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Densification of plasma sprayed YSZ electrolytes by spark plasma sintering (SPS)

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Abstract

Solid oxide fuel cells (SOFC) are promising candidates for alternative power generation systems due to their high-energy conversion efficiencies, and low emissions of environmentally hazardous by-products. Plasma spray (PS) is an effective, and relatively inexpensive process for fabricating high performance yttria stabilized zirconia (YSZ) electrolyte for SOFC. Yet, because of the numerous inter-granular defects introduced to the electrolyte by the plasma spray process, the electrolyte is not gas tight and consequently, the energy efficiency of the cell is severely curtailed. In order to improve the performance of the SOFC, spark plasma sintering (SPS) is introduced as a post-spray treatment to enhance the density of the PS YSZ electrolyte rapidly, and effectively. In this study, spark plasma sintering (SPS) was performed at 1200, 1400 and 1500 °C. Each sintering cycle had a holding time of 3 min. Single and multiple SPS cycles (3 min at preset temperature per cycle) were used to treat the plasma sprayed yttria stabilized zirconia (PS YSZ) electrolytes. The microstructure of as-received and SPS treated electrolytes as examined by scanning electron microscopy (SEM) demonstrated a microstructure transition above 1200 °C, where the typical plasma sprayed lamella structure transformed to a granular-type structure. The porosity of as-received and SPS post-treated electrolytes, which were determined by a mercury intrusion porosimeter (MIP) revealed a significant reduction in pores at 1500 °C. Average pore size reduced from 0.2 to 0.08 μm. The ionic conductivity of the electrolytes is evaluated by AC impedance spectroscopy to characterize the effect of SPS on enhancing the ionic conductivity of the electrolytes.

Keywords: Ionic conductivity; Mechanical properties; Plasma spraying; Porosity; Spark plasma sintering; Thermal conductivity; YSZ; ZrO_2

1. Introduction

Efficiency and environmental safety have become major considerations for new energy systems in recent years because of the restricted energy resources on Earth. Solid oxide fuel cells (SOFC) can directly convert the chemical potential of fossil fuels to electricity. The high conversion efficiencies (~65%), and low environmental hazards of SOFC make them promising candidates for future power generation systems.[1–4] Y_2O_3 stabilized ZrO_2 (YSZ) is one of the most common materials used as electrolyte in SOFC based on the following advantages: it has an adequate ionic conductivity; it is stable in oxidizing and reducing environment; and, it does not degrade readily from chemical reactions at the electrode materials. Cubic zirconia stabilized with 8 mol% yttria (8YSZ) is commonly used in solid oxide fuel cells (SOFC) as the electrolyte material due to its attractive ionic conductivity at high operating temperatures (~1000 °C), and this ensures stability of the YSZ at room temperature. However, the mechanical strength of 8YSZ is poor, hindering the fabrication of self-supported electrolyte plates for use in planar SOFC systems. Tetragonal zirconia stabilized with 3 mol% Y_2O_3 (Y–TZP) has a high bending strength at room temperature[5] and reasonable ionic conductivity at 1000 °C. Although the ionic conductivity of Y–TZP is lower than 8 mol% YSZ, handling is easier during the cell fabrication process. Hence, Y–TZP is also considered as a worthwhile electrolyte material[6] when the cell is designed as an electrolyte supporting one.

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Plasma spray is a quick and relatively inexpensive process for the fabrication of high performance YSZ electrolyte.[1–4,7,8] Yet, because of the numerous intergranular defects (pores) introduced to the electrolyte by the plasma spray process, the electrolyte is not gas tight and consequently the energy efficiency of the cell is severely curtailed.[9] Just as in any other plasma sprayed ceramic coatings, porosity in plasma sprayed YSZ electrolyte exists in two levels. Pores in the size-range 1–10 μm that arise from entrapped gas, unmelted particles, cracking or premature solidification by some particles, while pores <0.1 μm are formed as a result of poor interlamellar contacts.[10] The latter type of pore is rather predominant in plasma spayed YSZ electrolyte, and it causes the pores in the electrolyte to be interconnected, which is the main factor that lowers the energy efficiency of the electrolyte by allowing the reacting gases to pass through the electrolyte. Also, poor contacts amongst the lamellae decrease the mechanical property of the electrolyte, and cause premature failure of the electrolyte. In order to improve the performance of the cell further, effective post-spray treatment is necessary to bring the YSZ electrolyte to its full density. And spark plasma sintering (SPS) is an expeditious and effective post-spray heat treatment method.

