

Thermal and Structural Properties of Ultra Low Thermal Expansion Cordierite Ceramics

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Abstract

The important crystallographic properties of cordierite are its low thermal expansivity and an anisotropy of thermal expansion coefficient. These properties are also durable against the thermal changes of environment, Krosaki Harima Corporation designed the ceramics, NEXCERA™. Some microscopic experiments have been carried out from different angles of view for the purpose of clarifying a reason to cause the thermal characteristics of this ceramics. An in-situ X-ray powder diffraction experiments under low to high temperature, demonstrate the low expansivity of cordierite lattice parameters. Volume fraction of cordierite in the cordierite ceramics composed of cordierite and interstitial amorphous phase is almost ninety percent estimated with backscattered electron images (BSE) images using Scanning Electron Microscope (SEM). By taking the thermal expansion coefficient and the volume fraction into consideration, the possibility that the thermal expansion of cordierite is suppressed by the existence of the amorphous is suggested. In addition, the amorphous phase may affect the change in the volume thermal expansion of the whole ceramics.

Key Words: Cordierite, Ceramics, Low thermal expansion, Volume fraction, NEXCERA™

INTRODUCTION

Characteristic properties of cordierite are well known as, i) ultra low thermal expansion and ii) anisotropy of the thermal expansion coefficient (Hochella Jr. et al, 1979, Ikawa et al., 1986). For these thermal properties, they are durable against high temperature and/or thermal change of environments. And a cordierite based polycrystalline ceramics, NEXCERA™, enables very high precision measurement when this ceramics is used as a material of an instrument. NEXCERA™ has been developed as a cutting edge material with almost zero thermal expansion coefficient around the room temperature and superior mechanical properties (Nose et al., 2001).

In order to develop these excellent thermal properties, NEXCERA™ has been analyzed with several points of view, i) the thermal expansion properties within extended temperature range, ii) characteristics of microstructures using analytical electron microscope and SEM, and iii) finding an improved sintering conditions.

The purpose of present study is to acquire fundamental data which will be fed back to improve the ceramics making full use of characteristics of cordierite.

THERMAL EXPANSIBILITY

The textural change of cordierite and interstitial amorphous phase was not found in situ experiment of high temperature transmission electron microscopy (TEM) up to 800°C. Only the diffraction contrast of cordierite slightly changes during experiment (Toh et al., 2011). This result suggests that a small amount of lattice modification. In order to examine the temperature range in which the thermal expansion coefficient is almost zero, the high temperature X-ray diffraction (XRD) have been carried out.

In the present study, XRD experiment was carried out on a powder and a bulk sample. A powder sample was prepared by crushed bulk sample using an agate mortar, then the powder of the small particle size (2-5 μm) was separated by elutriation. A bulk sample experiment was using thinned and polished specimen. The XRD measurements were carried out using a Rigaku Ultima IV diffractometer with heating and cooling specimen stage. The main experimental conditions are listed in Table 1. After taking the XRD pattern the Rietveld analysis with RIETAN-FP software (Izumi and Momma, 2007) was applied for refinement of lattice parameters.

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Table 1. Main experimental conditions of X-ray diffraction

Voltage (kV)	40
Current (mA)	40
Scan range (deg)	4 - 80
Temperature range (°C)	-150 - +1200
Heating rate (°C/min)	10
Specimen heating apparatus	Rigaku SHT-1500

Figures 1 and 2 show examples of the results both of the XRD pattern measured at 25°C and the Rietveld analysis of a powder sample and that of a bulk sample, respectively. In each figures, the top pattern is XRD intensities and the below one shows residual substances of the fitting by the Rietveld analysis. The results of the analysis indicate that

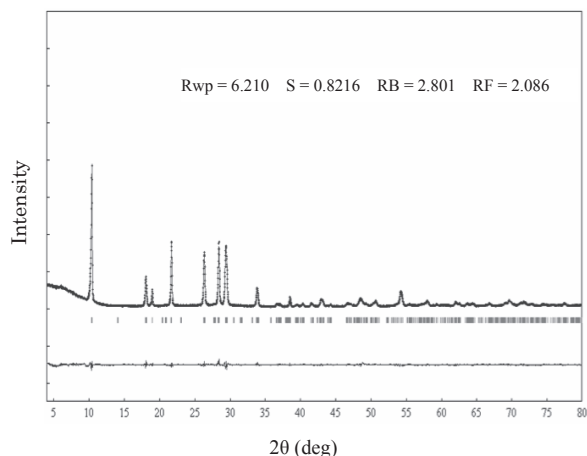


Figure 1. An example of result of the XRD and the Rietveld analysis of the powdered sample measured at 25°C. The top pattern is XRD intensities and the below one shows residual substances of the fitting by the Rietveld analysis.

