# Centrifugal sintering of BaTiO$_3$/Ni layered ceramics

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## Abstract

Centrifugal sintering is an advanced technology that is specifically designed to sinter structures under constrained conditions, such as films on substrates and multi-layered ceramics. This technology consists of loading high centrifugal acceleration more than 100 km/s$^2$ onto specimens and heating. Owing to the distinctive pressing measure, pressing without molds, and anisotropic shrinkage during sintering are achieved. This process has been found to be a successful strategy for eliminating shrinkage mismatches in multi-layered ceramics, leading to a crack-free homogeneous microstructure. This distinctive feature of centrifugal sintering arises from anisotropic shrinkage that is caused by chief densification progress along the radius of rotation.
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## 1. Introduction

Ceramic parts tend to be downsized towards further improvement of properties, which is especially apparent in the electric device application. Among the application, ceramics components are sintered on substrates or with other components such as electrodes. Because of the other components, sintering of ceramics progresses under complicated stress conditions. Normally, sintering is accompanied by a linear shrinkage ratio larger than 10%. Hence, the shrinkage mismatch between ceramics and other materials is the main reason for the occurrence of residual stress. In most cases, these stresses cannot be released during sintering, leading to crack formation or de-lamination.[1] One approach to avoid the formation of these macro defects consists in controlling the viscous nature of sintering.[2] The common procedure for the control in industry is to mix a glass phase with ceramic powders. Other method is to apply external pressure, which was demonstrated by applying centrifugal force in the present study. The later is advantageous to obtain pure thick films without glass phase. Conventionally, the pressure

sintering has been carried out using molds that frequently cause surface reaction. On the contrary, centrifugal pressing utilizes the body force arising from the mass of the components, which is effective to minimize solid contact with other materials.

In this paper, trial results of centrifugal sintering of layered ceramics are reported.

## 2. Experimental

### 2.1. Equipment

Fig. 1 shows the schematic of the equipment used. Specimens are placed in a ceramic rotor, which rotates up to 20,000 rpm. The radius of rotation is 80 mm, which results in a maximum acceleration of $\sim$350 km/s$^2$. The maximum rotation is limited by the resonance of the rotor, which is a function of its Young's modulus, mass and configuration. High Young's modulus and low density are desirable material properties to achieve high rotational speed. Therefore, ceramics are good candidates for the rotor material. Furthermore, high tensile strength at high temperature is required. Based on the above requirements, Si$_3$N$_4$ and SiC are adopted for the rotor material. In our design, the rotational number
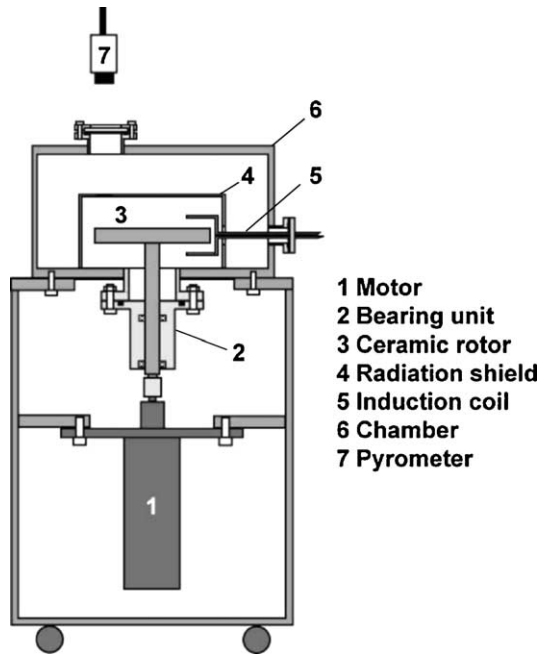
Fig. 1. Schematic of centrifugal sintering equipment.

1 Motor
2 Bearing unit
3 Ceramic rotor
4 Radiation shield
5 Induction coil
6 Chamber
7 Pyrometer

of resonance is settled at ∼30,000 rpm. Heating is carried out by an induction heating. The maximum temperature is 1000 °C. Temperature is monitored by a pyrometer. A chamber is kept airtight, so that an atmosphere of $N_2$, Ar or vacuum can be available during sintering.