SPS is a new sintering process, which can sinter ceramic powders quickly to its full density at a relatively lower temperature compared to conventional sintering methods.[11–16] In the SPS process, a graphite die set is filled with the raw material powder, and placed between the lower and upper electrodes. A pressure is applied on the compact during sintering. A pulsed direct current (dc) is then applied to the sintering powder, and the activation of powder particles is achieved by the application of electrical discharges. For electrically conductive powders, heating up is mainly due to the Joule effect. For non-conductive powders, heating is likely achieved through heat transfer from the die and punches. For conductive powders, electrical discharges can occur along the particles' surface during the SPS process. For oxides, ion conduction takes place at high temperatures. With the application of an alternating DC current, thermal and electrical breakdown phenomena are most likely to occur at high temperatures for non-conductive ceramic powders, and skin current can be formed.[17,18] With the alternative current, powder contacts and gaps works like small capacitors, and plasma may be generated by the electrical discharges across these capacitor gaps. The application of an external electric field leads to improved densification during sintering and requires a considerably shorter time cycle compared to conventional methods of sintering. The high-temperature sputtering phenomenon generated by spark plasma, and spark impact pressure eliminates absorptive gas and impurities present on the surface of the powder particles. There are several anticipated merits of SPS: 1. Generation of spark plasma; 2. Effect of electric field; 3. Effect of electric current on diffusion in conductor or skin current on the semiconductor and insulator; 4. Impact of spark plasma; 5. Rapid Joule heat and rapid cooling. Due to the afore-stated advantages, SPS is deemed as an effective post-spray process for plasma sprayed YSZ electrolyte in this study.

Presently, SOFC operate in the range 900–1000 °C. Thermal shock resistance and thermal cycle tolerance of its components is hence critical for the efficiency and reliability of the SOFC. These properties are greatly affected by the thermal conductivity of the electrolyte. Yet, while thermal properties of YSZ as thermal barrier coatings have been widely addressed,[10,19,20] there are scarcely any substantial study carried out on the thermal properties of YSZ as SOFC electrolyte. Besides the thermal properties, the mechanical properties of the YSZ electrolyte such as micro-hardness and Young's modulus are also factors that affect the reliability of SOFC.

In this article, freestanding 3 mol% YSZ electrolytes are prepared by plasma spray, and post-spray treated by SPS at temperatures 1200, 1400 and 1500 °C. The effect of SPS on the microstructure, mechanical properties, porosity, thermal and ion conductivity of the plasma sprayed YSZ discs is investigated and discussed.

2. Experimental procedures

Commercial 7 wt.%Y_2O_3 (3 mol%Y_2O_3) stabilized ZrO_2 (Y–TZP) (Praxair, USA) is used as feedstock powders for sample preparation. Plasma spraying of YSZ discs are carried out using the Model 4500 computerized 100 kW plasma spray system (Praxair, USA). The plasma spray processing parameters are shown in Table 1.

Freestanding YSZ discs 1–2 mm thick are obtained after removal from a substrate. The discs are then further processed by SPS using the Dr. Sinter 1050 (Sumitomo Coal Mining Co., Japan) SPS system. The spark plasma sintering (SPS) parameters are shown in Table 2.

Density of the SPS samples was measured using the conventional Archimedes technique. The microstructure

Table 1
Plasma spray parameters

Parameters (unit)	Value
Arc gas (Ar) flow (m^3/h)	1.52
Auxiliary gas (He) flow (m^3/h)	1.27
Carrier gas (Ar) flow (m^3/h)	0.34
Net power (kW)	16.0
Feed rate (RPM)	3.3
Stand-off distance (cm)	14

Table 2
Spark plasma sintering parameters for plasma sprayed YSZ

Sample	Temperature (°C)	Soaking time (min)	Numbers of cycles
A	1200	3	1
B	1200	3	2
C	1200	3	3
D	1400	3	1
E	1400	3	3
F	1500	3	1
G	1500	3	2
H	1500	3	3
I	1500	9	1

Table 3
Density of as-sprayed and SPS post-treated plasma sprayed YSZ electrolytes

