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X-ray powder diffraction phase analysis and thermomechanical properties of silica and alumina porcelains

José M. Amigó[a,*], José Vicente Clausell[a], Vicente Esteve[b], Juana María Delgado[b], María Mercedes Reventós[a], Luis E. Ochando[a], Tony Debaerdemaeker[c], Francisco Martí[d]

[a]*Departament de Geologia, Universitat de València, 46100-Burjassot (Valencia), Spain*
[b]*Departament de Química Inorgànica i Orgànica, Universitat Jaume I, Ap. 224, 12080-Castelló, Spain*
[c]*Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, 7900-Ulm, Germany*
[d]*Laboratorio Central, Nalda S.A., 46132-Almassera (Valencia), Spain*

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Abstract

Chemical and mineralogical characterization, using the Rietveld method, of some silica and alumina rich porcelains and its relationship with thermomechanical properties have been studied in this work. X-ray powder diffraction analysis allows to differ clearly between silica and alumina porcelains. X-ray study shows that both porcelains have a content of vitreous phase. This vitreous phase is higher in the silica than in the alumina porcelain. Dilatometric studies combined with powder diffraction methods shows a strong relationship between silica content and a lower expansion coefficients and between alumina content and a higher crash resistance. Lower contents in vitreous phase in porcelain yields to higher thermal expansion coefficients.

Keywords: Mechanical properties; Porcelain; Thermal expansion coefficient; X-ray methods

1. Introduction

The utilization of ceramic materials as electrical insulators goes back until 1850 when Werner von Siemens introduced in the construction of electrical air lines the use of electrotechnical porcelains.[1,2] With the denomination electrotechnical porcelains are grouped nowadays a series of ceramic materials with special electrical, mechanical and thermal properties that distinguish them of other industrial materials by its dielectric high-power and great resistance to the fracture. To obtain these properties, composition of porcelains has evolved from formulations with high silica and low alumina content to formulations with very low silica and high alumina content,[3] to improve a higher mechanical resistance.[4] Last studies pursue to obtain porcelains where there are no free quartz phase.[5,6]

Today, the greater part of ceramic industries uses in a routine way classic and some specialized techniques of chemical analysis in order to work with a little quantity of sample to be able to reduce sampling periods and to determine the elemental composition of raw material used as well as of the obtained industrial product. However, not always it is used the analysis of the mineralogical composition, which must be related to the chemical analysis. Though mineralogists use a great number of phase analysis methods, nowadays the X-ray diffraction[7–10] is one the most used for phase analysis of a single mineral or a group of useful minerals in industrial control.

For years many X-ray powder diffraction methods exist and are used. The basic principle[11] is that the integrated intensity of reflections for a compound in a multiphase powder diffraction pattern is related to the phase abundance in the mixture. But in some cases instrumental and sample-related effects (e.g. preferred-orientation, separation of overlapping and broad

* Corresponding author.
E-mail address: jose.m.amigo@uv.es (J.M. Amigó).

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reflections, detection of trace and amorphous components,...) can influence the accuracy of results. Improved analysis methods are continuously sought, but without accomplishing a satisfactory level yet. Rietveld refinement was originally developed as a method of refining crystal structures using powder neutron diffraction data,[12] later the pattern-fitting structure-refinement method of Rietveld to X-ray powder diffractometer patterns was adapted[13,14] and finally was revealed its application in quantitative phase analysis.[15] This method requires a knowledge of the approximate crystal structures of all phases of interest in the mixture. The Rietveld method of analysis provides many advantages over conventional quantitative analysis methods. As the method uses a whole pattern-fitting algorithm, all lines for each phase are explicitly considered, and even severely overlapped lines are usually not a problem. Thus is not necessary to decompose patterns into separate Bragg peaks, as is often the case for traditional methods. The use of all reflections in a pattern rather than a few minimizes the effects of preferred orientation, primary extinction, and non linear detection systems. Also, failure to consider a phase in the analysis will yield obvious differences between the observed and calculated diffraction pattern and reveal unsuspected minor phases. The Rietveld method of quantitative phase analysis was utilized because minimizes or eliminates many current problems present in traditional methods.[16–20]

The aim of this work is the characterization and quantification of mineral and amorphous phases present in some electrotechnical porcelains using chemical and X-ray powder diffraction analysis by the Rietveld method. In particular, the abundance of SiO_2 (quartz), Al_2O_3 (corundum) and $3Al_2O_3{\cdot}2SiO_2$ (mullite) determined in different porcelains have been studied. Depending on starting composition and calcining conditions normally silica and alumina porcelain can be formed. The quality of porcelain as electrical insulator is related to many factors, including the proportion of corundum, quartz, mullite and glass present in the porcelain. By the other part, the content in quartz and corundum have been correlated with some thermomechanical properties.

