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The role of C-impurities in alumina dielectrics

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Abstract

This work forms part of an extensive study on the effect of impurities on the structure and dielectric loss in alumina ceramics. In this case, the carbon impurity has been chosen since it can be an important contaminant in fusion reactors. Hot-Pressing at 1500 °C in a carbon rich atmosphere has been found to be a powerful method to introduce carbon in two different alumina powders. Due to the presence of C in the samples, they acquire a black colour. To check the ability of C to penetrate into alumina, microstructure (SEM,TEM) and chemical analyses (ICP-AES and EA) have been performed. The existence of pyrolitic carbon at the alumina grain boundaries in the as-sintered state has been observed. The dielectric properties (permittivity and loss tangent) as a function of frequency (from 0.1 Hz to 20 GHz) and DC conductivity of the sintered material were measured by means of several techniques. The most dramatic effect is that the DC conductivity is strongly enhanced when carbon reaches concentrations higher than about 0.5% wt. Oxidation of these samples by a treatment at 1500 °C in air reduces the C content and restores a white exterior colour. In general this treatment strongly reduces the dielectric loss. Changes between reduced and oxidised microstructures were analysed by SEM.

Keywords: Al_2O_3; Carbon-doping; Dielectric properties; Electric properties; Hot pressing; Microstructure-final

1. Results and discussion

1.1. Sample synthesis and processing

Two pure alumina powders were used in this study:

1. A commercial one, from now on called JP39SD.
2. A synthesized one following the Pechini wet method, called CIT.

Both well characterized powders were placed inside of a highly densified graphite mould and hot press sintered at 1500 °C and $4.7 \cdot 10^4$ N/m^2 during an hour in a rotary pump vacuum atmosphere. Pressure was applied in steps of 5200 N/m^2 from 1200 °C during temperature increase. The borders and regions in contact with the graphite moulds were removed, leaving a sample of 30 mm in diameter from the rod centre and 2–3 mm in thickness.

1.2. Analytical results

The carbon content of final samples was analysed by the combustion-IR absorption method, using a Leco CS-244 and Carlo Erba EA 1108.

These analyses reveal that a significant amount of carbon was introduced inside the whole alumina sample. Carbon content is clearly dependent on powder characteristics, since CIT samples allow the incorporation of much less carbon than the JP39SD ones. The same analyses were performed on samples after being oxidized at 1500 °C during 10 h in air. Carbon content was observed to decrease (recovery of the characteristic white colour of alumina on surfaces is observed), but a detailed carbon analysis indicates the existence of carbon still deep inside the sample. All these data appear in Table 1. It must be mentioned that the analyses include a portion of the whole sample (from surface to centre) and therefore represent average values (this is relevant in the case of oxidised samples).

1.3. Microstructure

1.3.1. SEM study

The surfaces of polished samples, thermally etched (15 min at 1450 °C) were studied with the aid of a SEM [JEOL 6400]. JP samples present a microstructure of

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Table 1
Carbon contents (% weight) in the samples before and after oxidation

	CIT	JP39SD
Sintered	0.24	0.77
Oxidized	0.07	0.31

very small rounded grains (around 500 nm) (like Fig. 1) compared with the polygonal 6-μm grains shown on CIT samples (see Fig. 2).

1.3.2. TEM study

XEDS spectra obtained from inside alumina grains, grain boundaries and triple points, showed the presence of carbon agglomerates at the grain boundaries and triple points.[1] The same analysis revealed the absolute absence of carbon inside the alumina grains. We have also been able to determine the exact structure of the carbon previously observed by SEM. Results indicate that while graphitic carbon is observed at grain boundaries, pyrocarbon structure is observed at triple points.[1] Carbon clusters are also present in some alumina grains surfaces.

