Alumina Additions Affect Elastic Properties of Electrical Porcelains

The partial substitution of alumina for feldspar in an electrical porcelain leads to an increase in Young's modulus from 38.27 to 62 GPa, reaching the maximum value when the firing temperature is 1350°C.

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The manufacture of electric porcelains has increased in recent years because of the need for electrical transmission insulators with improved mechanical properties. Among the materials available for this application, the best are the alumina-based porcelains because of their singular electromechanical properties. Alumina has been introduced into the classic triaxial porcelain body composition to replace some of the feldspar and flint in order to improve its elastic properties.

Much has been written to clarify why the incorporation of alumina into porcelain bodies produces a strength increase.[1] However, the theories remain controversial. Although some authors attribute the increase in strength to the increase in the mullite content associated with a decrease in the quartz content, others have found no relationship between mechanical strength and mullite content.[2]

It has been reported in a review of electrical insulating ceramics by Rigterink and Williams[3] that few engineers have specified and used high-alumina ceramics for many new electrical applications. More recently, engineers have been reconsidering using porcelain for economic and technical reasons—it has been the material of choice by many of them.

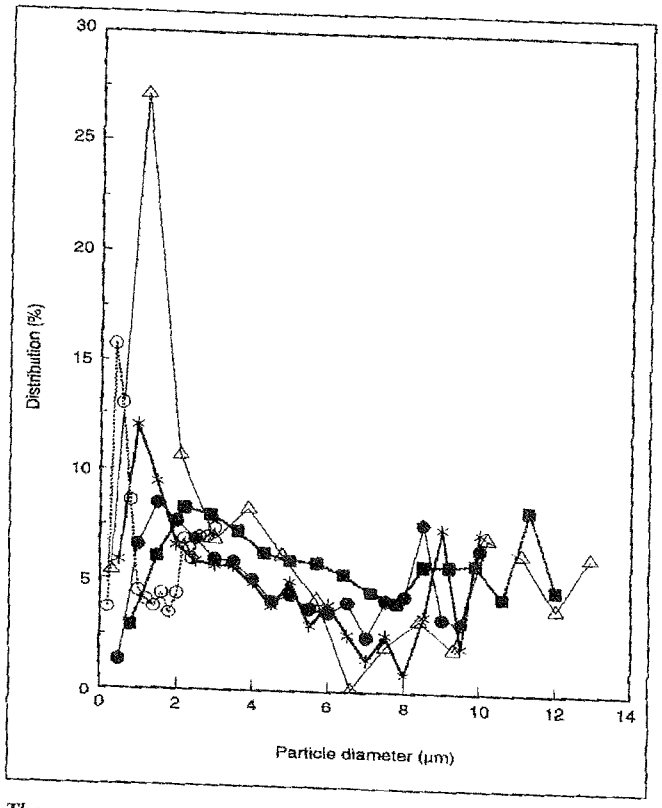
Mullite compositions also have attracted attention. Warshaw and Seider[4] have made a comparison of the strength of triaxial porcelains containing alumina and flint. They have found that the compositions containing alumina are free of internal cracks, and, therefore, are stronger than those with comparable quartz compositions. Kalnin *et al.*[5] have shown that the elastic modulus and, therefore, the flexural strength of a quartz-free body increases in proportion to the amount of mullite present over the range 11–36 wt%.

The results of Khandelwal and Cook[6] on the correlation of the crystalline constituents with the strength of porcelain are such that an increase of alumina in crystalline form as well as in the glassy phase results in increased strength. However, the mullite content does not affect the strength of the porcelain.

