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Cubic yttria stabilized zirconia sintering additive impacts: A comparative study

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Abstract

To evaluate the impact sintering additives have on the processing and performance of 8 mol% yttria stabilized zirconia (8YSZ), the 25–1525 °C sintering kinetics, phase purity, microstructure, and electrical properties of a single batch of 8YSZ powder surface-coated with 1, 3 and 5 mol% of barium, bismuth, calcium, cobalt, copper, iron, lithium, magnesium, manganese, nickel, strontium or zinc were investigated via constant heating rate dilatometry, X-ray diffraction, scanning electron microscopy, and AC impedance spectroscopy. For electrochemical applications where dense 8YSZ is required, iron was found to give the best combination of 8YSZ cubic zirconia phase stability, high oxygen ion conductivity, and enhanced densification kinetics. 5 mol% iron was found to reduce the 8YSZ sintering temperature by ~150 °C.

Keywords: Zirconia; Sintering additive; Dopant; Sintering Aid

1. Introduction

8 mol% Yttria stabilized zirconia (8YSZ) is used in a variety of applications including solid oxide fuel cells [1,2], oxygen sensors [3,4], electrolyzers [5], biocompatible implant coatings [6], and thermal barrier coatings [7]. Because sintering additives can induce changes in sintering temperature, fracture toughness and/or electrical conductivity [8–18], an understanding of 8YSZ sintering additive impacts is critical for tailoring the fabrication and/or high-temperature operational stability of these devices. To evaluate the relative impact of different 8YSZ sintering additives (be they intentionally added dopants/sintering aids or unintentionally added impurities), constant heating rate dilatometry on a single batch of 8YSZ powder surface-coated with 1, 3 and 5 mol% of Ba, Bi, Ca, Co, Cu, Fe, Li, Mg, Mn, Ni, Sr or Zn was performed. Further, since retention of the cubic 8YSZ crystal structure and a high ionic conductivity are often important in electrochemical applications, X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS) were also performed.

2. Experimental methods

2.1. Sample preparation

To eliminate interpretation difficulties caused by differences in 8YSZ particle size, particle size distribution, impurities etc., a single batch of TZ-8Y YSZ powder (Tosoh USA; Grove City, OH, USA) was used for the experiments reported here. As indicated by the manufacturer's certificate of analysis, this powder was 13.45 wt% Y_2O_3 (i.e. $Y_{0.1450}Zr_{0.8550}O_{1.927}$, $(Y_2O_3)_{0.07817}(ZrO_2)_{0.9218}$, or 7.817 mol% yttria stabilized zirconia) and had a SiO_2 content of 175 ppm. According to the manufacturer, and confirmed here via scanning electron microscopy, this spray dried powder had a 13.6 m^2/g specific surface area and consisted of 21 nm diameter crystallites agglomerated into 600 nm diameter (d_{50}) particles forming the walls of hollow, 60 μm diameter (d_{50}) spray dried granules. To eliminate possible silica contamination from glassware and cross-contamination between sintering additives, dedicated

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Nomenclature

8YSZ	$(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$
A	sample cross-sectional area
c_{Bulk}	oxygen vacancy concentration in the bulk
$C_{G.B.}$	grain boundary impedance arc capacitance
DS	cubic zirconia destabilization into monoclinic and/or tetragonal zirconia.
d	grain size
$\delta_{G.B.}$	electrical grain boundary width
EIS	electrochemical impedance spectroscopy
ε_o	permittivity of free space
$\varepsilon_{T,Creep}$	true strain induced by creep
$\varepsilon_{T,Dens}$	true strain induced by densification
$\varepsilon_{T,Dil}$	true dilatometer-recorded strain
$\varepsilon_{T,Mass\ Loss}$	true strain induced by sample mass loss
$\varepsilon_{T,Phase\ Change}$	true strain induced by phase changes
$\varepsilon_{T,Total}$	total true strain
k_{gb}	grain boundary dielectric constant
l	sample length
l_o	original sample length
LPS	liquid phase sintering
M_{Bulk}	oxygen vacancy mobility in the bulk
$PLC(T)$	percent linear change in sample length, $\left((l-l_o)/l_o\right)100$
R_{Bulk}	bulk impedance arc resistance
$R_{G.B.}$	grain boundary impedance arc resistance
ρ_{Arc}	the post-sintering, 25 °C relative density measured by the Archimedes method
ρ_{Dil}	the post-sintering, 25 °C relative density measured by the dilatometer using Eq. (1)
$\rho(T)$	relative density
$\rho_{th}(T)$	theoretical density
q	charge
σ_{Bulk}	bulk oxygen ion conductivity
σ_T	total oxygen ion conductivity
$\sigma_{G.B.}$	total grain boundary oxygen ion conductivity
$\sigma^{sp}_{G.B.}$	specific grain boundary oxygen ion conductivity
SEM	scanning electron microscopy
SSS	solid state sintering
T	temperature
TGA	thermo-gravimetric analysis
XRD	X-ray diffraction