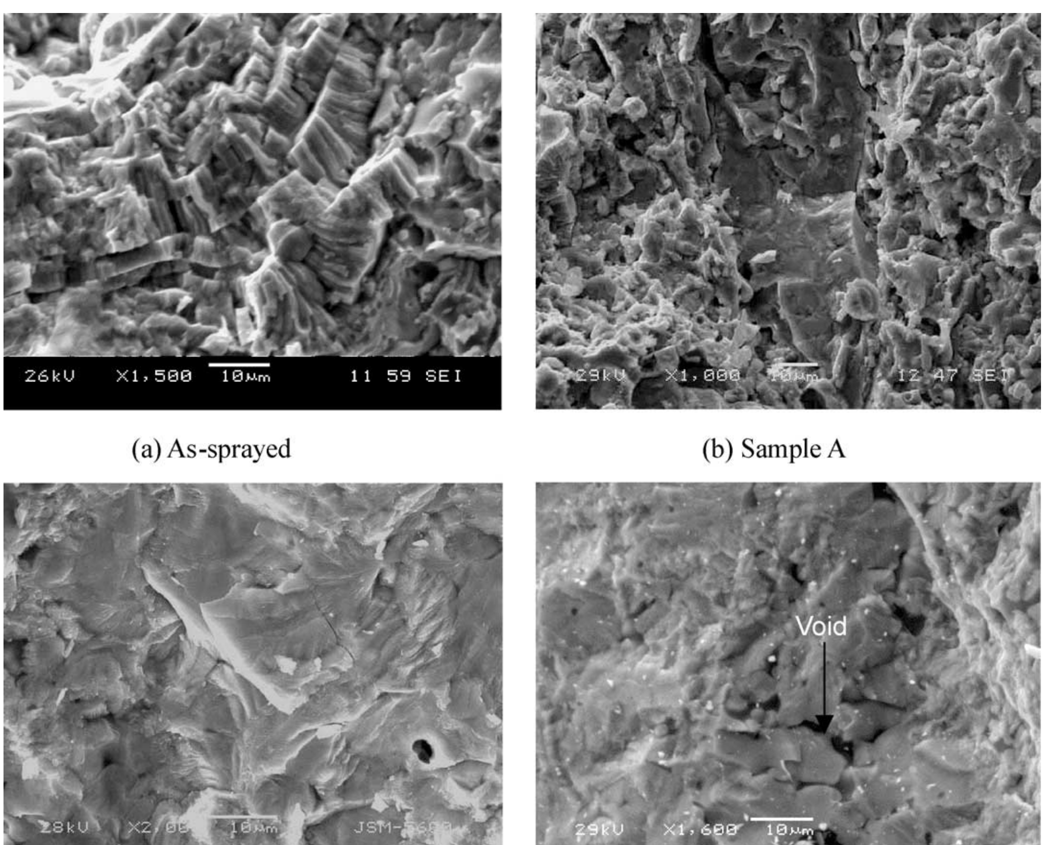
As-received	5.24 g/cm^3		
SPS samples at various temperatures (°C)	Number of SPS cycles		
	1	2	3
1200	5.35 g/cm^3	5.37 g/cm^3	5.53 g/cm^3
1400	5.35 g/cm^3	5.39 g/cm^3	5.71 g/cm^3
1500	5.86 g/cm^3	5.88 g/cm^3	5.89 g/cm^3
Theoretical density		5.90 g/cm^3	

of the SPS samples was inspected by the Jeol JSM-5600LV/(Jeol Pte Ltd, Tokyo, Japan) scanning electron microscope (SEM). Phase analysis was done on the Philips MPD 1880 (Philips, Netherlands) X-ray diffractometer system. The phase composition of samples before and after SPS was evaluated by the Rietveld refinement method.

In order to compare the porosity and the pore size distribution of as-sprayed and SPS treated electrolytes, porosity measurement was performed on as-sprayed YSZ and Sample F using the mercury intrusion porosimeter (Auto-Pore II Micromeritics, USA). In this technique, mercury is intruded into the electrolyte to measure the pore size. The technique is based on the non-wetting characteristics of mercury. Pore sizes are determined by Washburn's equation:[10]

$$P_r = -2\gamma \cos\theta, \tag{1}$$

where γ is the surface tension of mercury and θ is the contact angle between mercury and the pore wall. P_r is



(a) As-sprayed (b) Sample A

(c) Sample F (d) Sample I

Fig. 1. Fracture surface of as-sprayed and SPS-treated plasma spray YSZ.

the applied external pressure that ranged from several bars to several tens of thousand bars. The variation of the external applied pressure caused changes in the intruded volume. This in turn is related to pore-size distribution. This technique requires pores that are inter-connected, a common feature in plasma sprayed YSZ electrolyte.