For this study all the samples used are from group C-100 (porcelain as ceramic insulating materials) and two kinds of porcelain have been used:

1. Silica porcelain: corresponding to sub-group C-110
2. Alumina porcelain: corresponding to sub-group C-120

Both sub-groups with specifications according to IEC 672-3 standard.[21]

2. Chemical analysis

Materials used in this work correspond to silica and alumina porcelains obtained firing different formulations of raw materials. Chemical analysis was performed by fused pellets. Fusion was reached with a Claisse Fluxy equipment using lithium metaborate in a ratio 1:10. Data were acquired with a SRS-3000 Brüker sequential spectrometer. Results are listed in Table 1.

3. X-ray powder diffraction

Samples of commercial porcelains were obtained from industrial furnace. Finely crushed porcelain samples were split using a rotatory splitter and grounded in a micronizing mill. In all porcelains studied, 0.8 g of micronized material was mixed with 0.2 g of laboratory reagent ZnO (zincite) by hand using a mortar and a pestle. XRD data were obtained on dried material. Samples were manually pressed into standard sample holders. Preferred orientation was not present, in addition the Rietveld method minimizes this effect because uses the full pattern, in this case no mineral phases present in these porcelains have not this effect significantly. Powder diffraction patterns were taken at room temperature (22 ± 2 °C) using a Bruker D5000 X-ray powder diffractometer with Bragg–Brentano geometry. Experimental conditions are summarized in Table 2.

Intensities were collected by step-scanning from 5 to 90° (2θ) and a counting time of 10 s for each step. A total of 18 h was needed for each sample. The goniometer was controlled by the PC software package DIFFRAC plus for Windows NT, supplied by Brüker/Socabim.

Quantitative analysis of present phases was performed using a modified version[19] of the computer program DBW3.2,[14,17] adapted to run on PC computers.[22] If all crystalline phases in the mixture are included in the analysis, then the sum of the weight fractions of all phases determined is 100%. When amorphous or non determinated crystalline phases are present in the sample, the absolute weight fractions of each of the analyzed phases

Table 1
Chemical analysis (%)

Oxide	S1	S2	S3	S4	S5	S6	S7
SiO_2	50.94	50.20	49.10	46.50	66.80	66.40	66.20
Al_2O_3	44.70	45.60	46.30	47.90	28.40	28.70	28.70
TiO_2	0.53	0.59	0.48	0.46	0.54	0.57	0.57
Fe_2O_3	0.39	0.44	0.41	0.48	0.39	0.49	0.49
CaO	0.17	0.18	0.21	0.17	0.31	0.34	0.29
MgO	–	–	–	–	–	–	0.31
Na_2O	–	–	–	0.52	0.90	0.82	0.82
K_2O	3.30	3.03	3.56	3.67	2.59	2.71	2.59
Minor components	–	–	–	0.27	0.02	–	–
Total	100.03	100.04	100.06	99.97	99.95	100.03	99.97

Table 2
Data collection by X-ray powder diffraction

	Experimental conditions
Diffractometer	Brüker D5000
Radiation type, source	X-ray, sealed tube, Cu $K\alpha$
Instrument power	40 kV, 30 mA
λ Discrimination	Secondary graphite monochromator
Detector	Scintillation
Divergence slit	0.2 mm
Receiving slit	2 mm
Scatter slit	0.6 mm
Specimen form	Horizontally packed powder in an airtight diffractometer holder
Particle size	Sample grounded in micronising mill to pass 60 μm
Range of 2θ	From 5 to 90°
Step	0.02°
Time per step	10 s
Specimen motion	None
Intensity measuring procedure	Numerical registration of peak heights

can be determined by adding a known amount of an internal standard. The difference between 100% and the total of the absolute abundance represents the amount of amorphous and/or crystalline phase omitted from the analysis. In all cases, refinement involved the sequential variation of scale factor, peak-width parameters, Pearson VII profile function coefficients for each phase, and zero displacement correction. During the course of refinement, atomic coordinates, occupancies, and temperature factors for each phase were usually fixed and starting atomic structural parameters were taken from the literature.