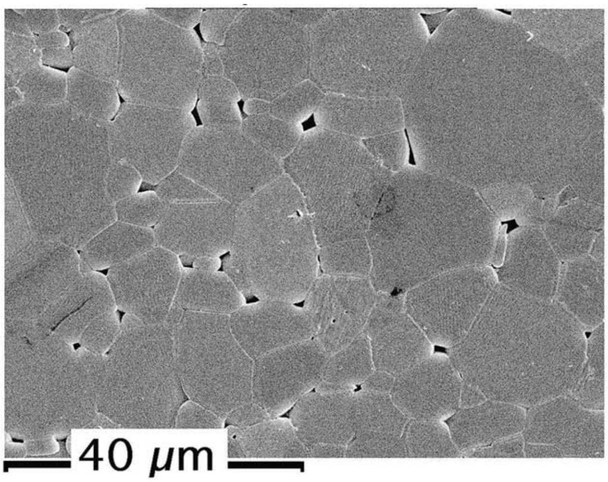

Fig. 1. SEM microstructure of the CIT sample after hot pressing and oxidation at 1500 °C.

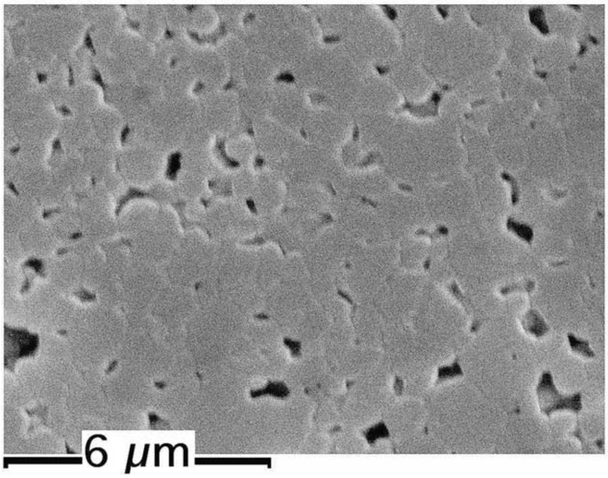

Fig. 2. SEM microstructure of the JP39SD sample after hot pressing and oxidation at 1500 °C.

It is worth noting that in all the samples their grain size increases after the long oxidation treatment, as a result of the loss of the grain boundary phase and the grain re-sintering through boundary diffusion.

1.4. Density

Density was calculated from sample water immersion data following the Archimedes immersion technique.[2] Due to the best powder compressibility, CIT alumina samples have reached almost the theoretical density (TD), with a mean value of 99.8% TD, while the JP39SD hot-pressed ceramics present densities around 97% TD. After the oxidation treatment, in both materials their densities decrease, although the CIT structure keeps much more dense (98% compared to 90% TD on JP39SD samples). Porosity remains at triple points, indicating the existence of an active movement of grain species through the grain boundaries to refill the volume left after carbon elimination.

1.5. Conductivity

Conductivity was measured in static air (closed system) by means of a two electrodes system up to 500 °C at a heating rate of 4 °C/min.

Fig. 3 shows the obtained values for samples, before and after oxidation. The most outstanding result is that for the higher C content sample (JP39SD) the conductivity is many orders of magnitude higher than in the other cases, and it does not follow a thermally activated behaviour.

It is also worth noting that heating and cooling curves can be quite different. The highest difference appears precisely in the JP39SD sample. When the sample reaches a temperature above 450 °C the conductivity drops rapidly and this decrease continues at the constant temperature of 500 °C. This change is permanent; therefore the cooling curve is different from the heating one. For that reason both curves are shown in the Fig. 3. The change can be attributed to the sample surface oxidation. In the Differential Thermal Analysis (DTA) curve, two peaks are obtained; one around 350 °C and the other around 1300 °C (heating at 1 °C/min). Therefore, the carbon loss seems to occur in two steps. The first peak would then correspond to the large change observed in the conductivity and would be associated to the burning of carbon weakly bound to the alumina. In the CIT sample the same process takes place, but at a lower scale.