### 2.2. Procedures

In order to clarify the effect of centrifugal force on constrained sintering, sintering of laminated ceramics was performed. Here, $BaTiO_3$ (Koujyundo Chemical Laboratory Co. Ltd., 99.9% purity, 1 μm) and Ni (Koujyundo Chemical Laboratory Co. Ltd., 99.9% purity, 2–3 μm) powders were sheet-casted and stacked alternately. In addition, LiF (Koujyundo Chemical Laboratory Co. Ltd., >99.9% purity) and $BaCO_3$ (Koujyundo Chemical Laboratory Co. Ltd., 99.95% purity) were added to $BaTiO_3$ to achieve low temperature sintering.[3] The amount of additives was weighed to be $BaCO_3$ of 2 mol% to that of $BaTiO_3$, and LiF of 0.5 wt.% to that of a mixture of $BaCO_3$ and $BaTiO_3$. The layers were fabricated by sheet casting in which slurry was prepared mixing with poly vinyl butyral (PVB) and dibutyl phthalate (DBP) in an ethanol medium. The solid loading of the slurry was adjusted to be 20 vol.%, and the content of the binder was 40 vol.% to the volume of the powder. Here, the volume ratio of PVB and DBP was chosen to be 2:1. After drying, the thickness of the sheet was found to be 60 μm. These sheets were layered and then warm-pressed under 10 MPa at 100 °C. Finally, the thickness of green compact became 1.3 mm. Those compacts were subjected to centrifugal sintering where sintering temperature of 1000 °C was maintained for 20 min in vacuum. Applied centrifugal acceleration was

87 km/s$^2$ generated by rotational number of 10,000 rpm. Meanwhile, the pellets of each powder were sintered with or without centrifugal acceleration, in which the sintering temperature was varied from 700 to 1000 °C and held for 20 min. Here, the centrifugal acceleration was set also to be 87 km/s$^2$. Archimedean method and dimensional measurement were adopted to analyze sintering behavior, and SEM observation was performed for microstructural analysis.

## 3. Results and discussion

Sintering curves of $BaTiO_3$ and Ni are shown in Fig. 2. In the case of $BaTiO_3$, full densification was almost achieved above 900 °C, which was a result of liquid formation at low temperature due to the addition of LiF, which forms a liquid phase above 610 °C. This densification behavior was in good agreement with a previous report.[3] There was no clear difference in sintering curves between centrifugal sintering and conventional sintering. In the case of Ni sintering, densification improvement by several percents was observed for centrifugal sintering compared to conventional sintering. The difference in the effect of centrifugal acceleration was possibly caused by the difference in their densities: $BaTiO_3$ of 6.0 g/cm$^3$ and Ni of 8.9 g/cm$^3$. Based on the density difference, the maximum pressure for these pellets was estimated to be 0.9 and 1.3 MPa for $BaTiO_3$ and Ni pellets, respectively. Although the densification curves were almost similar between centrifugal sintering and conventional sintering, the liner shrinkage behavior was quite different between them as shown in Fig. 3. For conventional sintering, shrinkage occurred homogeneously, while anisotropic shrinkage was observed for centrifugal sintering. The anisotropy in shrinkage is caused by uni-axial pressing promoted by the centrifugal force. These results indicate that the applied centrifugal force was not strong enough to enhance sintering, yet it was enough to promote the rearrangement of particles. Importantly, shrinkage along the tangential direction of rotation was maintained below 10%, and shrinkage mismatch between $BaTiO_3$ and Ni was kept below 5%. In contrast, conventional sintering showed the mismatch of ∼10%. Therefore, co-firing of both materials is difficult for conventional sintering. To overcome such large mismatch in conventional sintering, shrinkage adjustment is carried out by adding a second phase.[4] However, additional phases, which might result from unwanted reactants leading to deterioration of properties should be into consideration.