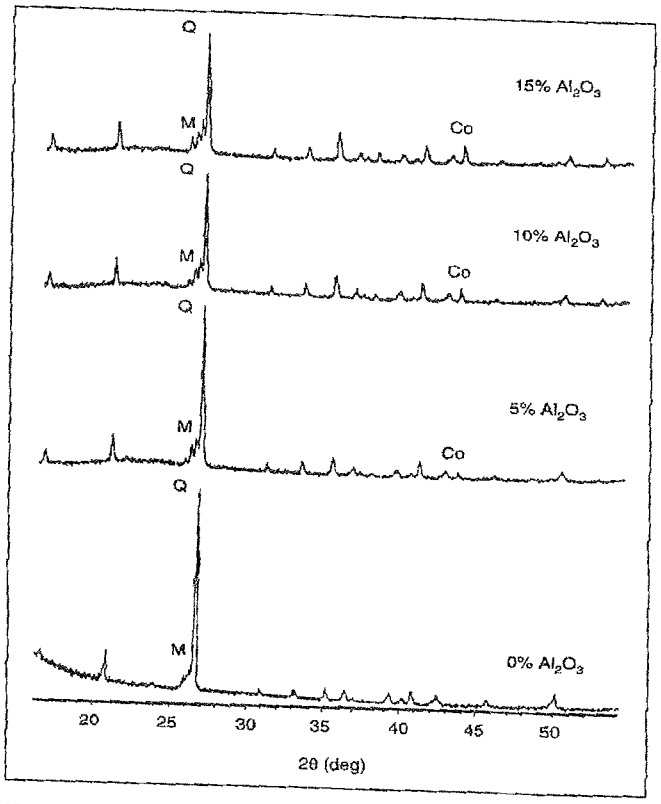
Kreimer and Chistyakova[7] have reported that, on the basis of their statistical analysis, the strength of alumina-containing porcelain is increased with an increase in the proportion of one of the crystalline phases. This is caused by a reduction in the proportion of the second crystalline phase and glassy phase.

Orlova *et al.*[8] suggest that, to obtain a electrical engineering porcelain having high electrophysical and mechanical properties, it is advisable to use alumina containing no spherulites of corundum and an average corundum particle size not exceeding 3 μm and with no tendency to form aggregates.

We provide in this article additional information on the incorporation of alumina in porcelains. The elastic constants of electrical porcelain in relation to alumina additions, phase composition and firing temperature are analyzed. We present data that show that the variation in alumina



There was a wide range in the particle-size distribution of the raw materials used in this study ((●) silica, (×) clay, (△) ball clay, (■) feldspar and (○) alumina).



XRD of samples fired at 1300°C with different alumina concentrations, showing changes in (Q) quartz, (M) mullite and (Co) corundum peaks.

Elastic Constants, Quartz:Mullite Ratios, and Shrinkage of the Bodies Fired at Different Temperatures

Body	Shrinkage (%)	Young's modulus (GPa)	Shear modulus (GPa)	Poisson's ratio	Quartz: mullite ratio	Peak height of corundum (mm)
			Fired at 1270°C			
P1-(0%)	5.275	47.90	20.37	0.18	5.89	
P1-(0%)	6.050	51.58	21.78	0.18	3.21	13.00
P1-(0%)	6.425	53.04	22.42	0.18	2.82	37.00
P1-(0%)	6.225	46.41	19.76	0.17	3.96	32.00
			Fired at 1300°C			
P1-(0%)	4.975	49.64	21.00	0.18	6.41	
P1-(0%)	6.206	56.78	24.02	0.18	4.42	4.00
P1-(0%)	7.025	60.98	25.61	0.19	3.00	6.40
P1-(0%)	8.049	62.12	26.09	0.19	2.80	8.00
			Fired at 1325°C			
P1-(0%)	3.182	43.57	18.66	0.18	3.53	
P1-(0%)	3.407	50.31	21.19	0.19	3.33	4.00
P1-(0%)	6.358	57.83	24.01	0.20	2.37	6.00
P1-(0%)	7.778	64.89	27.25	0.19	2.00	7.80
			Fired at 1350°C			
P1-(0%)	4.650	53.36	22.33	0.20	2.31	5.50
P1-(0%)	7.539	66.31	27.60	0.20	1.75	7.00

Effects of Alumina

In summary, the porcelain disks were produced from four raw materials containing four different concentrations of alumina. The raw materials were homogenized in water and drained. The resulting agglomerates were ground and sieved (–325 mesh) to obtain a fine powder.