Another very important point is that conductivity (σ) is a non-linear function of C content. If we take as a

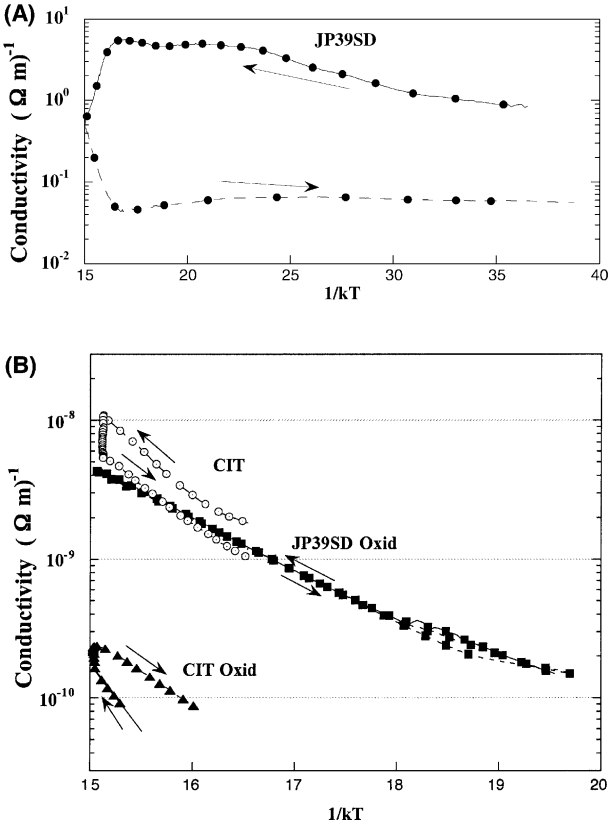

Fig. 3. Conductivity up to 500 °C of carbon-doped samples as a function of the inverse of temperature. The heating and cooling cycles are indicated by arrows. (A) Hot pressed JP39SD; (B) oxidised JP39SD (squares), hot pressed CIT (circles) and oxidised CIT (triangles). Note the differences in vertical and horizontal scales.

reference the σ value near 450 °C, we can see in Fig. 4 that there is a small increase of σ from 0.07 to 0.31% C and a very large one (around eight orders of magnitude) from 0.31 to 0.77%. If we consider values of σ obtained in other samples doped with C and Cr simultaneously[3] (and taking into account that Cr almost does not change DC conductivity at these temperatures) we obtain that between 0.4 and 0.5% an abrupt change occurs, indicating very probably a percolation process.

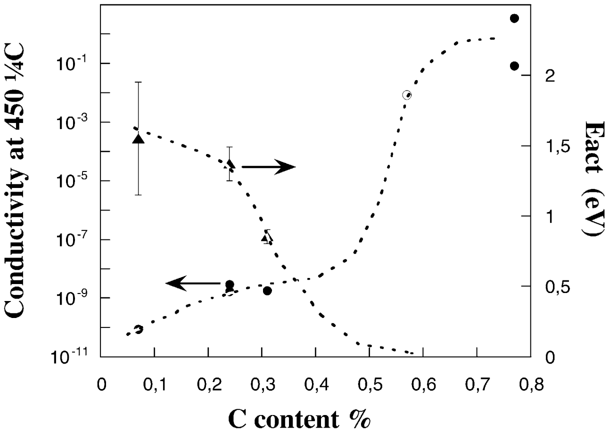

Fig. 4. Conductivity at 450 °C (triangles) and activation energy (circles) of carbon doped alumina samples as a function of their carbon content. The open circle represents a sample doped with carbon and chromium.

The high temperature side of the conductivity curves have been fitted to Arrhenius curves to obtain the activation energy of each process. The result is also plotted in Fig. 4. Some reduction is observed with carbon content (or σ value). In the JP39SD case, no value can be obtained since a strong decay of σ occurs, as explained above.

1.6. Dielectric measurements

Hot pressed and oxidised samples were dielectrically characterised as a function of frequency using as much as possible dielectric equipments.

