Preparation of Cordierite/ZrO$_2$ Nano-Composite Powders by a Colloidal Coating Process

En-Hai SUN, Taka-fumi KUSUNOSE, Tohru SEKINO, Tomohiko ADACHI, Masashi WADA and Koichi NIIHARA

Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihogaoka, Ibaraki-shi, Osaka 567-0047

Abstract: Cordierite/ZrO$_2$ nano-composite powders were prepared by a colloidal coating process. Cordierite particles are embedded within a continuous layer of fine amorphous ZrO$_2$ that was provided by the colloidal processing after drying. Tetragonal ZrO$_2$ was first formed at 650°C and monoclinic ZrO$_2$ phase was identified at the calcination temperature of 800°C. After calcination at 850°C, crystallized ZrO$_2$ particles with the size from 10 nm to 30 nm homogeneously covered the surface of cordierite particles. Cordierite/ZrO$_2$ nano-composite powders prepared by a colloidal coating process show better sinterability than that of cordierite/ZrO$_2$ powder mixtures prepared by a conventional mixing method, and were sintered to a density of over 96% at a low temperature of 1300°C.

Key-words: Cordierite, ZrO$_2$, Nano, Coating, Sinterability

1. Introduction

Cordierite (2MgO·2Al$_2$O$_3$·5SiO$_2$) is a technologically important material with wide-ranging uses and applications, because of its low thermal expansion and dielectric constant, along with good chemical and thermal stability. However, difficulty in sintering has long been a problem, since its sintering temperature range is narrow and near cordierite’s incongruent melting point. Near the melting point, water molecules in the cavities of the cordierite structure vaporize, therefore cracks and pores are left within the sintered body. These problems lead to relatively poor mechanical properties, which have prevented their more widespread applications.

Investigations have thus been carried out to introduce ZrO$_2$ dispersion into cordierite ceramics in order to enhance the mechanical properties of cordierite. Crystallization and colloidal methods in which metal-alkoxides were used as starting materials have been attempted to achieve better microstructure for improved mechanical properties of cordierite. From an economic point of view, however, these methods are not appropriate processes since they are very complex processing and the starting materials of colloidal synthesis are fairly expensive. Furthermore, in these cases, more than 6 vol% (or 10 mass%) of the ZrO$_2$ dispersion is necessary. Otherwise the effect of the dispersed ZrO$_2$ on sinterability and mechanical properties would be unremarkable.

The properties of advanced ceramics such as strength are well known to depend strongly on the characteristics of microstructures. Niihara reported that mechanical properties could be notably improved by dispersing nano-size second phase particles. Sol-gel coating technique is thought to be one of the promising processes to introduce nano-size particles into matrices. In this method, second phase material is firstly introduced as colloidal morphology, and then crystallized after calcining. This helps in the homogenous incorporation of dispersions or additives, avoiding agglomeration of second phase powder and hence refraining from oversized particles.

Powders prepared by sol-gel coating have been utilized in several ceramic preparation works. For example, De Jonghe et al. prepared SiC whiskers and Si$_3$N$_4$ powders coated by Al$_2$O$_3$. Sacks et al. developed a process for preparing mullite-based ceramics by coating ZrO$_2$ and SiC with an amorphous SiO$_2$ layer. Zirconia-toughened alumina, mullite and spinel have been also prepared from coated powders. All these powders exhibited an enhanced sinterability, and the sintered composites displayed an appropriate microstructure for better mechanical properties. Furthermore, in this powder preparation method, alkoxide is only used for second phase (i.e., for coating phase), thus the composite powders can be obtained at a lower cost than the fully sol-gel derived composite powders.

In order to improve the sinterability of cordierite powder with a small amount of ZrO$_2$, we have focused on applying this colloidal coating process to prepare cordierite/ZrO$_2$ composite powders. In the present work, cordierite powder has been coated by colloidal ZrO$_2$, and the crystalline and phase transformation behavior of ZrO$_2$, as well as powder morphologies, have been investigated. The sinterability of the prepared powders has also been evaluated in relation to the nano-structure of the composite powders.

