MORPHOLOGICAL AND STRUCTURAL ANALYSIS OF CERAMIC MATERIALS COMPOSITE BY KAOLINITE AND ALUMINA

ANÁLISIS MORFOLÓGICO Y ESTRUCTURAL DE MATERIALES COMPÓSITOS CERÁMICOS DE KAOLINITA Y ALÚMINA

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ABSTRACT

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In this work, we report the preparation, structural and electrical characterization, morphological analysis and hardness measurements of ceramic materials composed of kaolinite $Al_2(Si_2O_5)(OH)_4$ and alumina Al_2O_3. Samples were prepared from mixtures of precursor oxides starting with 100% alumina and increased the kaolinite concentration on steps of 10% up to complete 100% of kaolinite. The samples were sintered by the method of solid state reaction at temperatures of 1150, 1250 and 1350 °C. We found that the alumina samples are stable at the different temperatures of synthesis. The samples of kaolinite at 100% suffer a change phase depending on the sinterization temperature, noting that at 1350 °C yields 87% mullite and 13% cristobalite. The presence of quartz was only detected in samples with 100% kaolinite for sinterization temperatures of 1150 and 1250 °C. All samples with a mixture of alumina and kaolinite showed the presence of mullite, which is increased when the content of kaolinite is high or when the sinterization temperature is increased. This allows us to infer that the introduction of alumina optimizes the process of mullite formation by their reaction with the SiO_2 that remainder from the kaolinite. The sample with 100% alumina has a Mohs hardness of about 5, and this is increased with the content of kaolinite, until a Mohs hardness of about 6 to the sample with 100% kaolinite. The dielectric constant of these materials is around 27.82.

Key words: Ceramics, kaolinite, mullite, alumina.

RESUMEN

En este trabajo reportamos la preparación, la caracterización eléctrica y estructural, el análisis morfológico y las medidas de dureza de materiales compuestos de caolinita $Al_2(Si_2O_5)(OH)_4$ y alúmina Al_2O_3. Las muestras fueron preparadas a partir de mezclas de óxidos precursores iniciando con 100% de alúmina, la concentración

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de caolinita se fue incrementando en pasos de 10% hasta completar el 100%. Las muestras fueron sinterizadas por el método de reacción de estado sólido a las temperaturas de 1150, 1250 y 1350 °C. Se encontró que las muestras de alúmina son estables a las diferentes temperaturas de síntesis. Las muestras de caolinita al 100% sufren un cambio de fase dependiendo de la temperatura de sinterizado, encontrando que a 1350 °C se produce 87% de mullita y 13% de cristobalita. La presencia de cuarzo fue solamente detectada en muestras con 100% de caolinita para temperaturas de sinterizado de 1150 y 1250 °C. Todas las muestras con una mezcla de alúmina y caolinita muestran las presencia de mullita, la cual se incrementa cuando el contenido de caolinita es alto o cuando se incrementa la temperatura de sinterizado. Esto nos permite inferir que la introducción de alúmina optimiza el proceso de formación de mullita debido a la reacción del SiO_2 que sobra de la caolinita. La muestra con 100% de alúmina tiene una dureza Mohs de aproximadamente 5, y está se incrementa con el contenido de caolinita, hasta alcanzar una dureza de cerca de 6 para la muestra con 100% de caolinita. La constante dieléctrica de estos materiales es de aproximadamente 27.82.

Palabras clave: Cerámicos, caolinita, mullita, alúmina.

1. Introduction

In recent years, the study of ceramic materials has been particularly important because the stability of their mechanical and physical properties at high temperatures which is especially useful for technological applications (**Aksay & Dabbs**, 1991). The development of research on ceramic materials is significant because, among other factors, the metallurgical production worldwide has a projection to decrease, which enables the ceramic to be an adequate substitute for applications based on metals. In some cases the production of ceramics have disadvantages such as large sintered-drying time and high manufacturing costs that prevent processing at industrial level (**Heimann**, 2010). One of the main difficulties on the synthesis of ceramic materials is the use of crucibles which remain chemically stable relative to the material that is produced (**Weber & Thompson**, 1957). For this reason, it is necessary to investigate methods to obtain ceramic materials in a controlled and efficient form, in order to reduce processing time and costs.