polyethylene ball milling jars, polyethylene coated magnetic stir bars, and polypropylene beakers were used for each of the twelve sintering additives.

Dissolved nitrates were used to introduce sintering additives into the 8YSZ powder. All the nitrates (Alfa Aesar; Ward Hill, MA, USA) had nominal purities greater than 99.99%. Prior to use, the water content in each nitrate was measured to five significant figures through thermo-gravimetric analysis (TGA) from 25 °C to temperatures as high as 850 °C. In all cases, the measured water of hydration coefficients rounded to the single digit values provided by the manufacturer.

To prepare 1, 3 and 5 mol% surface-coated 8YSZ powders for dilatometry, appropriate amounts of barium nitrate, bismuth nitrate, calcium nitrate, cobalt nitrate, copper nitrate, iron nitrate, lithium nitrate, magnesium nitrate, manganese nitrate, nickel nitrate, strontium nitrate, or zinc nitrate were dissolved into 22 mL of 018.2 $M\Omega$/cm Milli-Q deionized water (Milli-Pore; Billerica, MA, USA). Sintering additive mole percentages were calculated as the ratio of the moles of nitrate cation to moles of 8YSZ. For instance, 0.9310 g of $Bi(NO_3)_3 \cdot 5.1720H_2O$ was added to 7.506 g of $Y_{0.1450}Zr_{0.8550}O_{1.927}$ to produce a 3% Bi-8YSZ powder with a composition of $Bi_{0.3000}Y_{0.1407}Zr_{0.8293}O_{1.915}$. For each sintering additive, the dissolved nitrate, 55 g of 3 mm diameter YTZ® tetragonal yttria stabilized zirconia milling media (Tosoh USA; Grove City, OH, USA), and 7.5 g of 8YSZ powder were placed inside a sealed 40 mL polyethylene bottle and ball milled at 50 rpm for 16 h. After removing the milling media, the water was evaporated from the ball-milled colloidal suspensions by stirring the suspensions in 600 mL polypropylene beakers under a fan. The dried, sintering-additive-nitrate-coated 8YSZ powders were then ground using an alumina mortar and pestle pre-cleaned with 30 μm diamond suspension, and sieved through a 150 μm polyethylene coated stainless steel mesh to break up agglomerates. Afterwards, 1.25 g of powder was uniaxially pressed to 46 MPa in a 1.27 cm diameter steel die to make cylindrical samples with heights ranging from 4.040–4.089 mm. After sample pressing, mass, height and diameter measurements were taken for sample volume/mass green density determinations.

Prior to dilatometry experiments, alumina spacers were produced by uniaxially pressing 3.3 g of AKP-50 alumina powder (Sumitomo Corporation of America; Los Angeles, CA, USA) to 32 MPa in a 1.27 cm diameter steel die. The resulting cylindrical spacers were fired to 1450 °C at 5 °C/min, held there for 20 h, and cooled back to room temperature at a nominal rate of 5 °C/min. In separate 25–1525 °C dilatometry tests, the resulting 10.7 mm thick, >95% dense alumina pellets only displayed recoverable thermal-expansion induced strain.

2.2. Dilatometry measurements

Dilatometry was performed on doped and undoped 8YSZ samples using a 402C Dilatometer (Netzsch Instruments North America; Burlington, MA, USA) continuously flushed with 50 mL/min of air. To limit dilatometer contamination, each sample was sandwiched between two of the previously described alumina spacers so that the dilatometer pushrod and backstop were not in contact with the sample. In all dilatometry experiments, the entire length of the sample and spacers was 25.4 ± 0.1 mm. Dilatometry was performed from 25 °C to 1525 °C with a 5 °C/min heating rate, no high