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Sintering of gadolinia-doped ceria prepared by mechanochemical synthesis

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Abstract

Gadolinia-doped ceria (GDC) ceramics were prepared by mechanochemical synthesis of ceria and gadolinia (10 mol.%) powders with subsequent uniaxial pressing and pressureless sintering. The mechanochemical synthesis was conducted in an attritor with different dispersion media: neutral (distilled water), basic (aqueous solution of ammonia), acidic (aqueous solution of propionic acid), and non-polar medium (xylene with stearic acid). The effect of suspension composition and attritor milling time on the sintering behaviour and ionic conductivity of GDC was studied. An attritor milling time of 3–6 h was evaluated as the optimum milling time from the viewpoint of further sintering behaviour. Longer milling times resulted in nanometre-sized powders, whose sintering behaviour deteriorated due to powder agglomeration. The appearance of agglomerates in the non-polar medium was reduced. The ionic conductivity of the samples was evaluated by impedance spectroscopy and correlated with their microstructure.

Keywords: Milling; Sintering; Ionic conductivity; Gadolinia-doped CeO_2

1. Introduction

Thanks to its high ionic conductivity at relatively low temperatures, gadolinia-doped ceria (GDC) is a suitable material for solid oxide fuel cells (SOFC). A disadvantage of GDC ceramics can be seen in their high sintering temperature (>1500 °C), which makes their production economically demanding and complicates the co-firing of GDC solid electrolyte with the other SOFC components. One of the possibilities how to reduce the sintering temperature is to reduce the particle size.

A method that can yield fine homogeneous powders of GDC in a comparatively simple manner is the mechanical milling of pure oxides.[1,2] Intensive milling can reduce the particle size and also activate the material for the sintering process and thus subsequently reduce the sintering temperature.[3] Intensive mechanical treatment in ball mills or attritors is often accompanied by chemical reactions between the components, and by the appearance of chemical products that usually form at temperatures of about 1000 °C.[4] A negative feature accompanying the milling of fine particles is their agglomeration. A potential tool for eliminating the agglomerations is the choice of an appropriate milling medium.[5]

The aim of the present work is to describe the sintering behaviour and ionic conductivity of $CeO_2 + 10\,mol.\%\ Gd_2O_3$ ceramics in dependence on the conditions of mechanochemical synthesis of powders, i.e. the milling medium and milling time.

2. Experimental

For the mechanochemical synthesis of $CeO_2 + 10\,mol.\%\ Gd_2O_3$ a mixture was prepared, in the respective ratio, of CeO_2 powder (99.99%, $d_{50} = 3.7\,\mu m$) and Gd_2O_3 (99.99%, $d_{50} = 3.3\,\mu m$), and dispersed in aqueous, basic (aq. ammonia solution, pH 10) and acidic (aq. propionic acid solution, pH 3) medium and in a non-polar medium (xylene with stearic acid). The suspensions contained 15 wt.% of ceramic powder, eventual ratio of additives was 1.5 wt.%. The suspensions were milled for periods $t_m = 0.17$, 3, 6, 24, and 48 h in an attritor with PTFE vessel and zirconia balls at laboratory temperature and 200 rpm. The milled suspension was dried in a spray drier at 130 °C after which the powder was calcined at 500 °C/24 h (heating and cooling rate 10 °C/min). The size of crystallites ($D_{X\text{-ray}}$) was established via X-ray diffraction (by means of Warren method[6]) while the specific surface area of particles was determined using the BET method. The particle size (D_{BET}) was established from the specific surface area using the theoretical density $\rho_{teor} = 7.24\,g/cm^3$.

Bodies in the shape of prisms (4.4 mm × 3.6 mm × 50 mm) were produced via uniaxial pressing at a pressure of 400 MPa.

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After pressing, the samples were pre-annealed at 800 °C/1 h. The samples were sintered in a high temperature dilatometer in air atmosphere, with the temperature increasing constantly by 10 °C/min up to 800 °C, and by 5 °C/min up to 1550 °C. At 1550 °C there was a holding time of 1.5–3 h. The final relative density (ρ_{relf}) of sintered samples was determined using Archimedes' method, their microstructure was studied via scanning electron microscopy. The impedance spectra of sintered samples were obtained using the four-point method in the range from 25 to 800 °C.

