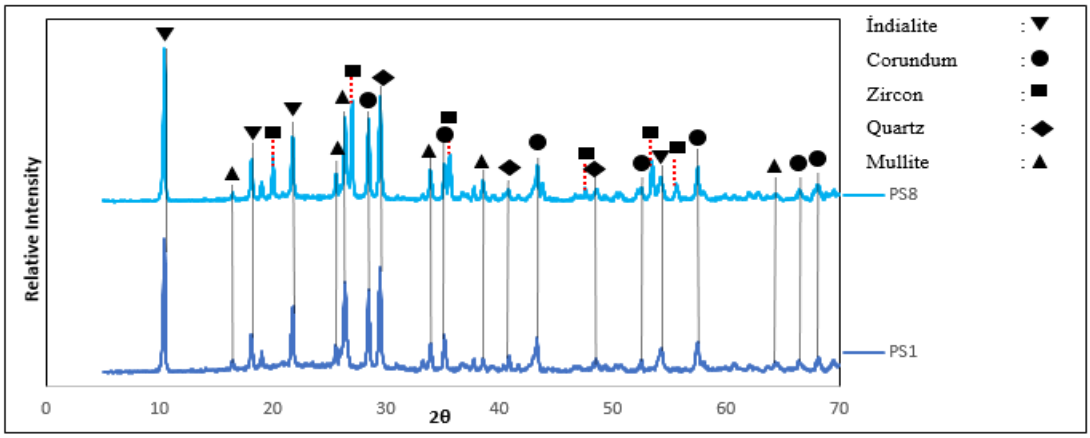
In a cordierite mixture consisting of clay, talc and alumina, at temperatures higher than 1250 °C, clay and talc transform into mullite and protoenstatite (MgO.SiO2). Later, cordierite phase is formed between 1250-1430°C from the combination of mullite and protoenstatite with alumina. In the formation of cordierite phase, both mullite and protoenstatite are exposed as SiO2 in the structure. However, alumina and MgO are only released from mullite and protoenstatite, where mullite plays the main role in cordierite formation. Because Al2O3 is the main component in cordierite formation compared to MgO. The coefficient of thermal expansion is more sensitive to MgO change than other ingredients [14].

Thermal expansion coefficient measurements of refractory samples are given in Table 10. According to Table 6; "PS1-Std." Talc raw material, which is used at the rate of 20.79% in the recipe composition, has been increased to 21.18% in the PS8 recipe. According to Table 5; It is seen that talc raw material contains 24.84% MgO according to its chemical composition. According to Mayer and Havas, it is known that the average coefficient of thermal expansion of MgO is 0.1x10-7°C-1. The percent increase in the MgO ratio in the PS8 coded recipe composition explains the decrease in the thermal expansion coefficient indicated in Table 10 [19]. PS1-Std. coded refractory body and PS8 coded refractory bodies are given comparatively in XRF (X-Ray Fluorescence) Table 11., XRD (X-Ray Diffraction) patterns are given comparatively in Graph 1.

Table 11 After sintering PS1-Std. and chemical analyses of PS8 coded refractory bodies (XRF)

(%)	*SiO_2*	*Al_2O_3*	*Na_2O*	*MgO*	*CaO*	*TiO_2*	*Fe_2O_3*	*ZrO_2*	*ZnO*	*K_2O*	*P_2O_5*	*HfO_2*	*A.Z.*
PS1Std	47.15	43.25	0.59	6.81	0.27	0.10	0.48	0.00	0.00	1.03	0.07	0.00	0.25
PS8	43.06	40.56	0.00	7.07	0.36	0.11	0.56	6.02	1.24	0.59	0.07	0.16	0.20

After the sintering process, indialite, corundum, quartz and mullite common phases were determined according to the XRD analysis results of the "PS1-Std. and PS8" coded refractory samples. Due to the addition of 8.47% zircon in the PS8 coded refractory body recipe, a different zircon phase was detected in the XRD analysis. For this reason, zircon phase was observed in the phase analysis of the PS8 coded body, different from the standard body. In the literature, studies on the observation of corundum and quartz phase are mentioned as follows; “The cordierite phase starts to form around 1200 °C, but rather than forming alone, corundum, enstatite, fosterite, spinel, anorthite and quartz phases are encountered with this phase depending on the operating conditions, and therefore, thermal expansion coefficients are obtained at high values” [20-23].



Graph 1 XRD diffraction patterns of refractory samples coded "PS1-Std" and "PS8" after sintering

In Graph 1, the microstructure images taken from the cross-sectional area of the PS1-Std coded and PS8 coded refractory samples, which were sintered in the furnace regime with a peak of 1300°C and a dwell time of 60 minutes, are given. While mullite crystals are clearly observed in the microstructure images of the PS1-Std coded refractory sample, with the addition of zircon in the PS8 coded refractory structure; Zircon appears as dispersed phases in a mullite matrix.