By means of powder X-ray diffraction, corundum (42-1468), quartz (33-1161) and mullite (15-0776) have been identified, using the complete ICDD powder pattern file as principal crystalline phases and the PC software DIFFRAC plus SEARCH for Windows. In all cases an amorphous phase was detected in the porcelains studied in this work. The amount of amorphous phase in porcelains depends on the exact conditions of production, especially the firing temperature. In spite of some physical problems in the determination of the glass abundance in porcelains by XRD, due to difficulties in accurately determining the level of background and the absence of a coherent diffraction pattern, some authors[7,17] have demonstrated that the algorithm used by the computer program DBW3.2 gives a correct estimation of the amount of amorphous material present.

Quantitative phase estimation obtained using Rietveld method are shown in Table 3.

Table 3
Quantitative X-ray phase analysis (%)

Sample	Corundum	Quartz	Mullite	Rutile	Albite	Glass
S1	33.22	12.07	3.34	0.24	–	51.06
S2	34.24	10.82	4.03	0.22	–	50.69
S3	35.27	8.47	5.04	0.13	–	51.10
S4	34.90	8.39	5.75	0.01	–	50.94
S5	8.81	23.02	5.42	–	0.05	62.69
S6	8.85	23.78	5.87	0.26	–	61.17
S7	8.52	22.63	5.06	0.20	–	63.59

4. Thermal properties

Fired samples of commercial silica and alumina porcelains without enamel have been yielded to a dilatometric study. Dilatometric diagram gives valuable information about thermal behavior. Changes of length in sample with temperature are reflected in this kind of curves. These changes are the result of reactions that can undergo in whatever the minerals present at the sample as well as between themselves.

The essay has been carried out with a BÄHR Thermo Analyse DIL 801 L dilatometer following the IEC 672-2 standard.[21] The initial length of samples was 47 mm. The essay was programmed with a heating speed of 5 °C per minute reaching a maximum temperature of 1250 °C in 4 h. Once this temperature is reached, it starts a high speed freezing process.

Dilatometric diagrams obtained for silica and alumina porcelain are presented in Figs. 1 and 2. In these figures two curves can be seen. The upper curve corresponds to the thermal expansion produced during heating; the lower one is the contraction suffered while freezing.[23,24] From these figures thermal expansion coefficients of both materials can be calculated at different temperature intervals. Dilatometric diagrams (Figs. 1 and 2) show a continuous but not linear rise with temperature. The characteristic feature of these kind of curves is the change of phase of quartz α–β close to 573 °C. This trait is due to a sudden shift in the slope of the curve at this temperature. This phenomenon is yielded in a major extension in silica porcelain (Fig. 1), and can be more easily appreciate in the dilatometric diagram than in alumina porcelain (Fig. 2).

Table 4 shows medium thermal expansion coefficients obtained for silica and alumina porcelains in the indicated intervals, according to the IEC 672-3 standard, along all the dilatometric diagram.

In same way Table 5 shows medium thermal expansion coefficients for several intervals around the temperature where the change of phase of quartz is yielded. Observing the results showed earlier, it can be remarked a major final thermal expansion coefficient in the alumina porcelain than in the silica one. Major thermal expansion coefficients are shown for alumina porcelain than for silica porcelain in all the intervals. This result can be attributed to the different chemical composition of both porcelains. Chemical analysis (Table 1) shows that raw material used for silica porcelain are sodium