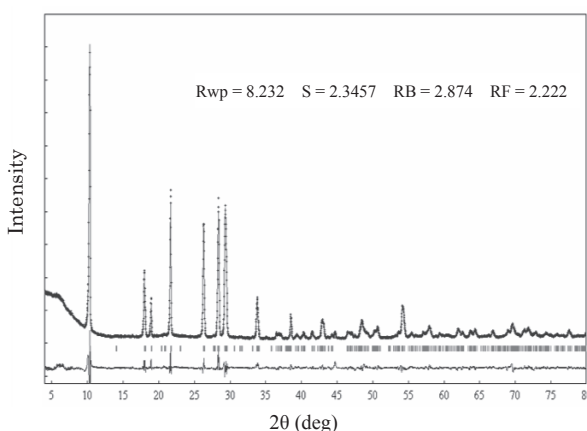


Figure 2. An example of result of the XRD and the Rietveld analysis of the bulk sample measured at 25°C. The top pattern is XRD intensities and the below one shows residual substances of the fitting by the Rietveld analysis.

the value RB and RF , which are factors reflecting the accuracy of the crystal structure parameter adopted by the present simulation, are low enough and imply that the fitting goes well in both cases. On the other hand, the value R_{wp} of the bulk sample showed clearly higher value (8.232) than that of powdered sample (6.210). This is more likely to be caused by the diffraction intensities of the bulk sample being higher than the powdered one. Since the S value, that is a substantial fitting parameter, is approximately one in the case of the powdered sample, the fitting was performed with high precision. In contrast, it may be necessary to take more examination of a crystal structure parameter, because the S value of the bulk sample was a relatively high.

In the present article, the value of thermal expansion shown in figures 3, 4 and 5 are normalized against the lattice parameters at 25°C.

The changes of lattice parameters along a , b and c -axis of the powder and the bulk samples are shown in figures 3 and 4, respectively. In the case of powdered sample, the length along the a - and b -axis increases with heating and that of c -axis decreases (Fig. 3). These tendencies are consistent with the real cordierite measured by XRD (Ikawa et al., 1986) and MD simulation (Miyake, 2005). In the case of bulk sample, the length along the a - and b -axis also increased with heating although a slight drop are seen at 400°C and that of c -axis shows decrease slightly (Fig. 4). The tendency of the temperature change is similar in both type of samples, but the values of expansion coefficients are slight different. These results indicate that the variation in thermal expansion coefficient of cordierite in the bulk sample is smaller than that of the powdered sample.

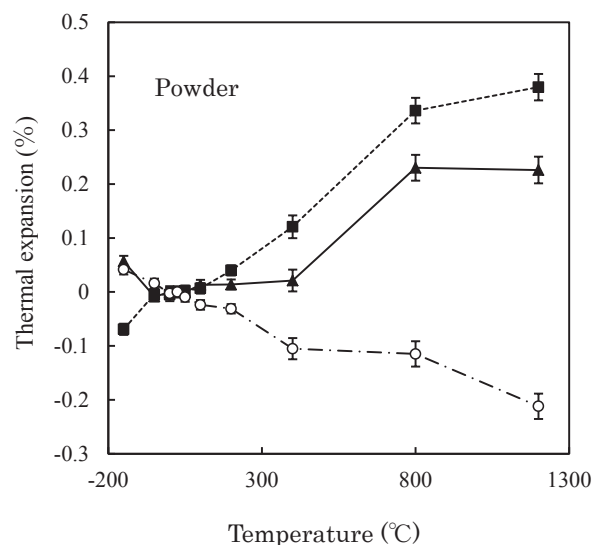


Figure 3. Change of the thermal expansion along a - (▲), b - (■) and c -axis (○) for a powdered sample.