3. Results and discussion

Table 1 and the graph in Fig. 1 give the size of particles prepared by milling in different media for periods of 10 min to 48 h. As expected, the size of crystallites decreased with the milling time, namely from a size that did not differ from the particle size of the raw powder (ca. 3 μm after 10 min milling) down to a size of the order of 20 nm (after 48 h milling), almost independently on the milling medium. The nanometre size of particles was confirmed by specific surface area measurement.

The final density values of sintered samples ranged over a wide density interval, from 73.2 to 99.1% t.d. (see Table 1). The dependence of final sample density on the milling medium and the milling time is given in Fig. 2. The lowest final densities were established for samples milled for the shortest period of time (10 min). With such a short milling time the necessary homogenization of powder mixture did not take place and the powder was not suitable for the preparation of high density bodies. Samples milled for 6 h (aqueous medium) or 3 h (non-polar medium) exhibited the highest sintered densities. In the milling time range from 6 to 48 h the final densities were seen to decrease with milling time. In this case, the intensive milling may have led to considerable powder agglomeration (be it primarily due to the high mechanical energy supplied into the system during milling or to the increasing tendency of the decreasing ceramic particles to agglomerate), which had a negative effect on the sintering process.

Table 1
Particle size after mechanochemical synthesis, and relative density of sintered bodies

Milling medium	t_m (h)	$D_{\text{X-ray}}$ (nm)	D_{BET} (nm)	Sintering (°C/h)	ρ_{relf} (%)
H_2O	0.17	744.0		1550/3	73.2
	3	363.1		1550/3	93.4
	6	255.9		1550/3	98.9
	24	53.70		1550/3	97.3
	48	26.50	29	1550/3	88.1
H_2O + ammonia	0.17	510.4			
	3	281.6		1550/3	92.6
	6	193.6		1550/3	98.1
	24	40.20		1550/3	96.7
	48	22.20	17	1550/3	91.3
H_2O + propionic acid	0.17	2983.9		1550/3	75.6
	3	476.1		1550/3	95.4
	6	287.6		1550/3	97.0
	24	49.8		1550/3	91.8
	48	21.3	18	1550/3	90.7
Xylene + stearic acid	0.17	3176.5		1550/2.2	86.5
	3	772.4		1550/3	99.1
	6	490.7		1550/1.5	98.5
	24	272.9		1550/1.5	98.2
	48	21.0	31	1550/3	98.2

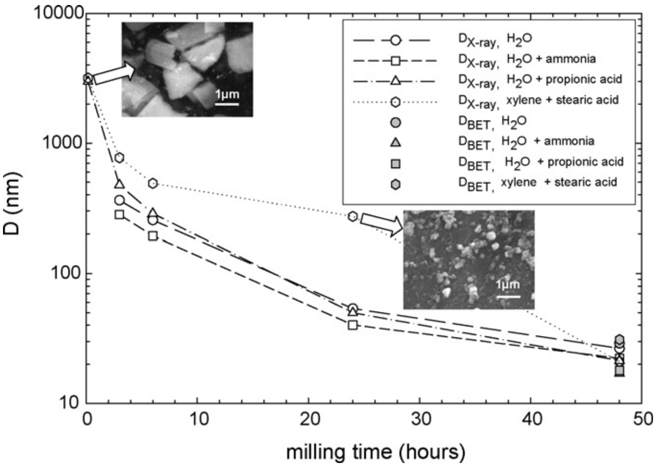

Fig. 1. The dependence of particle size on conditions of mechanochemical synthesis.