In recent decades, research on alumina-silicate ceramic materials has increased especially on mullite. Studies on raw materials, processing, heat treatment and mechanical behavior, among others, have been reported (Carty, 1998). Some of these studies have focused on the production of metakaolin in order to evaluate its performance as a function of the mineralogical composition (48-97%) of kaolinite (Burgoš, 2008). Furthermore, various concentrations of kaolinite have been tried at calcinations temperatures ranging from 700 to 1.600 °C for various heating times to examine the nucleation phenomenon of mullite; and mixtures of kaolinite have been treated with additives like silicic acid and aluminum hydroxide in order to achieve complete conversion to mullite (Schneider *et al.*, 2008). Fabrication of mullite refractory parts has been studied using some binders with aluminum phosphate and chromium, in order to compare the results with those obtained from commercial refractory mullite, clay and alumina (Torres & Mejía, 2007). Moreover, investigations have been developed that seek to create ceramic molds for use in some tests such as directional solidification of aluminum alloys; for which different concentrations of silica, bentonite, kaolinite, feldspar and several process for drying and thermal sintering were used (Rossíni & Arazi, 1970).

In this work we report the synthesis and characterization of structural, morphologic and hardness properties of ceramic materials composed by kaolinite $Al_2(Si_2O_5)(OH)_4$ and alumina (Al_2O_3) using the solid state reaction procedure and X-ray diffraction analysis (XRD), hardness measurements and electrical response.

2. Experimental

Samples were prepared from precursor powder oxides of alumina with substitutions of kaolinite from 0 to 100% (with increments of 10%), which were pressed to form pallets of *2.5 cm* diameter. Samples were dried in air and sintered at *1150, 1250, 1300* and *1350 °C* for *15 hs*. Structural characterization was carried out by using a Panalytical X-Pert PRO MPD diffractometer with CuKα (1,540598 Å). Refinements of the experimental data were performed through the GSAS and PowderCell 2.4 codes. From the X´Pert Highscore semiquantitative concentrations of samples were determined. Polarization curves were measured through a Radiant Technologies Polarimeter.

3. Results and Discussion

Figure 1 exemplifies the characteristic XRD results obtained for several concentrations of kaolinite in the samples sintered at 1350 °C. It can be seen that the intensity of the characteristic peaks of alumina (2Θ = 25.69, 35.16 and 43.43) decreases depending on the amount of kaolinite present in the samples. From the concentration of 20% kaolinite the diffraction pattern reveal the appearance of the characteristic

peaks of mullite (2Θ = 16.47, 26.91, 30.99 and 33.23) (Meng & Peng, 2013). For kaolinite concentrations above 90% traces of cristobalite and quartz are identified in the same angular positions reported for sintering temperatures of 1100 °C (Chen & Lan, 2000).

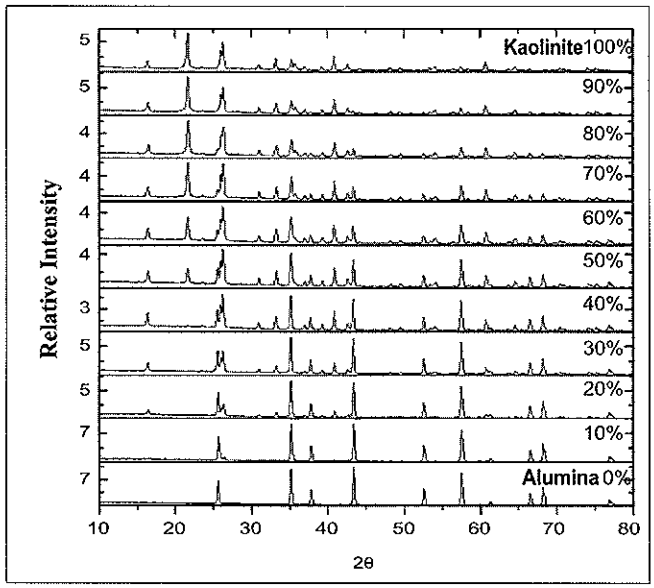

Figure 1: XRD pattern for alumina-kaolinite samples sintered at 1350 °C for several concentrations of kaolinite.

Using the semiquantitative phase analysis for the samples sintered at 1350 °C the weight percentage of the phases as a function of the kaolinite concentration were found as shown in Figure 2. It is observed that the weight percentage of cristobalite and mullite increases with the concentration of kaolinite. For all the sintering temperatures used in this work was determined that the weight percentage of cristobalite increases when we going from 90% to 100% kaolinite, which indicates that some percentage of the alumina reacts with the cristobalite that is produced after the process of mullite nucleation (**Rossíni & Arazi**, 1970). The presence of quartz was only detected in samples with 100% kaolinite for sinterization temperatures of 1150 and 1250 °C.