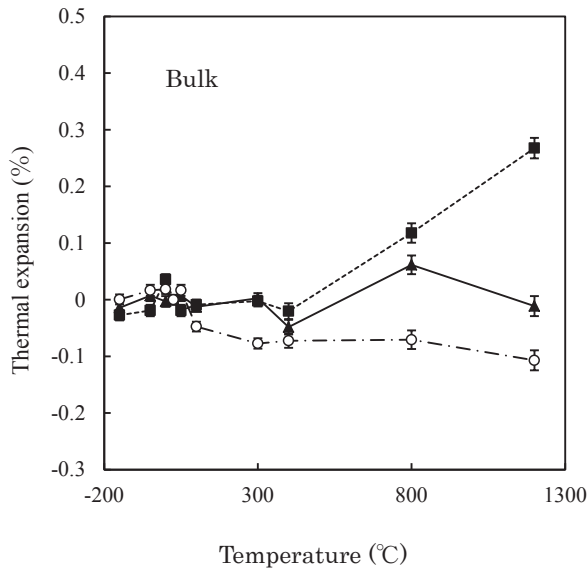


Figure 4. Change of the thermal expansion along *a*- (▲), *b*- (■) and *c*-axis (○) for a bulk sample.

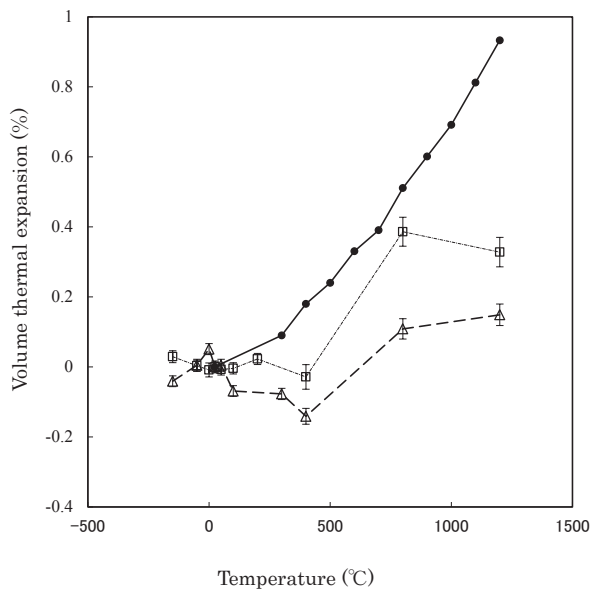


Figure 5. Change of the volume thermal expansion of macroscopic specimen (●), cordierite in powdered sample (□) and bulk sample (△).

Figure 5 shows the volume thermal expansion of macroscopic ceramics specimen, cordierite in the powdered sample and cordierite in the bulk sample. The result of a macroscopic measurement of the ceramics shows monotonous increase. That of powdered sample and bulk sample also increases with heating although slightly decrease at 400°C and 1200°C for powdered sample and 100°C, 300°C and 400°C for bulk sample. This figure shows that volume thermal expansion of cordierite in the bulk sample tends to be smaller than that of the powdered sample. Furthermore, volume thermal expansion of powdered sample is similar to the macroscopic measurement data.

VOLUME FRACTION

The microtexture of NEXCERA™ using TEM and SEM become clear that this ceramics is mainly composed of cordierite crystals of about 1-3 μm in diameter and amorphous is distributed as interstitial phase. In order to evaluate the effect of the amorphous phase on thermal expansion properties, a volume fraction between cordierite crystals and amorphous phase has been measured. In the present study, NEXCERA™ that has been sintered under atmospheric condition was measured.

Twenty-one BSE images were taken using Zeiss ULTRA 55 SEM in the EsB (Energy selective Backscatter) mode. As an example, one of these images is shown in Figure 6. In this figure, gray regions show cordierite, and white regions are amorphous phase. Since the images taken by the EsB mode are insensitive to the surface structure, the texture, which reflected only a difference in the chemical composition, can be shown in these images. The binarization was performed with deciding the threshold so that the area ratio of both phases in the original image was maintained (Fig. 7).