The densification curves for a samples prepared from powder milled in water with propionic acid (another two types of powders milled in neutral and basic aqueous mediums behaved in a similar way) and in xylene with stearic acid is given in Fig. 3. It is evident from Fig. 3 that for the two types of medium (aqueous and non-polar) there were some identical sintering characteristics: poor sinterability of 10 min milled powders and highest final densities for samples milled for 3–6 h. In addition to the above, there are differences in the sintering kinetics of nanometre-sized powders (milled for periods of 24 and 48 h). Samples prepared from nanometre-sized powders milled in aqueous medium had a higher green density than samples prepared by milling in xylene. It is known from the literature that more important than the green density value itself is the homogeneity of the particle and pore

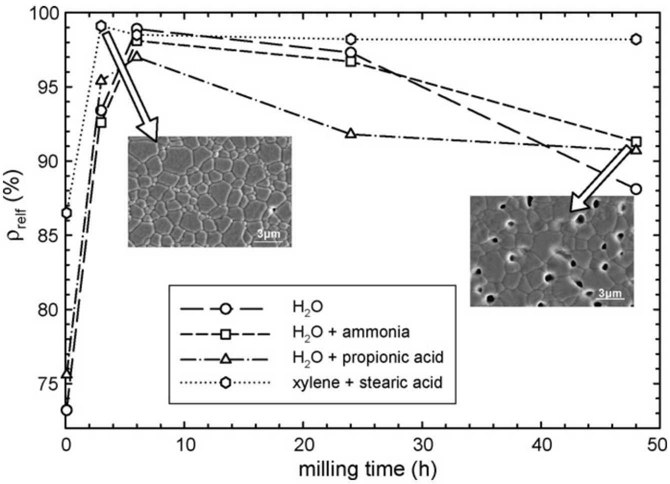

Fig. 2. The dependence of final relative densities on conditions of mechanochemical synthesis.

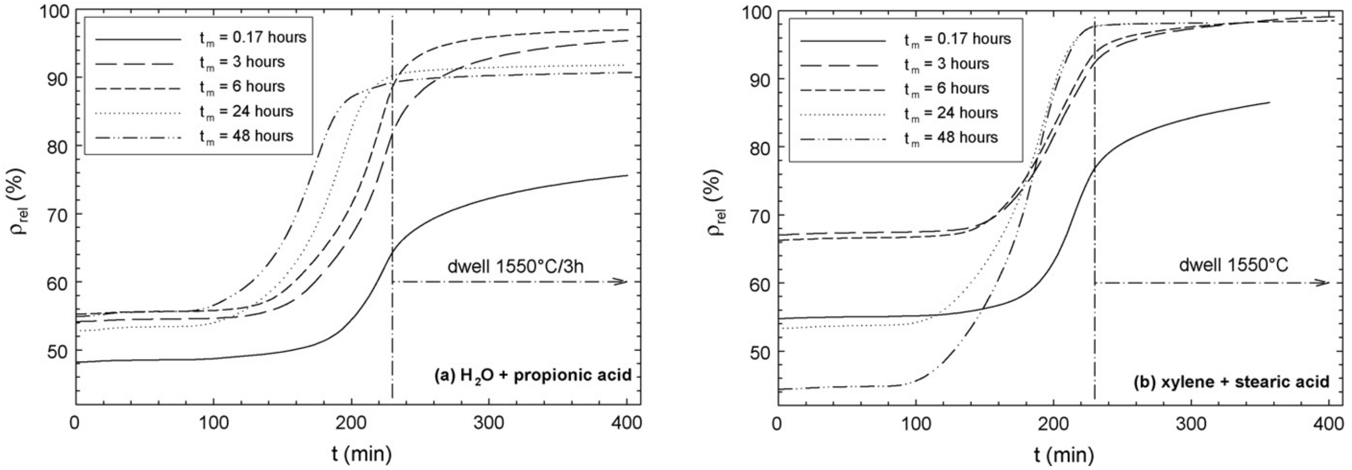

Fig. 3. Sintering kinetics of samples prepared from powders milled in (a) water with propionic acid and (b) xylene with stearic acid.

arrangement in green bodies.[7,8] It can be seen from Fig. 3 that the lowest green density was established for the sample milled in xylene for a period of 48 h; its relative density was in fact lower than 45% t.d. In spite of this, this sample featured very rapid sintering kinetics and acquired, eventually, a high final relative density (>98% t.d.). Similar behaviour was reported for non-agglomerated zirconia nanoceramics.[9–12] Homogeneous green structure with small pores, together with high sintering activity caused by very large specific surface of nanoparticles, can lead to high densification of samples with low green density (<45% t.d.). From the viewpoint of sintering behaviour the GDC powder milled 48 h in xylene holds much promise as regards the possibility of reducing the sintering temperature (in particular if shaping methods are used that are more advanced than uniaxial pressing).