SEM (Scanning Electron Microscope) images of PS1 and PS8 coded samples; BSE (Reflected Electron) cross-sectional surface images are given in Figure 1. EDX analysis was applied to determine the elemental compositions in selected areas of the samples whose surface and cross-section images were given. Images of the regions selected for EDX analysis are given in Figure 2 and Figure 3. Elemental distributions are given in Table 12 and Table 13.

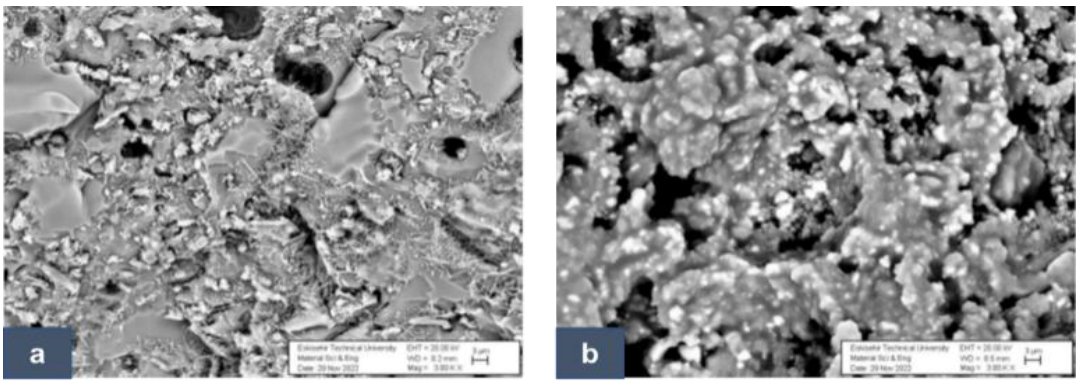


Figure 1 PS1-Std. and SEM analysis images of PS8 coded refractory samples; a) 3.00KX BSE image taken from the fracture surface of the PS1-Std coded sample, b) 3.00KX BSE image taken from the fracture surface of the PS8 coded sample

Kumar et al. in their study named “Processing and characterization of pure cordierite and zirconia-doped cordierite ceramic composite by precipitation technique”; There are two types of cordierite ceramics, porous and dense. Porous cordierite ceramic has much better thermal shock properties than dense one, but has poor mechanical resistance. In the study of Kumar et al., with the addition of pure cordierite (MgO: 13.8% wt., Al_2O_3: 34.8% wt., SiO_2: 51.4% wt.) and zirconia at the rate of 5-20% by weight it is understood that the mechanical and thermal properties of the samples are improved in direct proportion. When the PS1-Std and PS8 coded refractory samples are examined, it is seen that both bodies have a porous structure. In the microstructure images of the PS8 coded refractory sample, dark grains represent

alumina and white grains represent zircon grains.

In the SEM images of both samples, three points were selected from the surface and EDX analysis was applied to determine their elemental distribution. PS1-Std the EDX analysis of the coded refractory sample is given in Figure 2 and the elemental analyses of the selected points are given in Table 12 the EDX analysis of the PS8 coded refractory sample is given in Figure 3 and the elemental analyses of the selected points are given in Table 13 [24].

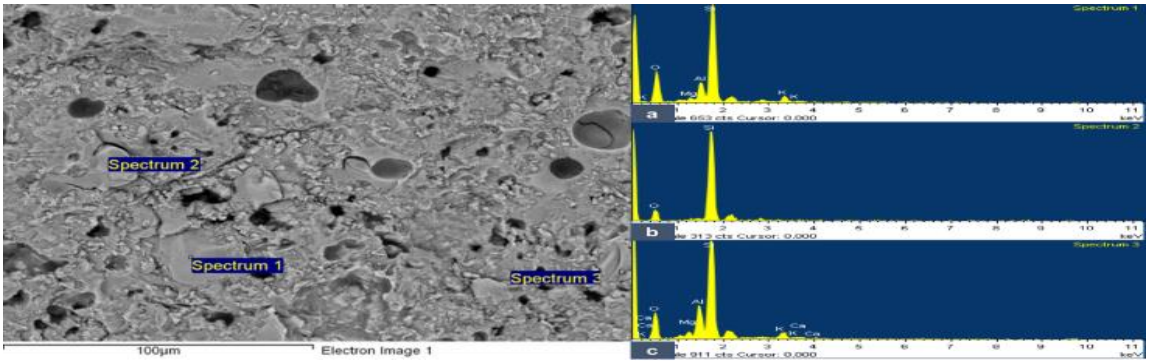


Figure 2 PS1-Std. SEM image of the coded refractory sample and three points selected for EDX analysis on the image; a) Spectrum 1, b) Spectrum 2 and c) Spectrum 3

PS1-Std. whose SEM images are given in Figure 1 a) within the refractory; black areas indicate that the sample has a porous structure. According to the EDX analysis of the points selected according to Table 12; It is seen that there is an elemental distribution forming the corundum, mullite, indialite and quartz phases. PS1-Std in the surface image of the refractory sample, acicular structures are more prominently seen. PS1-Std. XRD phase analysis and EDX analysis results of the sample confirm the formed phases.

