HIGH-FREQUENCY FIELD FIRING OF CERAMIC MATERIALS

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Firing is the heaviest energy consumer and lengthiest process in making ceramic components. Ovens currently used have low efficiency and cause stoichiometry deviations in ceramic materials because the firing is lengthy. It is therefore important to develop new firing methods. A nontraditional method is heating with UHF and HF fields [1]. An advantage over traditional methods is that the UHF and HF radiation is directed at the ceramic material, which increases the firing rate (the firing rate is reduced by factors of ten or more), while the costs of the equipment are reduced and it is possible to make materials having unusual properties [1].

Here we report experiments on firing various ceramics with an HF field. We used a standard VChD6-2.5/81 apparatus, which had power 2.5 kW at 81.36 MHz. The specimens were disks 10 mm in diameter and 2-3 mm thick, pressed at 150-250 MPa.

The specimens were placed in a crucible and covered with Al₂O₃ powder to reduce the heat loss. The crucible containing the specimens was then placed in the cavity and heated to the sintering temperature with an HF field (Fig. 1). The temperature was measured with a pyrometer. The pyrometer measured the temperature of the crucible containing the specimens, so the temperature of the specimens was higher than that measured by the pyrometer because the outer surface of the crucible was cooled by the air.

The specimens were perovskites (BaTiO₃ and CaTiO₃) and solid solutions based on them (BC-1 and THC-2500), together with high-alumina ceramics (BK-94 and BK-100), and a ceramic based on zirconium dioxide. The second group was chosen on the basis that the firing is performed at fairly high temperatures (1600-1800°C) and they are very important in constructional ceramic components.

Some of the firing results for perovskite materials and solid solutions based on them have been given in [4, 5]. Here we consider some properties of these specimens in more detail. Firstly, the materials in one group (BaTiO₃ and CaTiO₃) sinter in different ways. CaTiO₃ has the higher firing temperature in ordinary thermal sintering, whereas we found with the HF
treatment that CaTiO$_3$ sinters more readily than BaTiO$_3$. The CaTiO$_3$ specimens had residual porosity 2%, as against 15% for BaTiO$_3$. As the specimens were sintered at 1280°C, which is insufficient to sinter CaTiO$_3$ (usually, CaTiO$_3$ is sintered at 1400°C), that result is surprising.

The reason appears to be as follows. The value of tan $\delta$ increases with temperature, and the rise in loss in CaTiO$_3$ is much greater than that in BaTiO$_3$, so the CaTiO$_3$ is heated to a higher temperature. As the specimens were in a crucible, the temperature difference between a specimen and the wall was greater for CaTiO$_3$ than BaTiO$_3$. The sintering conditions were substantially disrupted. While the BaTiO$_3$ was sintered virtually throughout its volume, the CaTiO$_3$ began to sinter at the center of the specimen because of the greater heat transfer, and this then extended to the outer surface. One has as it were sintering in reverse.

When the structure of the ceramic has formed, the HF absorption decreases sharply [4, 5], so the firing of the CaTiO$_3$ continues longer. This is as was observed. The BaTiO$_3$ specimens sintered in 5-10 min, whereas the CaTiO$_3$ ones took 15-20 min. This would explain the low residual porosity in the CaTiO$_3$. The density of the BaTiO$_3$ ceramic differed by 2.5% from theoretical, whereas that of the CaTiO$_3$ ceramic differed by 8%.

The history has a considerable effect on the physical properties. For example, BaTiO$_3$ specimens made by the oxalate method sintered much more rapidly than ones made thermally from BaCO$_3$ and TiO$_2$. No changes in stoichiometry were observed. In that case, the porosity was much higher (about 40%) because various reactions may occur in such materials, which in the ordinary case are retarded [3, 6]. This is confirmed indirectly by the fact that there are substantial changes in the electrophysical parameters [4].

BK-94 and BK-100 materials sinter in an HF field at a temperature lower than in the ordinary method. The temperature of the crucible containing the specimens as measured by the pyrometer was 1340°C. For comparison, the temperature of the crucible containing ZrO$_2$ specimens was 1460°C. The sintering mechanism in the HF field clearly differs from the traditional one [1]. The density of Al$_2$O$_3$ specimens was 3.4 g/cm$^3$, while for ZrO$_2$ it was 5.3 g/cm$^3$. The porosities as determined by water uptake were 10 and 17% respectively.

The increased porosity and reduced density are due to the low sintering temperature. However, x-ray measurements showed that the Al$_2$O$_3$ ceramic had a cubic lattice, while the ZrO$_2$ ceramic, 60% of the volume was occupied by a phase having tetragonal symmetry. This shows that sintering has occurred because the structures of the initial powders were different. Also, the 60% content of tetragonal ZrO$_2$ shows that the sintering in an HF field enables one to obtain structures difficult to make in the usual way.

These studies show that one can sinter various ceramic materials in an HF field at 81.36 MHz.

REFERENCES