Paper

Sintering Behavior of Nanocrystalline CeO₂ by Master Sintering Curve Analysis

Masakuni OZAWA*

Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-8603, Japan.

Received December 3, 2017; Revised February 4, 2018; Accepted February 19, 2018

ABSTRACT

The master sintering curve was applied to nanocrystalline CeO₂ powder compact, and the sintering activation energy was determined to be \( Q = 405 \pm 40 \text{ kJ mol}^{-1} \). A classical model was applied to the initial sintering region and gave \( Q = 360 \pm 30 \text{ kJ mol}^{-1} \). The difference is attributed to the effect of the sintering driving-force between in initial and total sintering stages of nanocrystalline CeO₂ particles. The MSC model can be used to predict the total densification of present powder compact under time-temperature excursion. It is conducted that the MSC is an integral work of the sintering concept that is useful for modelling the densification of CeO₂.

KEY WORDS

CeO₂, sintering, master sintering curve, activation energy

1 Introduction

CeO₂ is an attractive substance for recent applications such as catalysts, fuel cells, buffer film of devices and so on. The thermal stabilization of CeO₂-based oxygen storage capacity sub-catalysts in automotive exhaust treatment is one of the important problems when they are subjected to elevated temperatures in catalytic reactions. In ceramic electrodes of solid state fuel cell (SOFC), the better sintering behavior is strongly required to fabricate a dense film material as a high performance ceramic fuel cell component. In the development CeO₂-based materials the sintering of nanocrystalline CeO₂ powders have been examined, however, a systematic approach using a certain theory in whole sintering history is not achieved. Regarding with theoretical approach, the question of sintering control is not resolved yet by temporary industrial technologies and researches. In the earliest quantitative sintering studies, many models have been derived to relate the sintering kinetics to the particle-particle configuration. Simplified geometries were considered for the sintering process to readily identify driving forces, including mass transport paths and geometric factors around particles. Although attempts made to extend the models for many powders system have been done, actually there was achieved to provide a limited success using detailed geometrical assumption. Su and Johnson have proposed the concept of a master sintering curve (MSC), which is different from previous approaches. They characterized the sintering behavior of a given powder and green-body regardless of the heating profile, and made the MSC model enable to predict the densification behavior using a minimal set of preliminary experiments e.g. by dilatometry technique. Other researchers applied the MSC theory to the sintering curves of several powders at temperatures-up experiments, and applied it to the sintering of other substances such as ThO₂, ZnO and BaTiO₃. In the present work, the non-isothermal sintering at different heating rates was studied for nanocrystalline CeO₂. The activation energy of sintering was estimated by the master sintering curve analysis, and compared with the initial sintering behavior using a classical model.

2 Experimental

The starting powder was synthesized by a homogeneous precipitation method. Aqueous solutions of both 0.3 M hexamethylenetetramine and 0.05 M cerium nitrate were separately prepared. Suitable amounts of these solutions were mixed together under stirring in order to obtain a homogeneous solution, hold at 90°C for 24 h. The precipitate was separated from the solution by filtration, and washed with water, then dried at 120°C for 10 h in air, followed by heat treatment at 900°C for 5 h in air.

The crystal phase of the powder was studied by X-ray diffraction apparatus (XRD; Rigaku, Rint2000) with CuKa radiation. The XRD indicated that the powder and sintered bodies consisted of fluorite-structured oxide phase of pure CeO₂, and the crystallite size by XRD was 62 nm in diameter. The morphology of powder and sintered bodies was observed by scanning electron microscopy (SEM; Hitachi, S4800). Fig. 1a shows a picture of the powder particles taken by SEM. The average particle size was 98 ± 20 nm in diameter and the particle shape was sphere-like.

* Corresponding author, E-mail: ozawa@imass.nagoya-u.ac.jp
** The content of this article had been presented at JSPMIC2017.
A dilatometry apparatus (Brucker AX, TD3000SA) was used for monitoring the sintering behavior of the powder compacts at various heating rates. Small pieces of rod-shaped powder compact (10 × 2 × 2 mm) were carefully prepared by uniaxial pressing at 50 MPa at room temperature. The heating-up procedure from 40 to 1650°C was performed with different heating rates of 5, 10, 15 and 20°C min⁻¹. The axial shrinkage of the specimens was measured with an accuracy of ±1 μm, and the relative density of the sintered specimen was calculated using thermal expansion coefficient and the density of CeO₂ (7.23 cm³ g⁻¹).