Table 12 PS1-Std EDX analyses of selected points on the SEM image of coded refractory samples

	Spectrum1		*Spectrum2*		*Spectrum3*	
	Wt.%	*A.W %*	*Wt. %*	*A.W %*	*Wt. %*	*A.W %*
Mg	01.17	00.98	00.00	00.00	01.43	01.19
Al	06.23	04.70	00.00	00.00	08.28	06.25
Si	38.50	27.90	46.70	33.30	36.50	26.50
K	03.21	01.67	00.00	00.00	02.51	01.30
O	50.80	64.70	53.20	66.60	50.60	64.40
Ca	00.00	00.00	00.00	00.00	00.54	00.27

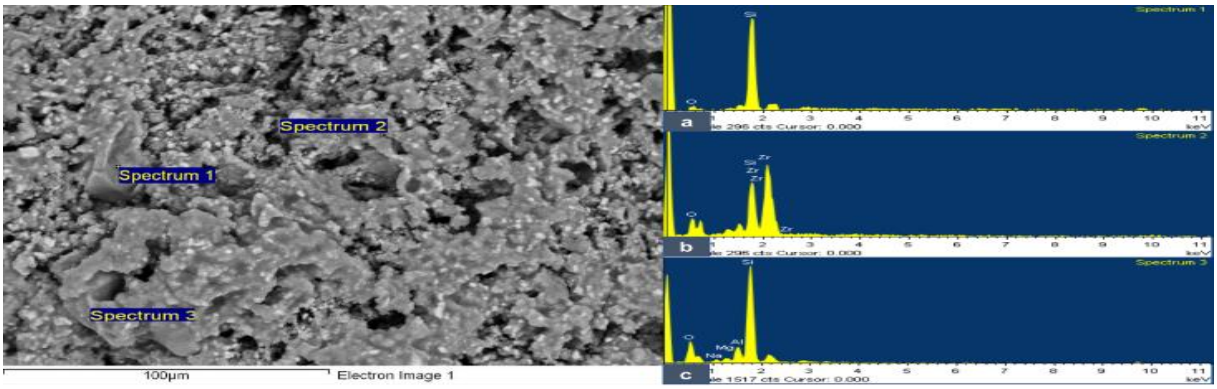


Figure 3 PS8. SEM image of the coded refractory sample and three points selected for EDX analysis on the image; a) Spectrum 1, b) Spectrum 2 and c) Spectrum 3

Within the PS8 coded refractory whose SEM images are given in Visual 1.b; black areas indicate that the sample has a porous structure. According to the EDX analysis of the points selected according to Table 12; It is seen that the phases that may occur are the elemental distribution forming the corundum, mullite, indialite, quartz and zircon phases. In Figure 1 b) PS8 in image. The reason why acicular and curved structures supporting primary or secondary mullite formation cannot be seen in the surface image of the refractory sample is due to the fact that zirconium dioxide forms a homogeneous structure on the mullite phases.

In Figure 2, PS1-Std. SEM image of the coded refractory sample is given. EDX analysis results of 3 different points selected on the relevant SEM image are given in Table 12. PS1-Std. When the XRD analysis of the refractory sample is examined; It is observed that indialite, corundum, quartz and mullite phases are formed. It is seen that the indialite phases are homogeneously distributed as small white grains. The structures displayed as blocks between the grains represent the quartz phase. Acicular mullite crystals are observed between quartz grains and indialite structures. In Figure 3, white dots represent ZrO_2, black dark regions represent pores and dark gray regions represent Al_2O_3 (corundum) grains. The XRD phase analysis of the PS8 coded sample confirms the phases formed when it is examined in terms of elemental analysis according to the EDX analysis results. In the patent study of Avedikian and his colleagues named "Sintered refractory product with improved resistance to thermal shocks"; "Mullite-zirconium dioxide grain is understood as a refractory grain in which chemical analysis obtained by sintering or melting reveals the presence of mostly (Al_2O_3), silica (SiO_2) and zirconium dioxide (ZrO_2); silica and alumina are available in the form of $2SiO_2$-$3Al_2O_3$ (mullite). Therefore, alumina (Al_2O_3), silica (SiO_2) and zirconium dioxide (ZrO_2) are the three main components by weight of a mullite – zirconium dioxide particle." have stated [25].