The powder was dry-pressed at 9 tons (8.1×10^4 N). The resulting disks contained large quartz particles and fine acicular mullite crystals. Variations in the XRD signals as a function of the alumina concentration were recorded. The quartz:mullite ratio as a function of temperature also was recorded.

The raw materials have a complex chemical composition, but these components can be combined[9] in a fluxing oxide mixture: K_2O, Na_2O, CaO,

concentration, at the expense of feldspar and flint, results in an improvement in Young's modulus. The increase in elastic modulus is attributed to the increase in mullite concentration and quartz dissolution at the highest firing temperature.

The Experiment

The sample compositions were prepared with kaolin (Técnica Minera, Jalisco, Mexico), feldspar and flint (Compañia Minera San José, Guanajuato, Mexico), Kentucky ball clay, and alumina (99.9%).

Four bodies were made with different alumina concentrations to study the effect of alumina on the elastic constant of the electrical porcelains. The original composition (body 1) was taken from the standard used for conventional electrical porcelain. Alumina addition was made at the expense of feldspar and quartz.

All the bodies had equal amounts of kaolin and ball clay—50 wt% kaolin, 25 wt% feldspar and 25 wt% flint. Uniform distribution of the raw materials was ensured by wet mixing. The suspensions were dried at 100°C for 2 h and pressed in disks 30 mm in diameter. The disks were sintered to different temperatures (1270, 1300, 1325 and 1350°C) and soaked for 2 h. The amount of shrinkage was measured after sintering.

The elastic constants of the porcelain disks were measured by the impulse excitation technique, a nondestructive method (Grindo-Sonic, J. W. Lemmens Inc., St. Louis, Mo.). The measuring instrument used pulse excitation principles to analyze the transient vibration of the test piece following a mechanical impact. The energy from the impact was dissipated in the form of a damped vibration, which depended on the geometry of the material as well as its density and elastic properties.

The instrument measured Young's modulus, shear modulus and Poisson's ratio and met standards ("Standard Test Method for Dynamic Young's Modulus, Shear Modulus and Poison's Ratio for Advanced Ceramics by Impulse Excitation of Vibration," ASTM Designation C 1259, American Society for Testing and Materials, West Conshohocken, Pa.).

SEM image of the general contrast observed in all the samples. Mullite (indicated by M) and quartz (indicated by Q) particles are easily recognized.

The crystalline phases present in the porcelain disks were identified by powder X-ray diffractometry (XRD) (Philips Electronic Instruments, Mahwah, N.J.) using Cu$K\alpha$ radiation at 35 kV and 15 mA. Scanning electron microscopy (Model 6400, JEOL, Palo Alto, Calif.) was used to analyze the microstructures of these phases.

The samples for SEM observation were polished and etched with hydrofluoric acid to dissolve the glassy matrix and enhance the crystalline morphologies. They then were glued onto the holder cylinder and covered with a thin gold film. The samples were ground, and the fine powder was analyzed by XRD.

Chemical Compositions of Raw Materials

Oxide	Composition (mol%)				
	Kaolin	Ball clay	Feldspar	Silica	Alumina
SiO_2	68.580	72.035	76.706	97.310	0.051
Al_2O_3	27.000	23.628	11.690	1.330	99.662
K_2O	0.980	0.399	7.409	0.376	
Na_2O	0.176		3.599	0.561	
Fe_2O_3	0.080	0.532	0.099	0.006	0.087
Rb_2O			0.022	0.020	
BaO	0.030		0.017	0.003	
CaO	0.510	0.544	0.398	0.390	
TiO_2	0.591	1.846	0.058	0.004	
P_2O_5	0.987	0.079			
SrO	0.114				
Cr_2O_3	0.010				
MgO	0.940	0.937			
Total	99.998	100.000	99.998	100.000	100.000