3 Results and discussion

According to the master sintering curve (MSC) theory proposed by Su and Johnson, the instantaneous shrinkage rate is given as

\[
\frac{-dL}{dt} = \gamma \Omega \left( \frac{\Gamma G D_v}{kT} + \frac{\Gamma G D_b}{G^2} \right)
\]

(1)

where \(\gamma\) is the surface energy, \(\Omega\) the atomic volume, \(k\) the Boltzman constant, \(T\) the absolute temperature, \(G\) the mean grain diameter, \(\delta\) the width of the grain boundary, \(D_v\) and \(D_b\) are the diffusion constants. Also, the grain diameter dependence term \(G^n\) is known as \(n = 3\) and \(n = 4\) in volume and grain-boundary diffusion mechanism, respectively. \(\Gamma\) is a scaling parameter about driving force, diffusion distance and geometric feature. This is essentially a function of time and can be integrated by \(t\) as

\[
\Theta(t,T(t)) = \int_0^t \frac{1}{T} \exp\left( -\frac{Q}{RT} \right) dt
\]

(2)

where \(R\) the gas constant, and the diffusion term in Eq. (1) by two mechanism are described as in \(D_v \exp(-Q/RT)\), where \(Q\) is activation energy and \(R\) is gas constant. Also, Eq. (1) should be described by a function of density \(\rho\) which is observed in dilatometry experiments. It is integrated by \(\rho\) as

\[
\Phi(\rho) = \frac{k}{\gamma \Omega D_b} \int_0^\rho \left( \frac{G(\rho)}{3\rho} \right)^n d\rho
\]

(3)

\[
\Phi(\rho) = \Theta(t,T(t))
\]

(4)

The MSC can be generally defined, if a certain relation between density and \(\Phi (=\Theta)\) stands for sintering with a constant scaling parameter \(\Gamma\) and activation energy \(Q\). Since \(\Theta\) is a function of temperature \(T\) (and time \(t\) at a constant heating rate), the MSC is generated by sintering experiments with several constant heating rates for the same green body. The density as a function of temperature (so called sintering curve) is computed to exchange to the relation of density versus \(\Theta\) under the assumption of the proper \(Q\) value in the MSC theory. The scaled parameter \(\Theta\) is calculated by Eq. (3) using various \(Q\) values, and then the best fit between four sintering lines (relative density vs. \(\Theta\)) is obtained by the least square method between experimental data and calculated values.

Fig. 2 shows the sintering curves (relative density versus temperature) for pure CeO₂, which were measured at various heating rates. The line was shifted to higher temperature side as increasing a heating rate, demonstrating the MSC description. One of the essential advantages for obtaining MSC is to give the activation energy from these sintering curves. In the present work, various \(Q\) values in the range from 200 to 1000 kJ mol⁻¹ were...
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...taken into account, so that an obtained $Q$-value was constructed according to Eq. (2). The resulting curves for different heating rates had to be fitted to one line, and new activation energy was chosen in the measured range, and then the calculation was repeated by leading to the best fit. Fig. 3 shows the mean residual squares of error for the various values of activation energy assumed.

Fig. 3  Plot of mean residual squares of error for the various values of activation energy assumed.

expected comparing with micron-sized powders by conventional methods. For example, superior sintering properties have been reported by several experiments of CeO$_2$ ceramics fabrication using powders from homogeneous precipitation method$^{20,21)}$.

The driving force for sintering is diffusion in present case so that the lattice instability e.g. defects and relaxation of cations will induce better sinterability. In general, the volume diffusion is dominant for an initial sintering, and then the grain boundary diffusion become a major driving force in intermediate and final stages, replacing the volume diffusion in bulk. In CeO$_2$, the diffusion rate and activation energy of each composition of Ce cation and oxide anion will be different. In fluorite-type oxides, an oxide ion easily diffuses and the diffusion of cations is relatively slow, bringing a slower sintering rate-limit. The better boundary diffusion in each grain boundaries, followed by pore elimination, can generally result in the final densification. But, it is difficult to determine the fraction ratio between both the diffusion mechanisms contributed in each stage. Also, the shape and diameter of grains, which should change, should affect the grain boundary diffusion in intermediate sintering stage. Furthermore, the segregation of oxygen defects at grain boundary often affects the sintering.