Table 13 PS1-Std. EDX analyses of selected points on the SEM image of coded refractory samples

	Spectrum 1		Spectrum 2		Spectrum 3	
	Wt. %	A.W. %	Wt. %	A.W. %	Wt. %	A.W. %
Si	46.70	33.30	15.10	16.50	39.80	28.40
O	53.30	66.70	35.00	66.72	51.70	64.90
Zr	00.00	00.00	49.90	16.78	00.00	00.00
Na	00.00	00.00	00.00	00.00	01.50	01.39
Mg	00.00	00.00	00.00	00.00	01.61	01.33
Al	00.00	00.00	00.00	00.00	05.39	03.98

4. RESULTS

In the study, in order to prevent deformation during sintering in bone porcelain products, bone porcelain is fired on a refractory carrier called sagar, which has a low thermal expansion coefficient and does not cause shrinkage or deformation problems during firing. In this study, it is aimed to develop a formulation as an alternative to the imported carrier saggars in bone porcelain production. Based on the chemical composition of cordierite, it is very difficult to develop cordierite as a ceramic material using only raw materials. There are two main reasons for this. The multiplicity of eutectic points and the difficulty of approaching equilibrium. Since the eutectic points are very close to each other, even the slightest deviation from the actual composition causes melting or the formation of unwanted phases. During firing, cordierite compositions show short firing intervals. That is, due to the proximity of various eutectic points, the amount of liquid increases rapidly and it is difficult for the structure to turn into a glassy state. The firing interval can be increased by adding some melting additives to the body.

In this study, PS1-Std. standard refractory recipe and PS2, PS3, PS4, PS5, PS6, PS7 and PS8 coded recipes were prepared. To the prepared prescription suspension; viscosity, thixotropy and 5 min. At the end of the period, wall thickness controls were carried out and rheological properties were determined. At this stage, the problem of sticking to the mold was observed in the PS2, PS3, PS4 and PS5 refractory casting mud suspensions prepared to improve the standard recipe. Therefore, in the continuation of the study, 0.42% bentonite addition was applied in PS6, PS7 and PS8 recipes. In order to determine the mechanical properties of PS6, PS7 and PS8 coded refractory bodies whose rheological properties are accepted within the criteria; shrinkage percentage, strength, deformation and water absorption under vacuum (%) tests were carried out. When comparing the three recipes developed, it was seen that the PS8 recipe was advantageous in terms of its mechanical properties. Dry shrinkage is 2.31%, biscuit shrinkage is 3.65% and baking shrinkage is 6.05%. The strength values obtained in terms of strength values were measured as PS1-Std < PS2 < PS3 < PS4 < PS5 < PS6 < PS7 < PS8. As it is known from the literature, porous refractories have higher thermal properties. For this reason, the high-water absorption value of the PS8 coded refractory sample was evaluated as positive in terms of its thermal properties.

Imported equivalent carrier sagar refractories are used against the PS8 coded carrier refractory body to preserve their mechanical and microstructural properties; The water absorption rate of the equivalent hose under vacuum is between 9.8-17% and its dry strength is specified as 10-15 kg/cm^2. If chemical analyses (XRF) of equivalent products are in charge; It is seen that SiO_2 expanded in the range of 16.82-50.03 percent (%) and Al_2O_3 expanded in the range of 40.41-81.45 percent (%). It is seen that the product of the Al_2O_3/SiO_2 ratio in the composition is called sagar, cordierite or mullite cordierite as superiority in Table 3. It is seen that the dry strength of the PS8 coded final product developed is 15.74 kg/cm^2 according to Table 9.

The water absorption under vacuum was measured as 17%. PS8 coded contents obtained after sintering were designed as 43.06% SiO_2 and 40.56% Al_2O_3 according to Table 11 in the chemical analysis of sagar refractory body bodies. In order to configure the mechanical properties of the cavities in the structure, 8.47% zircon was added to the PS8 coded recipe. In PS7 and PS8 coded prescriptions, improvement in mechanical properties is observed with the addition of zircon. In the study, the improvement in mechanical properties with the addition of zircon was supported by the appearance and microstructure of the mullite phase formed by XRD, SEM and EDX analyses in both structures. The developed refractory body can be shaped according to different bone porcelain product forms and used as a bearing refractory. It has been observed that the bearing refractory products for the bone porcelain firing process developed as a result of the project offer a 10% longer service life compared to the equivalent refractory products that were imported and used in production before the project.

Acknowledgments
This study has been prepared as the output of the project coded 121M997 “Development and Characterization of Carrier Refractory (Sagar) Formulation for Bone Porcelain Firing Process” supported by TUBITAK within the scope of ARDEB-1005-New Ideas and Products. We would like to thank TÜBİTAK for contributing to the realization of the study with the support of the project.

Funding
The author received no financial support for the research, authorship, and/or publication of this paper.

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No conflict of interest or common interest has been declared by the author.

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