It follows from the literature that the ionic conductivity of GDC ceramics depends on dopant concentration, sample porosity and grain size.[13] It is evident from Fig. 2 that our GDC ceramic had grains of 2–5 μm in size. To be able to compare the sintering behaviour of individual powders, the same sintering temperature of 1550 °C was chosen for all samples, which was high enough to neutralize the effect of different input sizes of powders on final grain size. The agglomeration of powders milled in aqueous medium for periods of 24–48 h showed significantly in the resultant microstructure. As can be seen from the microstructure of such a sample in Fig. 2, large inter-agglomerate pores remained preserved in the structure even in the case of a high sintering temperature. The temperature dependence of ionic conductivity of sintered GDC samples is documented in Fig. 4 for a sample prepared from powders milled for different periods of time in water with propionic acid. At elevated temperatures (>300 °C) there was an apparent increase in sample conductivity with temperature, which could be expressed by the Arrhenius dependence. It is evident from Fig. 4 that the ionic conductivity increased with increasing sample density, and for the most dense sample (density of 95% t.d.) it was $\sigma = 1$ S/m (at 600 °C). The activation energy of ionic conductivity was of average magnitude $E_a = 0.9$ eV, increasing slightly with increasing sample porosity. The increase of ionic conductivity of GDC ceramics with increasing density of samples was observed also by Torrens et al. (density range 86–98% t.d.)[2] and by Ivanov et al. (density range 94–100% t.d.).[14] Similarly to our results, these authors also mentioned a slight increase in E_a with density diminishing. From our results (see Fig. 4) it can also be seen that the ionic conductivity onset increased with increasing sample porosity (260 °C for a sample with a density of 95.4% t.d. compared to 310 °C for a sample with a density of 75.6% t.d.).

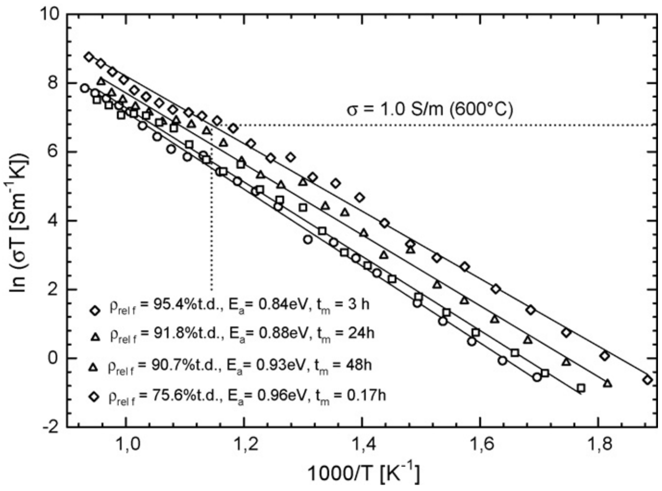

Fig. 4. Arrhenius plots of ionic conductivity of samples prepared from powders milled in water with propionic acid.

4. Conclusions

The subject of study was the sintering of uniaxially pressed CeO_2 doped with 10 mol% Gd_2O_3, prepared by attritor milling in aqueous mediums (neutral, basic and acid) and in a non-polar solvent medium. From the viewpoint of the final densities obtained, a milling time of 3–6 h proved to be optimum. Extending the milling time to 48 h led to nanometre-sized particles (∼20 nm) that, however, were agglomerated, which had a negative effect on the sintering behaviour of uniaxially pressed bodies. The appearance of agglomerates was slightly reduced in the non-polar solvent medium. The sintered bodies exhibited ionic conductivity, which increased with increasing density (i.e. decreasing porosity) of samples and with increasing temperature ($E_a \cong 0.9\,\text{eV}$); at a temperature of 600 °C the values reached were $\sigma \cong 1$ S/m.

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