A variable load microhardness tester (CSEM Instruments SA, Switzerland) evaluates the micro-hardness and Young's modulus. The thermal diffusivity and thermal conductivity of the samples are measured in the

Table 4
Phase composition in as-spray and SPS treated PS YSZ samples refined by Rietveld method

Sample	t-Zirconia	m-Zirconia
As-spray	0.869±0.005	0.131±0.005
A	0.8558±0.006	0.1442±0.009
D	0.864±0.007	0.136±0.005
F	0.862±0.007	0.138±0.006
H	0.884±0.007	0.116±0.006
I	0.927±0.014	0.073±0.011

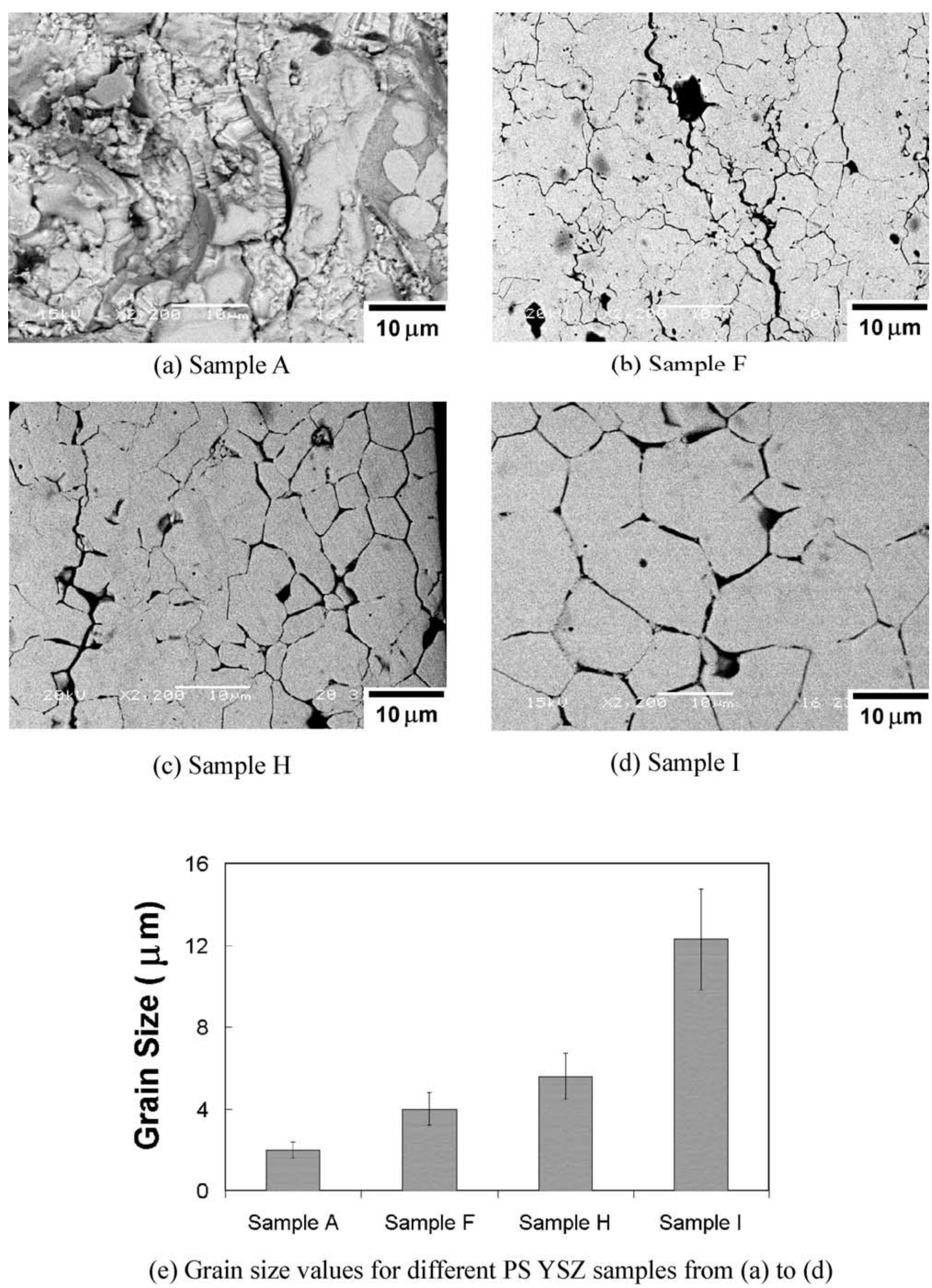


Fig. 2. Grain size evolution in PS YSZ samples with the change of SPS temperature and SPS cycles.

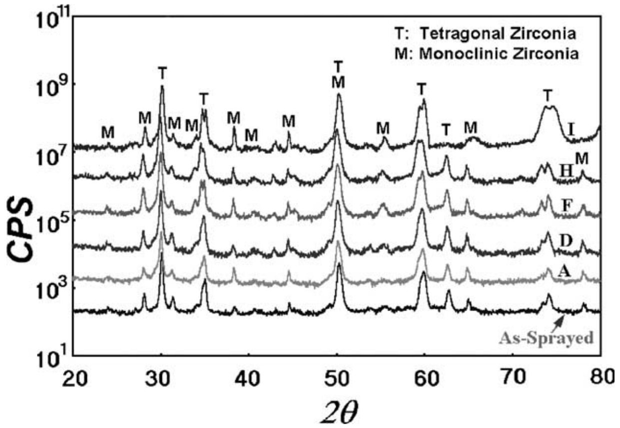


Fig. 3. XRD patterns for as-sprayed PS YSZ sample and sample SPS at different parameters.

temperature range of 22–1150 °C using a Netzch model 427 laser flash diffusivity apparatus (Germany).

The ionic conductivity of the plasma sprayed YSZ (PS YSZ) treated by SPS was measured by AC impedance spectroscopy. In order to compare the ionic conductivity of PS YSZ samples treated by SPS with that of YSZ samples compacted by SPS directly from YSZ powder, two YSZ powder samples (particle size range 30–50 μm) are compacted by SPS at 1200 °C, and 1500 °C over three consecutive SPS cycles (with 3 min at the preset temperature per cycle). These SPS settings were similar to those employed on Samples C and H. The ionic conductivity of these two samples is subsequently measured. The measurement system for the impedance included a program-controlled furnace, which can control the temperature within an error of ±1 °C and a computer-controlled frequency response analyzer (Gamry PC4/750 Potentiostat Instruments, Warminster, USA). The sintered electrolytes were first