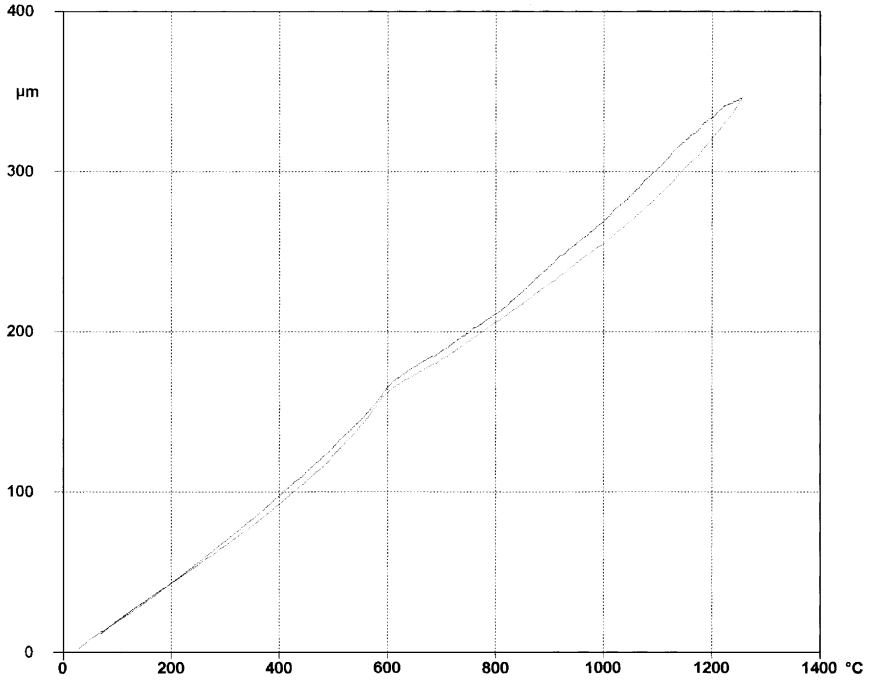

Fig. 1. Dilatometric diagram for silica porcelain.

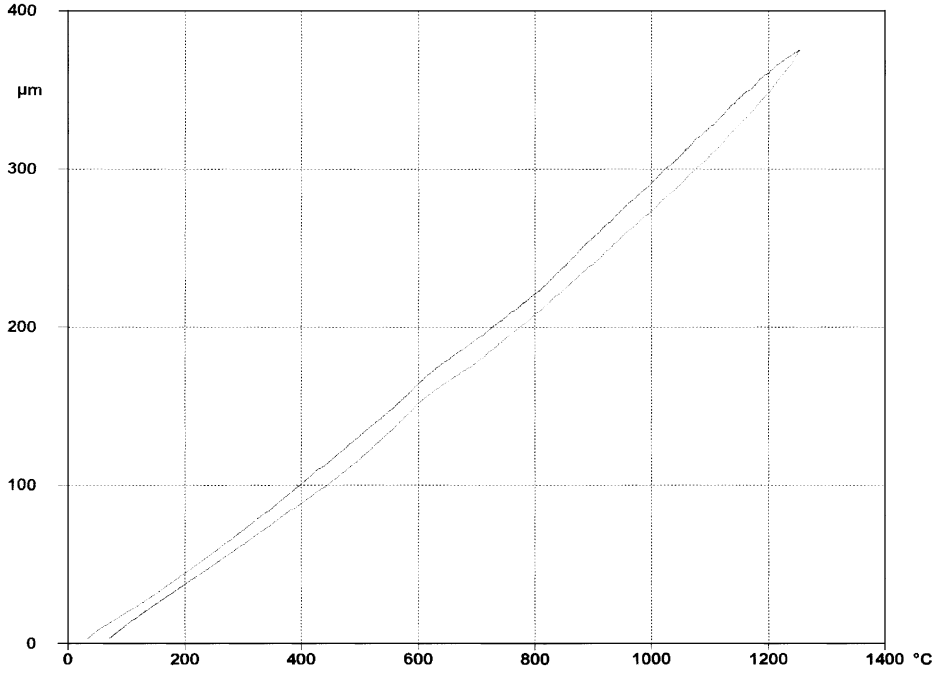

Fig. 2. Dilatometric diagram for alumina porcelain.

and potassium feldspars. Nevertheless, for alumina porcelains it is used potassium feldspar mainly. In general, sodium feldspars are more fluid than potassium ones at a given temperature, so silica porcelains will have more vitreous phase than alumina porcelain.