Microwave frequency measurements of the dielectric properties are based on resonant methods by using closed cylindrical resonant cavities. Sample permittivity and loss tangent are obtained from the comparison of the resonant characteristics with and without the sample inside a 30-mm diameter copper cavity.[4] At optimum conditions, this system allows the determination of permittivity, and loss tangent with values down to about 10^{-5}, with an error less than 0.1 and 10%, respectively. To reach these limits, samples were carefully grinded with the aid of a 15-μm diamond paste to assure a surface flatness and thickness error better than 10 μm.

The half-power-gap variation method[5] was used at frequencies below 100 MHz by using a commercial equipment (DPMS-1000, Japan E&M). It is a resonant technique in which the response of a resonant circuit is measured when the sample is between the parallel plates of a condenser and compared with the same measurement without the sample. This system allows us to measure loss tangent values as low as 3×10^{-6} with a precision better than 0.5% and permittivities better than 5%.

Finally at lower frequencies, a Chelsea Dielectric Spectrometer was used to perform the experiments from about 10^{-2}–10^{4} Hz. The measurement is based in the phase delay of the signal incident on a sample, placed between parallel electrodes, with respect to a reference signal. It has a higher limit in loss tangent, so in some of the samples used the measurements were not possible.

The obtained values of loss tangent for samples, before and after oxidation, are shown in Fig. 5. It must be noted that for C concentration higher than about 0.5% the samples cannot be measured in our resonant systems since they behave like a low value resistor.

Contrary to conductivity, the correlation of loss tangent with carbon is not so obvious. There is clearly a large enhancement of loss for the two highest carbon values (JP39SD sample), but in the case of CIT, almost no change is observed when oxidizing the sample. The reason could be established in the fact that even a quite

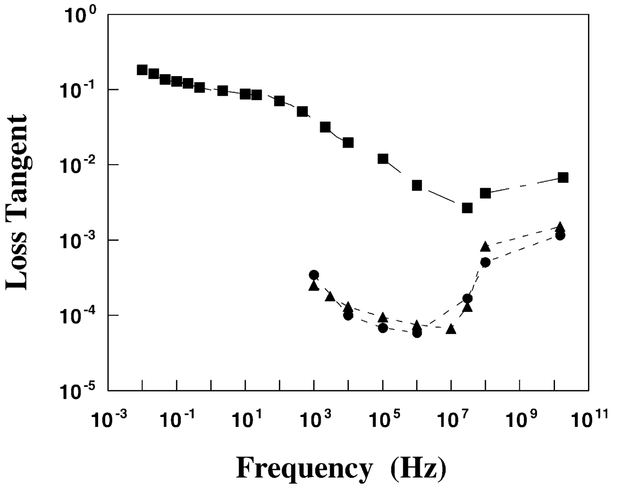

Fig. 5. Loss tangent as a function of frequency of JP39SD (squares), CIT (triangles) and oxidised CIT (circles).

thin oxidized layer (high resistivity) greatly reduces the conductivity (series-circuit), however, for loss tangent (AC process), the carbon-rich core still contributes to a large extent to the total loss. This is so because, in this region, the carriers can follow the external AC field even surrounded by the insulating layer. In other words, the loss tangent represents an average of contributions, whereas in the DC conductivity case the highest resistance control the final conductivity.

Looking at Fig. 5, we can see that even at carbon concentration where the sample is black, we can obtain values of loss in the range of 10^{-4} in the MHz's region. When C content rises, the loss spectrum undergoes a large degradation at very low frequencies extending to higher ones.

2. Conclusions

- Doping alumina with carbon has been achieved by hot pressing two quite different powders.
- Very low diffusion and surface re-sintering limit oxidation of the samples to the surface.
- Carbon content correlates more closely with DC-conductivity than with dielectric loss.
- A percolation effect for values higher than approximately 0.5% of carbon content causes a dramatic increase in conductivity.

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