Table 5
Porosity of as-sprayed and 1500 °C/3 min SPS post treated electrolytes

Sample	Porosity (%)	Average pore diameter (μm)
As-received	10.72	0.2182
1500 °C 3 min SPS treated	3.02	0.0801

coated with platinum paste on both sides as electrodes and fired at 1100 °C for 30 min. Two platinum wires adhered to the each side of the electrolyte were connected to the frequency response analyzer, one to counter and reference and the other to work terminals. Measurements were carried out in the temperature range 240∼1000 °C, and in the frequency range 1∼100 KHz.

3. Results and discussion

Table 3 gives the densities of as-sprayed and SPS-treated YSZ electrolytes measured by the Archimedes technique. It can be seen that the density of electrolytes is improved by SPS, and increasing the SPS temperature, or increasing the number of SPS cycles can densify the electrolyte effectively. Fig. 1(a) shows the microstructure of as-sprayed plasma sprayed YSZ disc, which has a lamellar structure. After SPS treatment at 1500 °C for 3 min (Sample F), the lamella microstructure of plasma sprayed YSZ converted completely to a fine granular structure, as shown in Fig. 1(c). With SPS temperature of 1500 °C and a total soak time of 9 min (Sample I), the grains coarsened, and there is also the observation of voids at the intergranular positions [Fig. 1(d)]. Fig. 2 shows the grain size evolution with the sintering temperature and sintering cycle. For the sample treated at 1200 °C for 3 min (Sample A), the grains