If expansion coefficients corresponding to the two first intervals (Table 5) are observed, it can be seen that for both porcelains coefficients are higher within the interval that contains the temperature of phase transformation (550–600 °C) than in the posterior interval (600–650 °C), with values going from 8.6×10^{-6} to 5.6×10^{-6} °C^{-1} for silica porcelain and 7.7×10^{-6} to 6.6×10^{-6} °C^{-1} for alumina porcelain. It should be remarked that difference between both coefficients for the same material is higher for the silica porcelain.

Different composition of porcelains, mainly in concentration of quartz, rebounds in dilatometric curves in an important way as well as in thermal expansion coefficients.

Table 4
Medium thermal expansion coefficients

Temp. interval (°C)	α Silica porcel. ($°C^{-1}.10^{+6}$)	α Alumina porcel. ($°C^{-1}.10^{+6}$)
20–100	5.3	5.4
20–300	5.4	5.7
20–600	6.2	6.3
20–1000	5.9	6.5

Table 5
Medium dilatometric coefficients

Temp. interval (°C)	α Silica porcel. ($°C^{-1}.10^{+6}$)	α Alumina porcel. ($°C^{-1}.10^{+6}$)
550–600	8.6	7.7
600–650	5.6	6.6
523–573	7.7	7.1
573–623	7.9	7.7
523–623	7.8	7.4
572–574	9.2	7.2

Alumina porcelain curves are smoother than silica ones. In silica porcelain curves it is observed at a glance the change of the slope due to the allotropic change of quartz. Beside of this, influence of concentration of quartz in the composition is clearly seen in thermal expansion coefficients at intervals (550–600 °C), (523–623 °C) with values of 8.6×10^{-6} and 7.8×10^{-6} $°C^{-1}$ for silica porcelain opposite to 7.7×10^{-6} and 7.4×10^{-6} $°C^{-1}$ for alumina porcelain. Moreover, difference in thermic expansion coefficients due to concentration of quartz is highly seen at the polymorphic interval (572–574 °C) with values of 9.2×10^{-6} $°C^{-1}$ for silica porcelain opposite to 7.2×10^{-6} $°C^{-1}$ for alumina porcelain.

5. Mechanical properties

The IEC 672-2 standard has been employed to characterize the mechanical resistance of samples of commercial silica and alumina porcelains. The essay has been carried out to raw samples, fired samples without and with two different industrial enamels (grey and brown) used for increase mechanical resistance.

6. Discussion

Results obtained are shown in the following figures. Fig. 3 shows results obtained for mechanical resistance as resistance to flexion measured in N/mm^2/MPa. For alumina porcelains with brown enamel, the average value obtained was 176 N/mm^2/MPa, and with grey enamel was 178 N/mm^2/MPa. For silica porcelains averages were lower, 125 and 121 N/mm^2/MPa respectively. Fig. 4 shows the variation of mechanical resistance. Fig. 5 shows the variation of mechanical resistance with the content of quartz, corundum, mullite and vitreous phase in a sample.

From the Fig. 3 we can conclude that mechanical resistance of fired samples with enamel have about 22% higher mechanical resistance than fired samples without enamel. Mechanical resistance obtained with different enamels are very similar.

Fig. 4 shows clearly the influence that content of SiO_2 and Al_2O_3 has on mechanical resistance. In the first case, an increase of the percentage of SiO_2 leads to a decrease of the mechanical resistance of the material. Otherwise, increasing the percentage of Al_2O_3 in the sample, increases the mechanical resistance.