2. Experimental procedures

Commercial cordierite powder (SS-600, Marusu Yuyaku Joint Vent., Seto-shi) was used as a starting powder. It was ball-milled for 24 h to reduce hard agglomeration before coating. The precursor of zirconia was commercial ZrCl$_4$ (Wako Pure Chemicals, Tokyo) that was dissolved in HCl (0.4M) aqueous solution. The precursor solution, in which the concentration of zirconium was kept at 0.01M, was first added slowly to cordierite slurry. After mixing for 8h, an excess of 25% ammonia solution was dropwise added to this suspension under intensively stirring. To precipitate all zirconium ions, the pH of the suspension was maintained at 10 or more during the hydrolysis. After the hydrolysis, the gel was washed by distilled water several times in order to remove chlorides from the solution. Subsequently, the slurry was washed with an excess ethanol to remove free water. After filtered, it was dried in air at 80°C.
Two compositions were prepared, cordierite +1 vol% ZrO₂ and cordierite +5 vol% ZrO₂, hereafter these powders will be referred to as CZ1 and CZ5, respectively. The crystallization and phase transformation behavior of zirconia in prepared powders was studied by thermogravimetric and differential thermal analyses (TG–DTA, DTG–50, Shimadzu Co., Kyoto) and in-situ high-temperature X-ray diffraction (HT–XRD, X1 system, Scintag Inc., CA, USA). TG–DTA was carried out in air, at a heating rate of 5°C min⁻¹ from room temperature to 1200°C. HT–XRD patterns were obtained at 45 kV and 40 mA using a Pt direct heating stage. The heating rate was fixed at 5°C/min in the range from room temperature to 1200°C and the measurement was carried out after soaking at each temperature for 10 min. From the TG–DTA and X-ray analyses, the calcination temperature was fixed. The average particle size of ZrO₂ was calculated using the (111) diffraction peak (2θ = 30.20 of tetragonal ZrO₂ by the Scherrer formula as follows:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

where \( D \) is the crystalline size, \( \lambda \) is the wavelength (Cu Kα), \( \beta \) is the corrected half-width of corresponding 2θ peak and \( \theta \) is the diffraction peak angle. IR spectroscopy (JIR–Winspecioo, JOEL Ltd., Tokyo) measurement was performed by KBr method for the dried and calcined at 850 and 1100°C powders. Pure KBr pellet was used as a reference. Particle morphology and microstructure of the composite powders were investigated by transmission electron microscopy (TEM; Model H–8100T, Hitachi Co.).

For sinterability evaluation, the calcined composite powders were ground by wet ball-milling for 24 h with zirconia ball in ethanol solvent and further dry-milled for another 12 h. The resultant granules were pressed uniaxially at 19.4 MPa and then cold-isostatically-pressed (CIP) at a pressure of 196 MPa. The green compacts were sintered in air from 1100 to 1400°C for 2 h.

For comparison, 5 vol% non-stabilized monoclinic ZrO₂ powder (TZ–0, 30 nm, Tosoh Co.) dispersed cordierite powder was prepared by the conventional mixing method, and sintered at the same conditions. This sample and pure cordierite were labeled as CZSM and CZO, respectively. Crystalline phase was identified by using X-ray diffractometer (50 kV, 150 mA, RU–200B, Rigaku Co., Ltd.) with Cu Kα radiation. The bulk density of sintered specimens was determined by the modified Archimedes’ displacement method (Boiling water method, ASTM C–20), and the relative density was then estimated from the starting compositions and the phase information provided by XRD analysis.

3. Results and discussion

The result of the TG and DTA curves for CZ5 powder are shown in Fig. 1. Endothermic peaks around 90 and 260°C each with a weight loss, and an exothermic peak around 650°C was observed. The endothermic peak around 90°C corresponds to evolution of physically absorbed water and remained NH₄Cl. Another endothermic peak around 260°C may be attributed to the dehydration of Zr(OH)₄ gel to form amorphous ZrO₂. The theoretical weight loss of Zr(OH)₄ dehydration is 22.6%. In the present powder, Zr(OH)₄/cordierite ratio is 0.56 in mole, which corresponds 0.15 in weight. Therefore, estimated weight loss of the present powder can be calculated as 3.39%, which is in good agreement with the experimental loss of about 3.3% at 260°C.

Tetragonal ZrO₂ was found to form first at 650°C from HT–XRD analysis as shown in Fig. 2. This results clearly indicate that the exothermic peak of DTA curve around 650°C corresponds to the crystallization of amorphous ZrO₂. Monoclinic ZrO₂ phase was identified at the temperature of 800°C in an XRD pattern enlarged by the computer program, although the main peak of monoclinic ZrO₂ at 28.2° is not clear because of small scale. Except for cordierite and ZrO₂ phases, no other additional phases, such as ZrSiO₄, were detected up to 1200°C in this investigation.

