NANOSCALE DENSIFICATION MECHANISM OF GADOLINIUM-DOPED CERIA UPON SINTERING

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Abstract
Densification mechanism of gadolinium-doped ceria (GDC) caused by sintering are nanoscopically investigated by XRD, laser scattering particle size analyzer, and positron lifetime spectroscopy. XRD reveals that the crystallite size grows with increasing sintering temperature. The average particle size reaches 1.88 µm by sintering at 1273K. Positron lifetime spectroscopy reveals the densification of interfaces among crystallites. The results suggest that both crystallite interfaces and particle-grain boundary contribute to the densification in GDC.

1. INTRODUCTION
Solid oxide fuel cells have been intensively studied due to their high power conversion efficiency. There has been a long-standing problem of extremely high operating temperature for solid oxide fuel cells. Gadolinium-doped cerium oxides are one of the most promising candidates as the electrolytes operated at intermediate temperature [1-3]. The total ionic conductivity of GDC is governed by the local atomic structure of transgranular [4], which is expected to be correlated with sintering. Zhang et al. [5] showed that the loading of transition metal oxide has an influence on sintering behaviour and ion conductivity of GDC. In the present paper, the densification mechanism is discussed on atomic scale based on the data by XRD, laser scattering particle size analyzer, and positron lifetime spectroscopy.

2. EXPERIMENTAL
Gadolinium-doped cerium oxides (GDC) were prepared using oxalate coprecipitation method [6]. The cerium and gadolinium nitrate mixed solution at a molar ratio of Ce³⁺/Gd³⁺ = 4/1 was dropped into a stirred oxalate acid solution to produce the oxalate precipitate. The precipitates were calcined at 873K for 1 h in the air to form oxides. They were compacted into a pellet by uniaxial pressing (20MPa) and sintered in the wide temperature range (873 - 1273K) for 6 h in the air. The lattice constants of GDC and CeO₂ were determined by XRD using NaCl internal standard. The crystallite sizes of samples were estimated from (111) peak broadening using Scherrer’s equation. The grain size distribution analysis was conducted by laser scattering particle size analyzer. Positron lifetime spectroscopy was conducted using ²²Na positron source at room temperature. The positron lifetime spectra were numerically analyzed using the POSITRONFIT code [7].

3. RESULTS AND DISCUSSION
Fig.1. shows the XRD patterns of GDC sintered at 1073K for 6h in the air. The XRD pattern indicates that GDC has a fluorite type structure without any other phases. All peaks of GDC are shifted to low angle region against to the corresponded ones of CeO₂ indicating the expansion of interplanar spacing for GDC by Gd doping. The lattice constants calculated for GDC and CeO₂ are 0.5429 nm and 0.5415 nm, respectively. The
crystallite sizes of GDC estimated with Scherrer’s equation increases monotonically along with sintering temperature and reaches ~50nm at sintering temperature of 1273K (see Fig.2). Average grain sizes are 1.47\( \mu \)m and 1.88\( \mu \)m at sintering temperatures of 873K and 1273K, respectively, being increased by ~28%.

**Fig.1.** XRD patterns of GDC and CeO\(_2\) sintered at 1073K for 6h.

**Fig.2.** Crystallite sizes of GDC and CeO\(_2\) sintered at 873K, 973K, 1073K, 1173K, and 1273K.
Fig. 3 shows positron lifetime spectra for GDC sintered at 873K, 973K, 1073K, 1173K, 1273K, 1373K, and 1473K. With increasing sintering temperature, positron lifetime spectra decay more rapidly indicating the densification of local atomic structure. The average sizes of GDC crystallites evaluated from XRD data are by far smaller than the typical positron diffusion length in solids of ~ 300 nm [9]. Positrons implanted in GDC crystallite can thus efficiently diffuse out and annihilate at interface among crystallite. We therefore conclude together with larger average particle sizes evaluated by laser scattering particle size analyzer that positron are annihilated at interfaces among crystallites. Similar observations were reported for yttria-stabilized zirconia by Cizek et al. [10].

In the present work, the densification of particle grain-boundaries presumably associated with the neck is clearly observed by which is generally discussed for sintering mechanism. In addition to that, positron lifetime spectroscopy evidences the densification of crystallite interfaces. It is therefore inferred based on the present observation that the crystallites interfaces contribute to the densification as well as the particle-grain boundary.

4. Conclusions

Densification mechanism of gadolinium-doped ceria (GDC) induced by sintering are nanoscopically investigated by XRD, laser scattering particle size analyzer, and positron lifetime spectroscopy. XRD reveals that the crystallite size grows with increasing sintering temperature. The average size of particle reaches to 1.88µm by sintering at 1273K. Positron lifetime spectroscopy reveals the densification of interfaces among crystallites. The results suggest that both crystallite interfaces and particle-grain boundary contribute to the densification in GDC.

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References