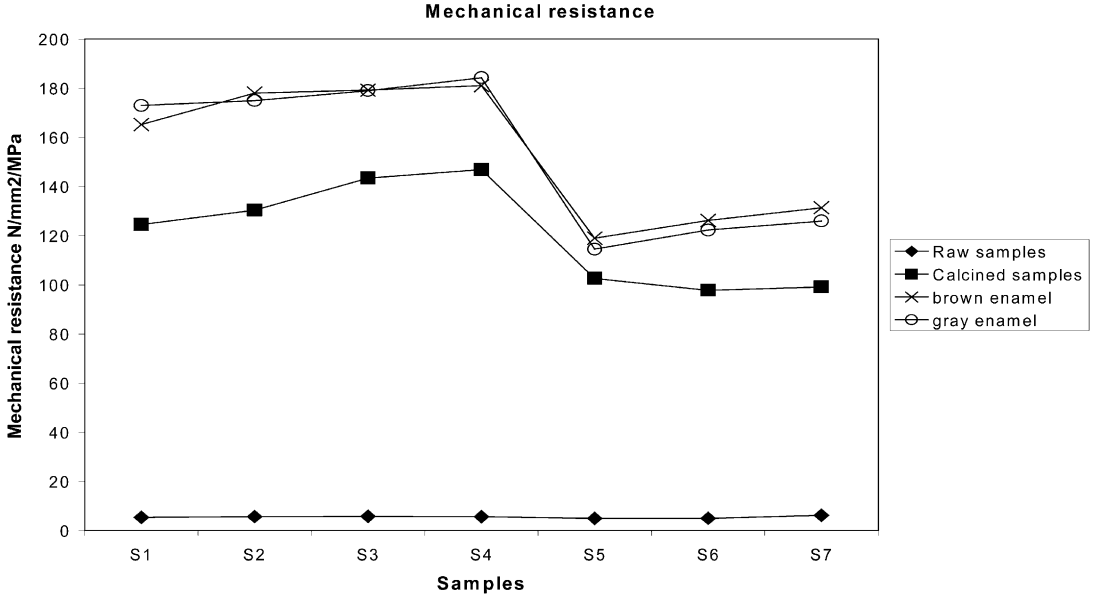

Fig. 3. Mechanical resistance of samples.

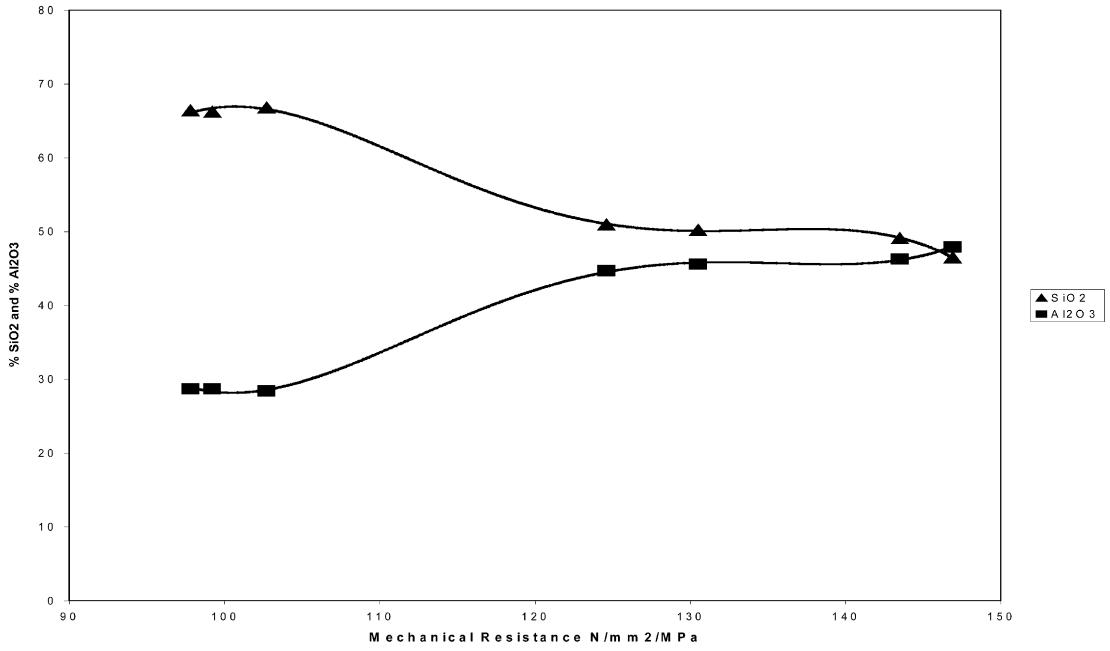

Fig. 4. Mechanical resistance vs content of SiO_2 and Al_2O_3.