To simplify the factor in diffusivities, we examined the initial sintering behavior using a classical model applied to the uptake region of densification$^{22)}$. Fig. 5 shows a modified plot in the reverse temperature region of 0.73-0.9 (approximately 900-1100°C in Fig. 2), using the initial sintering rate according to Eq. (4).

\[
\ln \left( \frac{C_d \rho_n Q}{RT} \right) = - \frac{nQ}{RT} + C
\]

, where $n$ is a factor depending on sintering mechanism. It is suggested that $n = 1$ for viscous sintering, 1/2 for volume diffusion and 1/3 for grain boundary diffusion mechanism. Fig. 5 indicated almost linear relation for all data measured at different heating rates, and $nQ = 180 \pm 15$ kJ mol$^{-1}$ was obtained by a linear fitting procedure.
If \( n = 1/2 \) (volume diffusion) the \( Q \) is \( 360 \pm 30 \) kJ mol\(^{-1}\) and if \( n = 1/3 \) (grain boundary diffusion) the \( Q \) is \( 480 \pm 45 \) kJ mol\(^{-1}\). \( Q \) of \( 360 \pm 30 \) kJ mol\(^{-1}\) is lower and \( 480 \pm 45 \) kJ mol\(^{-1}\) is higher than the value of \( 405 \pm 40 \) kJ mol\(^{-1}\) by MSC in extended sintering region to higher density at elevated temperatures.

The microstructure of the sintered bodies, including grain sizes, was observed in the SEM images for examining the effect of the quenching temperature during sintering, as shown in Fig. 1. The starting powder was \( 98 \pm 20 \) nm in diameter and weekly aggregated as shown Fig. 1a. The increase of grain size was not observed at the temperature region up to \( 900^\circ\text{C} \) and partially sintered to make the microstructure with grain boundaries between particles (Fig. 1b). The temperature of \( 900^\circ\text{C} \) corresponds to the initial sintering region as discussed above. At \( 1300^\circ\text{C} \) (Fig. 1c), a porous structure was made by sintering, which was typical intermediate microstructure during sintering stage, followed by grain growth in each small area of aggregates resulting in connected structure with grains of average size of \( 252 \pm 40 \) nm. The grain growth was obvious (763 ± 90 nm) in the densified body at \( 1500^\circ\text{C} \). The morphology changes of a sintering powder compact are quite dependent on each starting powder when they are used to calculate properties such as mass diffusivities and sintering. The inhomogeneous microstructure and heat conducting phenomena of powder compact in micrometer-scale should exist for a portion of most sintering experiments, leading to some experimental errors in activation energies. It seems that large derivative in \( Q \) is induced by doping of foreign elements such as rare earths. Unfortunately, little attention has been given to the elemental impurity effects on experimental variables of CeO\(_2\) in sintering. The experiments about pure CeO\(_2\) in several studies as
well as ours have produced activation energies in agreement within 290–440 kJ mol$^{-1}$ in previous references$^{23,24}$.

In fluorite-structured CeO$_2$, the formation of oxygen vacancy induces the reduction of Ce$^{4+}$ to Ce$^{3+}$ (with larger ionic radius). Thus, the formation of species of CeO$_2$ in grain boundary area should bring inhomogeneous chemical state. Such chemical bond may inhibit diffusion in grain boundary, because large cation lead to such anti-sintering effects (e.g. in the system of La doped ZrO$_2$)$.^{23,29}$ Furthermore, other factor is grain growth phenomenon during sintering process. We have studied it in sintering experiment using the similar powder as in this paper, and the inhomogeneous distribution of grain diameter was observed$^{20}$ In this work, the inhomogeneous distribution of grain-diameter is not assumed in our analysis using MSC. Such microstructure should bring longer and more complex path network in grain boundary than those under assumed condition.

The results in this work support that the MSC is an integral work of the sintering which contains the increase of grain boundary in intermediate sintering stage. The concept and data treatment of MSC are useful for practical modelling the densification of active nanoparticles in the wide range up to elevated temperatures.

5 Conclusion

In this work, the master sintering curve was successfully applied to nanocrystalline CeO$_2$ powder compact. The sintering activation energy was determined to be $Q = 405 \pm 40$ kJ mol$^{-1}$. A classical model was applied to the initial sintering region and gave $Q = 360 \pm 30$ kJ mol$^{-1}$. The difference is attributed to the effect of the sintering driving-force between in initial and total sintering stages of nanocrystalline CeO$_2$ particles. The MSC model can be used to predict the total densification of present powder compact under time-temperature excursion. It is conducted that the MSC is an integral work of the sintering concept that is useful for modelling the densification of CeO$_2$.

Acknowledgment

This work was financially supported by the Project of Creation of Life Innovation Materials for Interdisciplinary and International Researcher Development of the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by Grant-in-Aid for Scientific Research No. 17H03100 from the Japan Society for the Promotion of Science.

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