Also a systematical study of the effect of sintering temperature on the structure of the ceramics was performed as shown in figure 3. Comparing the x-ray diffraction patterns of the mixtures after the compaction and the sintering process is observed the phase transformation from kaolinite to mullite. Note the disappearance of the characteristic peaks of kaolinite (2Θ = 12.41 and 24.97), result that is consistent with those reported by other authors (**Torres & Castelló**, 2011). Figure 4 shows the dependence of the weight percentage of the different phases as a function of the sintering tempera-

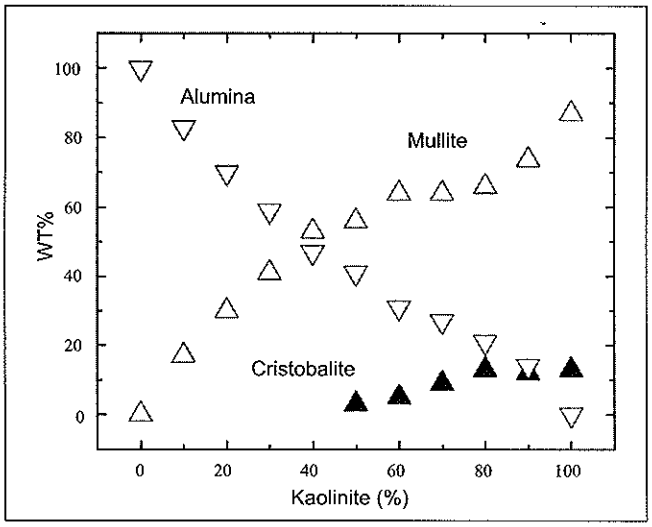

Figure 2: Weight percentage of the phases as a function of the kaolinite concentration for the alumina-kaolinite samples sintered at 1350 °C.

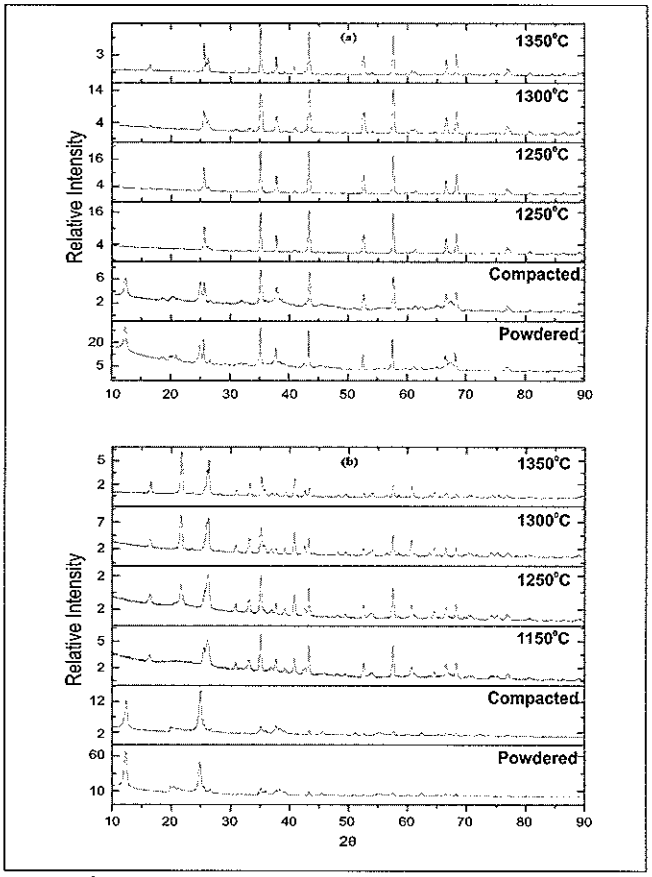

Figure 3: Diffraction patterns of samples prepared at several sintering temperatures for a) 20% and b) 80% of kaolinite. For comparison the patterns of the powdered and compacted samples before the sinterization process are also shown.

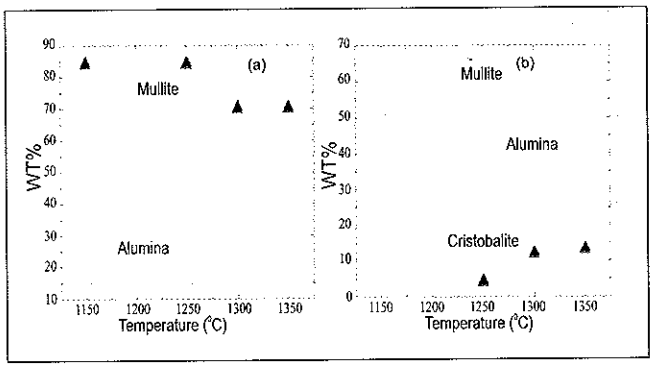

Figure 4: Quantitative analysis of the weight percentage of the phases as a function of the sintering temperature for a) 20% and b) 80% of kaolinite.

ture, for the samples prepared with 20% and 80% kaolinite. For the samples with 80 % of kaolinite was observed that as the sintering temperature increases the mullite concentration increases, which may be due to the presence of cristobalite.

Hardness analysis of these materials was performed by abrasive wear test. For this test we use an experimental setup consisting of a rotating disk with oxide aluminum sandpaper on the top that have 180 granules per square centimeter.