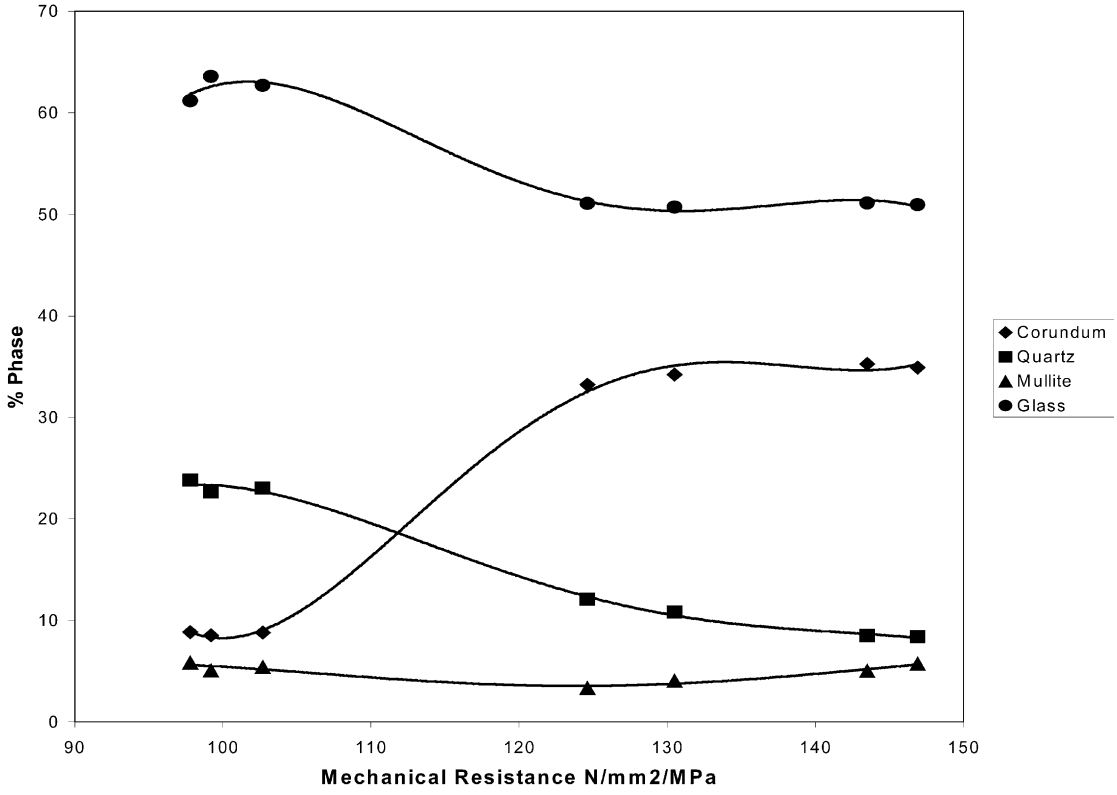

Fig. 5. Mechanical resistance vs content of quartz, corundum, mullite and vitreous phase.

In Fig. 5 it is observed the influence of the content of several phases common in ceramic material have on mechanical resistance. An increase of vitreous phase decreases the mechanical resistance of the sample. This also happens with quartz. Raising the percentage of quartz present in the sample, it decreases the mechanical resistance. Otherwise, increasing the percentage of corundum in a sample, increases the mechanical resistance. By the way, in this case, as the percentage of mullite it is very similar in all the samples, a relationship between the content of mullite and mechanical resistance cannot be established. Nevertheless, from the references, an

increase of the content of mullite[1] should lead to an increase of mechanical resistance.

In general, chemical analysis of studied porcelains does not show important differences in the majority of oxides determined, only percentages of silica and alumina show significant variations in silica and alumina porcelains. This is reflected in the mineralogical analysis performed by X-ray powder diffraction, which results show a minor content of corundum in the silica porcelains being major in the alumina porcelains.

From the dilatometric study it can be concluded that the less vitreous phase in porcelain, the more thermal expansion coefficient. That is because alumina porcelains have major thermal expansion coefficients in all the studied intervals.

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