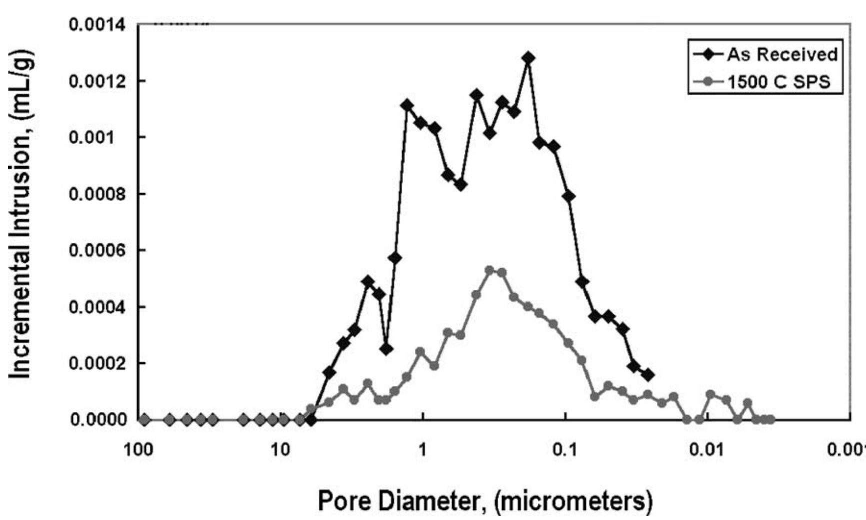


Fig. 4. Pore size distribution of the PS YSZ electrolytes before and after SPS.

are fine columnar grains with an average of grain size of about 2 μm in the plasma sprayed lamellae (Fig. 2a). For the SPS samples treated at 1500 °C with one 3-min cycle, and three 3-min cycles (Samples F and H), the grains are still relatively small, around 5 μm. Yet the densification of the samples treated with three SPS cycles is higher than that of the sample with one SPS cycle. For the sample treated at 1500 °C for 9 min (Sample I), the coarsening of the grain is quite obvious, with the grain sizes around 10–20 μm. Fig. 2(e) illustrates the trend observed in the grain size as a function of treatment temperature. From the earlier results, one can conclude that multiple SPS cycles with short duration helps the densification of plasma sprayed YSZ samples with a lower risk of grain growth.

The XRD patterns of plasma sprayed YSZ samples before (as-sprayed) and after SPS are shown in Fig. 3. The samples composed mainly of tetragonal zirconia. In order to reveal the X-ray radiation counts diffracted from the secondary phase (monoclinic zirconia, or baddeleyite), the XRD data are plotted logarithmically with respect to counts per second (CPS). The phase composition in the samples was evaluated with the Rietveld refinement method, and listed in Table 4. Results show that there is no significant phase change after SPS treatment.

The MIP results showed that the porosity of the samples is greatly reduced by 1500 °C/3 min SPS post-spray treatment (Sample F), and the pore size distribution of the PS YSZ electrolyte is also decidedly modified after SPS (Fig. 4). It can be seen that the amount of pores in the size-range of 1–1 0 μm is extensively reduced. It can also be observed that the fine pores with a pore size <0.1 μm are significantly reduced. These pores are likely to be the inter-lamellae pores[8] and the reduction or elimination of these pores would enhance the impermeability to reactive gases, and strengthen the inter-lamellae bonds. The reduction of