Formulations of the Produced Bodies

	Composition (wt%)				
	Kaolin	Ball clay	Feldspar	Silica	Alumina
Body 1	30	20	25	25	0
Body 2	30	20	25	20	5
Body 3	30	20	25	15	10
Body 4	30	20	20	15	15

Chemical Composition of the Produced Bodies

	Composition (mol%)			
	Body 1	Body 2	Body 3	Body 4
SiO_2	76.465	73.622	68.759	64.926
Al_2O_3	16.081	21.007	25.934	30.342
K_2O	2.320	2.301	2.282	1.912
Na_2O	1.093	1.067	1.037	0.857
Fe_2O_3	0.157	0.161	0.165	0.164
Rb_2O	0.011	0.009	0.009	0.007
BaO	0.014	0.014	0.014	0.013
CaO	0.459	0.439	0.419	0.399
TiO_2	0.562	0.562	0.562	0.559
P_2O_5	0.312	0.312	0.312	0.312
SrO	0.034	0.034	0.034	0.034
Cr_2O_3	0.003	0.003	0.003	0.003
MgO	0.469	0.469	0.469	0.469

Chemical Composition of the Produced Samples in a Simplified Form

Component*	Composition (mol%)			
	Body 1	Body 2	Body 3	Body 4
RO	4.758	4.695	4.632	4.059
RO_2	79.155	74.291	69.428	65.593
Al_2O_3	16.083	21.007	25.934	30.343
Total	100.000	100.000	100.000	100.000

*R is radical, RO is the fluxing group, and RO_2 is the refractory group.

MgO, SrO, BaO and Fe_2O_3, refractory SiO_2, Cr_2O_3, and TiO_2. Alumina is the variable compound used in this study. Therefore, the composition of the bodies can be described as a function of only three variables—RO, RO_2 and Al_2O_3, where R indicates a radical.

The particle size of the raw materials is an important parameter, because it defines the compaction of the product. It has been reported in the case of quartz that large particle sizes result in a product with a high density of cracks. The preparation of a compound of different-sized particles often results in better compaction.

This is the case of the raw materials used in this work—alumina is in the range 0.4–3 μm (mean value of 1.22 μm), feldspar is in the range 0.8–12 μm (mean value of 5.6 μm), ball clay is in the range 0.3–12.9 μm (mean value of 2.99 μm), kaolin is in the range 0.5–10 μm (mean value of 3.39 μm) and flint is in the range 0.3–10 μm (mean value of 4.25 μm).

Major changes occur in the elastic properties when the alumina concentration is varied. At 1270°C, Young's modulus increases as the alumina content increases. However, the highest value (53.04 GPa) is attained for the sample containing 10% alumina rather than the one with 15% alumina. It is speculated that the firing temperature was insufficient to sinter the body completely. Optimal sintering conditions need to be established.

At 1320°C, a direct proportion relationship between the alumina content and Young's modulus again is observed. The sample with 15% alumina presents the largest value (62.12 GPa). When the temperature is increased to 1325°C, Young's modulus decreases in all the samples except that with 15% alumina. This result is due to the temperature being too high for sintering.

Bloating of body 1 was observed. Young's modulus increases only for the body with 15% alumina—from 62.12 to 64.89 GPa. Increasing the temperature to 1350°C further increases Young's modulus to 66.31 GPa. This corresponds to an increase of 44% in Young's modulus with respect to the body without alumina.

XRD analysis indicates that the quartz:mullite ratio decreases as the alumina content increases—i.e., the alumina increase produces more mullite and a corresponding decrease in quartz, increasing Young's modulus. The unreacted corundum concentration causes no significant microstructural modification. However, corundum does affect the mechanical properties of the porcelains produced in this study.