Sintering of thick films has similar problems. These include crack formation and separation of film from the substrate. In this case, shrinkage adjustments are not very effective. The way to achieve one-dimensional shrinkage, i.e., no shrinkage along the parallel direction to the surface of substrate, is substantial solution. Application of centrifugal sintering might be one option. So far, it was confirmed that the acceleration of 87 km/s$^2$ was beneficial to suppress macro defects of copper film with a thickness of 20 μm.[5]
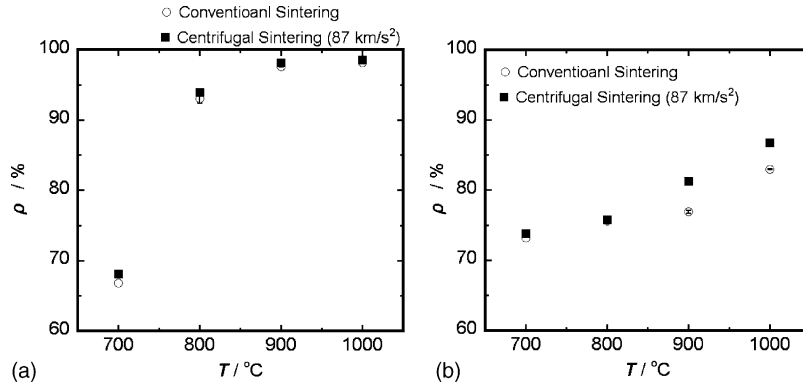
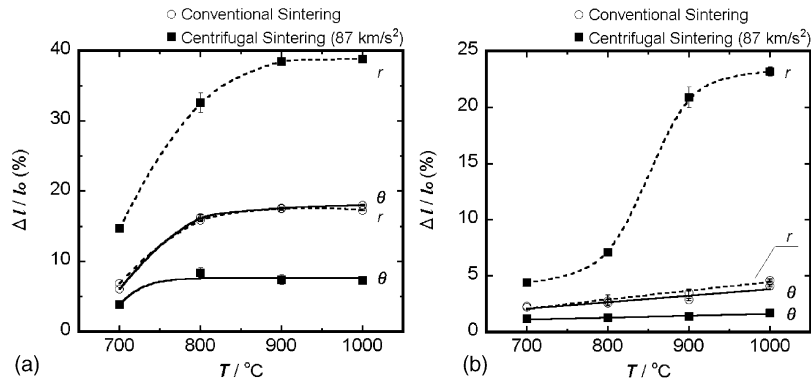Fig. 2. Sintering curves of (a) BaTiO$_3$ and (b) Ni as a function of firing temperature.



Fig. 3. Linear shrinkage, $\Delta l/l_o$, of (a) BaTiO$_3$ and (b) Ni as a function of firing temperature, $T$. Shrinkage direction is denoted as $r$ and $\theta$ indicating radius and tangential directions, respectively.
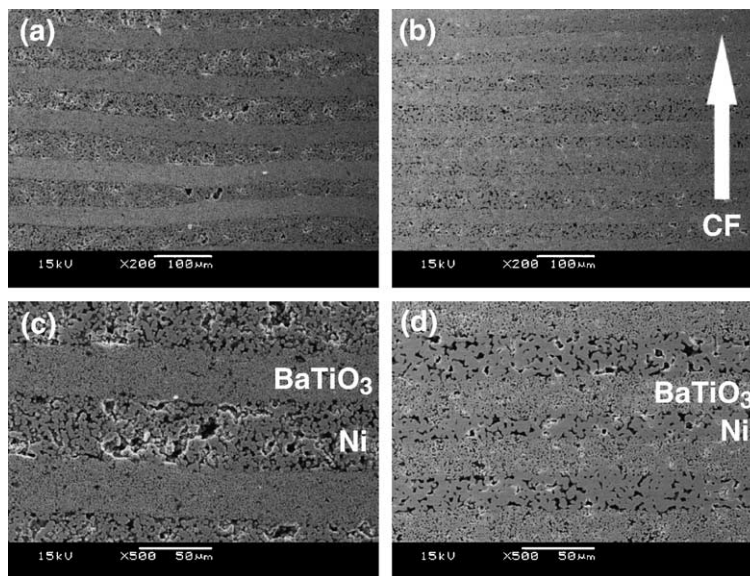


Fig. 4. Microstructure of multi-layered ceramics. (a) and (b) show the microstructure of ceramics by conventional sintering and centrifugal sintering, respectively. (c) and (d) are enlarged parts of (a) and (b), respectively. Arrow in (b) indicates the direction of centrifugal acceleration.

The advantage of centrifugal force as mentioned above was confirmed by the sintering of layered ceramic components. Here, $BaTiO_3$ and Ni were co-fired. The microstructure of the cross-sectional area is shown in Fig. 4. In comparison with a SEM photograph of conventional sintered specimen (Fig. 4a), all of the layers sintered under centrifugal force showed homogeneous microstructure. On the contrary, conventional sintered specimen included large pores with a crack-like shape, which was a result of constraint due to a shrinkage mismatch between both layers.

## 4. Summary

Ceramics processing assisted by centrifugal acceleration has been demonstrated for constrained sintering. In the constrained sintering, shrinkage mismatch between materials inherently causes macro-defects such as crack or de-lamination. It was found that those macro-defects were suppressed by applying the centrifugal acceleration during firing. This advantage of centrifugal sintering originates in anisotropic shrinkage in which densification mainly proceeds from a shrinkage in the direction of radius of rotation. Hence, layered ceramics settled in perpendicular to the radius direction does not shrink in lateral direction, leading to less shrinkage mismatch between the layers.

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