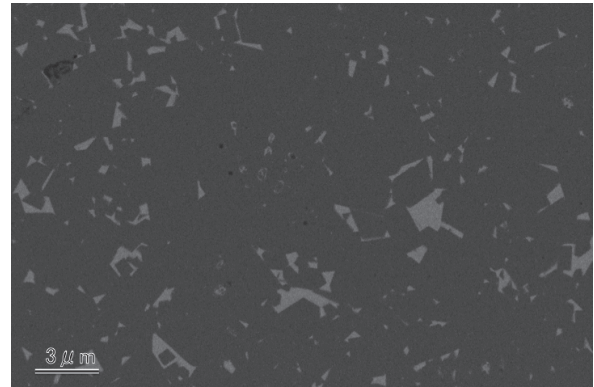


Figure 6. Original SEM image of NEXCERA taken with the EsB mode.

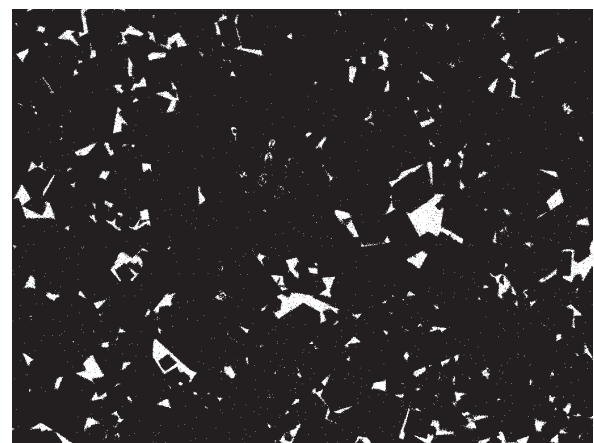


Figure 7. Binarized image of NEXCERA made by processing the figure 6. Area and a scale are same as the original image.

Photoshop software provided by Adobe Corporation was used in the present binarization. Then the black and white pixels were counted using the ImageJ software (<http://rsbweb.nih.gov/ij/index.html>). Volume fraction of each image was calculated, then these values were averaged to acquire volume fraction.

The result of volume fraction of cordierite in NEXCERA™ sintered under the atmospheric condition is approximately 92 percent. This value is almost two percent higher than the NEXCERA™ that has been sintered under the controlled atmosphere (Hattori et al., 2012).

DISCUSSION

Thermal expansion of lattice parameters

The XRD experiments show that the variation in thermal expansion of lattice parameters of powdered sample is smaller at around the room temperature (Figs. 3 and 4). On the other hand, the variation of thermal expansion coefficient of bulk sample is smaller than that of powdered sample at whole temperature range in the present experiment. The thermal expansion of powdered sample indicates that the result reflects a thermal expansion property of cordierite itself. Cordierite crystals in the powdered sample were likely to be able to expand freely, because they have been separated from an amorphous phase in the process of powdering. Smaller thermal expansion of the bulk sample, is caused by the presence of the amorphous distributed in interstices of cordierite crystals.

Thermal expansion of volume

As shown in figure 5, the volume thermal expansion of cordierite in the powdered sample is larger than that of bulk sample at whole temperature range. This result indicates that the volume thermal expansion of cordierite in the bulk sample was reduced because the amorphous phases distribute between cordierite crystals suppressed the expansion of cordierite as discussed in the previous section. It is thought that the volume expansion of the powdered sample was not affected by the amorphous phases, the result of powdered sample is also considered to provide the volume thermal expansion of cordierite itself. Another characteristic point in figure 5 is that a difference between the volume thermal expansion of bulk sample and macroscopic specimen is larger than that of powdered sample. The line graph of macroscopic expansion is the sum of cordierite crystal and amorphous phase, whereas the graph of the bulk shows only a cordierite. Therefore it can be understood that the difference comes from the volume thermal expansion of amorphous phase.

Volume fraction

The volume fraction of amorphous phase in NEXCERA™ is approximately eight percent. The amorphous phase shows anhedral morphology and is distribute interstitially in the ceramics (Fig. 6). In spite of these textural characteristics, thermal expansion of cordierite seems to be affected by the amorphous phase as seen in the discussion above. Though a volume fraction of amorphous phase is only eight percent, taking the large amount of the gap between the macroscopic ceramics and the bulk in the volume thermal expansion (Fig. 5) into account, the thermal expansion coefficient of amorphous is suggested to be considerably large amount. Therefore, it may be possible to enlarge the temperature range of “zero” thermal expansion by controlling the volume fraction of amorphous phase in an appropriate value.

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