The volume fraction of the m-ZrO₂ phase (\( V_m \)) was deter-
mined by utilizing the following equation\(^\text{16}\) from X-ray diffraction analysis.

\[
V_m = \frac{\rho X_m}{1 + (\rho - 1) X_m} 
\]

where \(X_m\) is the integral intensity ratio and \(\rho = 1.311\). The \(I_m\) and \(I_t\) represent the integral intensities of the monoclinic and tetragonal phases, respectively.

Taking account of the low ZrO\(_2\) addition and the fact that m-ZrO\(_2\) main peak (111, 2\(\theta\)=28.2) and cordierite peak (202, 2\(\theta\)=28.4) overlap, a profile fitting analysis was carried out by a computer program (RAD-R, RINT, Rigaku Co., Ltd.). Volume proportions of the monoclinic phase \((V_m)\) and crystalline particle size \((D)\) of tetragonal phase are shown in the Table 1. The \(V_m\) increased till 950\(°\), and then kept at a value of \(~37.5\text{ vol\%}\) up to 1200\(°\). The particle size of ZrO\(_2\) increased gradually from 19 nm at 900\(°\) to 27 nm at 1200\(°\).

According to the phase diagram of ZrO\(_2\), pure ZrO\(_2\) is known to have the monoclinic structure at room temperature, which is thermodynamically stable below 1200\(°\), and have tetragonal structure at above this temperature. The t-ZrO\(_2\) can also exist at lower temperature when stabilizer is added.\(^{17-19}\) However, the phase formation and transformation behavior of hydrous-ZrO\(_2\) powders are affected significantly by various synthesis conditions or processing parameters such as pH, aging time, reaction temperature, precursor concentration, solvent type, and variation of precursor salt. And thus it does not always follow the traditional phase transformation route.\(^{20-23}\) In the current study, t-ZrO\(_2\) phase appears preferentially to the m-ZrO\(_2\) phase during crystallization of amorphous hydrous zirconia, which is consistent with earlier work on the tetragonal crystallization from amorphous zirconia gel materials as a traditional crystallization route.\(^{24,25}\) However, metastable t-ZrO\(_2\) phase was found to coexist with m-ZrO\(_2\) in the present composite when the temperature was dropped from 1200\(°\) to room temperature, even no any stabilizer of ZrO\(_2\) was added. The most possible consideration is that metastable t-ZrO\(_2\) phase was stabilized by MgO that diffuses from neighboring cordierite.\(^{19,20}\) In the present composite powder, the volume ratio of ZrO\(_2\) is as low as 5 vol\%, thus the free MgO is sufficient to partially stabilize ZrO\(_2\). In addition, metastable t-ZrO\(_2\) phase may be stabilized for those which size is less than the critical size (\(~30\text{ nm}\)) after heating cycle.\(^{24,27,28}\) More analysis such as the modification of cell parameters of t-ZrO\(_2\) is needed to clarify it.

The volume proportion of the monoclinic phase is much smaller than that of Guinebretière’s report,\(^{29}\) which is 0.65 at 1200\(°\), when zirconium-n-propoxide was used as the precursor of ZrO\(_2\). The great difference of the \(V_m\) is considered to be due to the difference of measurement method. In the present work, because in-situ high-temperature X-ray diffraction was used, more tetragonal phase may be detected than that analyzed at room temperature after calcined at high temperatures.

IR spectra of dried and calcined powders are given in Fig. 3. In the IR spectrum of dried powder, the –OH group bending vibrations at 1650 cm\(^-1\) was observed. The –OH band disappeared after calcining due to the removal of crystal water. The band assigned to the ring structure of SiO\(_4\) tetrahedron in cordierite was observed at 780 cm\(^-1\) for all powders.\(^{30}\) The vibration bands for all ZrO\(_2\) coated powders at 575 cm\(^-1\) (Zr-O) is in good agreement with those of ZrO\(_2\).\(^{31}\) The characteristic –NH absorbance band for NH\(_4^+\) at 1429 cm\(^-1\) was observed in the dried powder, indicate the remnant of NH\(_4\)Cl. The characteristic bands of other phases, such as spinel (MgO·Al\(_2\)O\(_3\), 700 and 526 cm\(^-1\)) and ZrSiO\(_4\) (900 and 640 cm\(^-1\)) were not observed, confirming again the results obtained from XRD analysis. From above results, the calcine temperature was fixed at 850\(°\), at which the formation of ZrO\(_2\) was completed.