Temperature/Mullite Effects

The results indicate the possibility of increasing the mechanical properties of electrical porcelains by modifying only the crystalline phase contents and optimizing the firing temperature. In this study, the addition of alumina produces a 44% increase in Young's modulus compared with the base material (no alumina), using a firing temperature of 1350°C.

The mechanical properties can be increased even further by adding higher concentrations of alumina. There have been reports of 40% alumina additions with increases of >125% in Young's modulus[8] after optimizing the firing temperature. However, the importance of the present work is the confirmation of the positive effect that the increase of the mullite content has on the mechanical strength of the porcelains.

Authors disagree on the function of mullite in controlling the strength of electrical porcelains. One group assumes that mullite has little effect in improving the mechanical properties;[6] another group opposes this idea.[10]

In this work, the addition of alumina favors an increase in mullite and decrease in quartz. Therefore, it is important to analyze the mechanism of strengthening as a function of all the crystalline phases present in the porcelain. The role of mullite, quartz, corundum and the glassy phases as well as the synergistic effect of all these phases must be understood.

Some authors have, for example, reported that, when the porcelain contains <10% residual quartz, an increase in mullite content occurs, leading to an increase in strength. However, when there are residual quartz concentrations >11%, an increase in mullite produces a decrease in strength.[7]

The mechanical properties of electrical porcelains improve with alumina additions of up to 15%, if the firing temperature is concurrently increased.

The maximum increase in strength is attained by increasing the mullite content in the fired porcelain while reducing the amount of the residual quartz. This strength can be further improved by increasing the amount of crystalline phases and accounting for their concentrations as well as establishing their role in the region of the phase diagram and optimizing the firing temperature. ■

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References

[1]Z. Ke, "Fracture-Initiating Flaws in Aluminous Electrical Porcelain," *Am. Ceram. Soc. Bull.*, **69** [3] 380, 382, 384, 386, 388, 390 (1990).

[2]E. de los Monteros, D. Alvarez-Estrada and R. Martínez-Caceres, "Porcelanas Aluminosas de Elevada Resistencia Mecánica, Obtenidas Mediante Arcillas Sericíticas," *Bol. Soc. Esp. Ceram. Vidrio*, [Aug.] 11–17 (1991).

[3]M. D. Rigterink and J. C. Williams, "A Half Decade of Improvement in Ceramic Insulating Materials," *Am. Ceram. Soc. Bull.*, **43** [12] 894–900 (1964).

[4]S. I. Warshaw and R. Seider, "Comparison of Strength of Triaxial Porcelains Containing Alumina and Silica," *J. Am. Ceram. Soc.*, **50** [7] 337–43 (1967).

[5]I. L. Kalnin, P. Cucka, S. I. Warshaw and R. Seider, "Strength and Elasticity of White Wares," *Am. Ceram. Soc. Bull.*, 47 [5] 498, 499, 502–504 (1968).

[6]S. K. Khandelwal and R. L. Cook, "Effect of Alumina Additions on Crystalline Constituents and Fired Properties of Electrical Porcelains," *Am. Ceram. Soc. Bull.*, **49** [5] 522–26 (1970).

[7]D.B. Kreimer and T. I. Chistyakova, "Influence of Phase Composition of Aluminous Porcelain on its Mechanical Strength," (translated from) *Steklo Keram.*, 489–91 (1990).

[8]R.E. Orlova, V. D. Beshentsev, I. Kh. Moroz and É. P. Bogdaniz, "Effect of Structure and Degree of Dispersion of Alumina on Properties of Porcelain," *Steklo Keram.*, 466–69 (1989).

[9]G. R. Shelton, "Method of Correlating Chemical Composition, Relative Amounts of Glassy Bond, and Properties of Ceramic Bodies," *J. Am. Ceram. Soc.*, **31** [2] 39–49 (1948).

[10]S. C. Sane and R. L. Cook, "Effect of Grinding and Firing Treatment on the Crystalline and Glass Content and the Physical Properties of Whiteware Bodies," *J. Am. Ceram. Soc.*, **34** [5] 145–51 (1951).