Figure 5 shows in a semi logarithmic scale the abrasive wear as a function of the percentage of kaolinite used for the material sintering at a temperature of *1350 °C*. Notice how the wear resistance of the material is improved as the kaolinite concentration increases. This result can be explained as due to the growth of the weight percentage of mullite and cristoballite when the kaolinite concentration increases, as shown in figure 2.

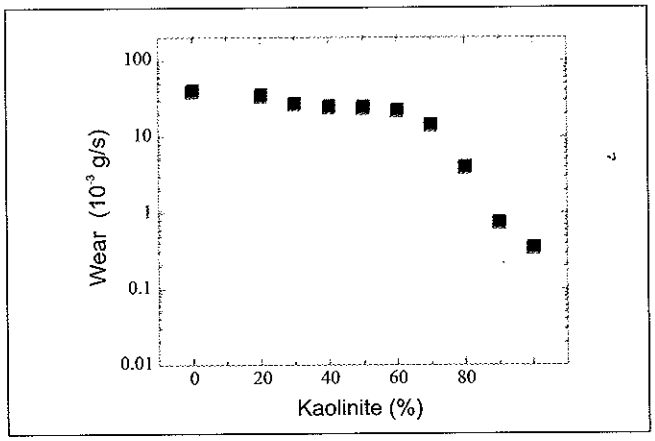

Figure 5: Abrasive wear dependence as a function of the kaolinite concentration. The sintering temperature of the material was 1350 °C.

From a comparative analysis with known hardness materials, we found that the sample with 100% alumina has a Mohs hardness of about 5 which increases with the content of kaolinite, until a Mohs hardness of about 6 for the sample with 100% kaolinite.

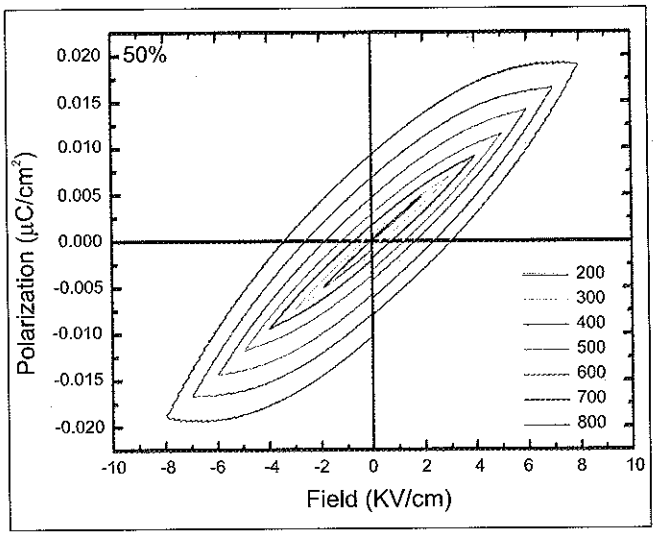

Figure 6: Polarization as a function of the electrical bias field for the sample with 50% of kaolinite, the voltage was changed from *200* to *800 V*.

Table 1: Dielectric constant (ε_r) for each of the voltages used on the measurement of polarization for the sample with 50% of kaolinite. The values of the electric field (E) and the saturation polarization (Ps) of hysteric curves are also shown.

Voltage (V)	E (V/m)*10^5	Ps (C/m^2)*10^{-2}	ε_r
200	1.94	0.005	29.29
300	3.05	0.007	27.61
400	4.02	0.009	27.18
500	5.03	0.012	27.29
600	6.01	0.014	27.78
700	7.01	0.017	27.72
800	7.99	0.019	27.90
Average ε_r		**27.82**	

Figure 6 shows the graph of polarization as a function of the applied field for the sample with a kaolinite concentration of 50%. In this graph are observed hysteresis curves by applying a bipolar triangular signal from *200 V* to *800 V* with *100V* increments. This behavior is evidence of a ferroelectric-like behavior. From the saturation polarization a relative

dielectric constant was obtained for each applied voltage, we found an average of 27.82 as presented in table 1. We notice that the value of the dielectric constant do not varies significantly with the concentration of kaolinite in the samples.

4. Conclusions

The synthesis and structural, morphologic, mechanical and electrical characterization of mullite obtained from alumina and kaolinite precursors were performed. Analyzing the weight percent of the phases present was identified the formation of secondary mullite as result of the transformation of kaolinite in mullite and cristobalite. Hardness test showed that the sintering temperature and the increasing of the kaolinite concentration improve the mechanical properties of the ceramic samples. From the saturation polarization of hysteric curves of polarization as a function of applied fields, the relative dielectric constant for the samples was obtained.

Acknowledgements

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