TEM observation was carried out for as-prepared powder and 850\(°\) calcined powder. TEM micrograph (Fig. 4(a)) of dried powder shows that cordierite particles are embedded in a continuous layer of fine amorphous ZrO\(_2\) particles. Energy dispersive X-ray (EDX) microanalysis (Fig. 4(b)) indicates the presence of ZrO\(_2\). After calcination at 850\(°\), nanometer-sized ZrO\(_2\) particles homogeneously dispersed.
on the surface of cordierite particles (Fig. 5(a)). The size of ZrO₂ particles is between 10 and 30 nm, which is consistent with the crystalline size obtained from XRD measurements. HR-TEM clearly shows that ZrO₂ particles are crystallized on the surface of cordierite particles (Fig. 5(b)).

Pressureless sintering of prepared composite powders has been carried out with various conditions. The relative density of sintered specimens for different sintering temperature is shown in Fig. 6. It can be seen that densification takes place above 1200°C for all specimens. However, cordierite/ZrO₂ composite powders prepared by the colloidal coating process (CZ1 and CZ5) show better sinterability than that of cordierite/ZrO₂ powder mixture prepared by the conventional mixing method (CZ5M). It should be noted both colloidal processed CZ1 and CZ5 powders could be sintered to sufficiently density of over 96% at a low temperature of 1300°C, showing the advantage of colloidal processing for cordierite/ZrO₂ nano-composites powders.

It has been reported that Y₂O₃ partially stabilized ZrO₂ is an active sintering additive in several systems, such as mullite (3Al₂O₃·2SiO₂) and Al₂O₃.35-34 Because of the ionic
radii ratio of Zr$^{4+}$/Al$^{3+} = 0.65$, it is reported that the substitution of Zr$^{4+}$ for Al$^{3+}$ is possible. Thus an eutectic phase which exists in the system Al$_2$O$_3$-SiO$_2$-Y$_2$O$_3$ always formed at the grain boundary when Y$_2$O$_3$ partially stabilized ZrO$_2$ was used, and consequently enhanced the grain boundary mass transport. However, this seems not to be the case for the present work. Since Y$_2$O$_3$ was not added, the presence of the eutectic phase that generated when Y$_2$O$_3$ partially stabilized ZrO$_2$ was used, was uncertain. More details would need to confirm whether a eutectic phase exists by transmission electron microscopy observations.

In the present work, the improvement of sinterability is considered to be mainly due to the formation of ZrSiO$_4$ phase. It is reported that the formation of zircon has been observed during crystallization of cordierite/ZrO$_2$ glass-ceramic and sintering of cordierite/ZrO$_2$ powder mixture at temperatures in excess of 1250°C. In our system, the results are consistent with the reports. From identification of sintered specimens by X-ray diffraction, ZrSiO$_4$ phase was detected at 1250°C in CZ5 composite (Fig. 7). The formation temperature of ZrSiO$_4$ in each composition increased in the sequence of CZ1, CZ5 and CZ5M. The formation of ZrSiO$_4$ is significantly affected by the structure of cordierite/ZrO$_2$ powder compacts. Finer size and more homogeneous dispersion of ZrO$_2$ in compacts, which favors diffusion, might enhance the reaction of cordierite and ZrO$_2$. Therefore, the 1 vol% ZrO$_2$ coated powder shows an obvious increase of relative density at low temperature of 1250°C.

There are some differences between HT-XRD pattern of CZ powder at 1200°C (Fig. 2) and XRD pattern of CZ5 specimen sintered at 1200°C (Fig. 7). In the case of sintered CZ5 specimen, only t-ZrO$_2$ phase was detected. The phase identification difference is considered to be due to the difference of measurement method. CZ5 specimen was measured after cooling from sintering temperature, thus it is possible that all ZrO$_2$ can remain as tetragonal phase by the stabilization of MgO.

The lowering of sintering temperature implies that the microstructure of the sintered composites might be fine, which may introduce enhancement of mechanical properties. Detailed investigation of the mechanical properties as well as microstructure feature of the composites will be reported in elsewhere.

4. Conclusions
Coating of cordierite particles with a continuous layer of amorphous ZrO$_2$ was obtained from the precursor of ZrCl$_4$. Stabilization of ZrO$_2$ to tetragonal phase was observed due to incorporation of a small amount of MgO from cordierite phase. After calcined at 850°C, the nanometer-sized ZrO$_2$ particles were homogeneously formed on the surfaces of cordierite particles. The size of ZrO$_2$ particles lies between 10 nm and 30 nm. These nano-composite powders show better sinterability than that of cordierite/ZrO$_2$ powder mixture prepared by conventional mixing method, and were sintered to a density of over 96% at a low temperature of 1300°C. The improvement of sinterability is considered to mainly due to the better nanostructure and the formation of ZrSiO$_4$.

References