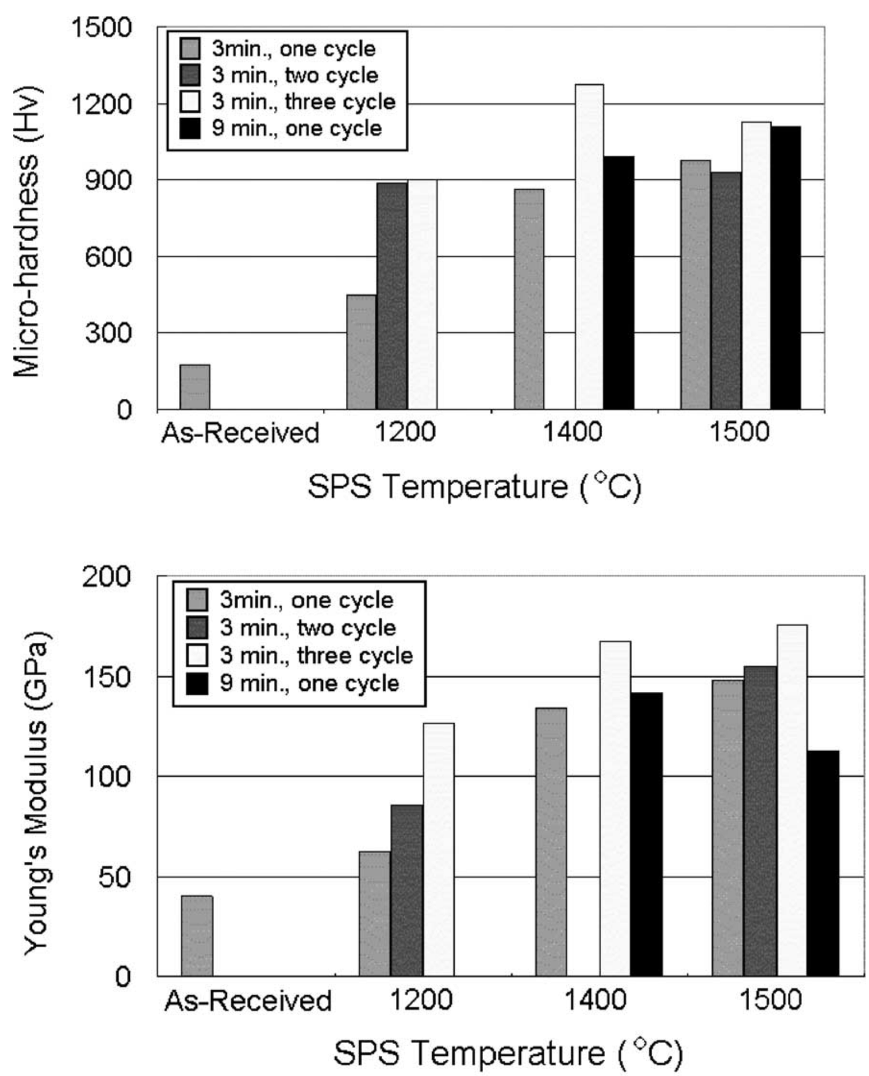


Fig. 5. Micro-hardness (a) and Young's modulus (b) of as-received and SPS-treated plasma sprayed YSZ discs.

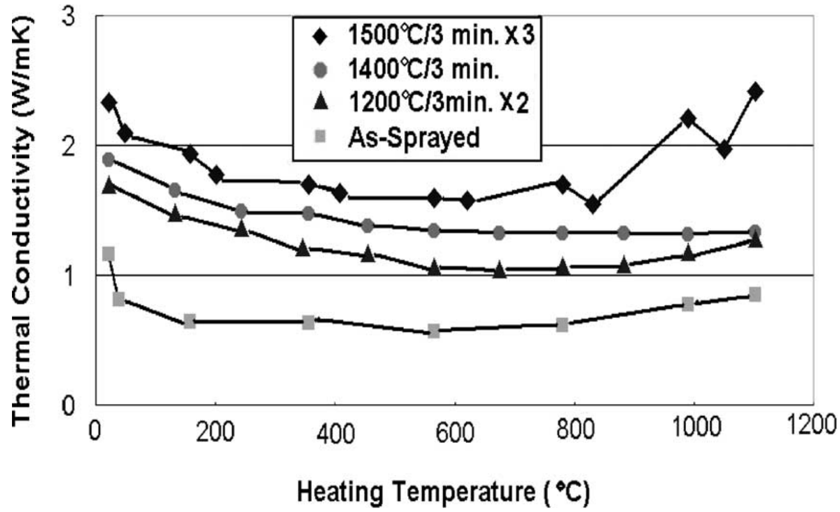


Fig. 6. Thermal conductivity of as-sprayed and SPS-treated plasma sprayed YSZ discs (different SPS temperature level).

pores with the size 0.1–1.0 μm is incomplete, and a considerable amount of pores with the size of this range still remains. The overall porosity is, however reduced considerably, with ~7% measured in the SPS treated electrolytes, as shown in Table 5.

The micro-hardness and Young's modulus of as-sprayed and SPS-treated plasma sprayed YSZ samples F, G, H and, I are shown in Fig. 5. It can be seen that at a fixed soak duration at the preset temperature of 3 min, the micro-hardness and Young's modulus increase synchronously with increase in SPS temperature or number of SPS cycles. But at a fixed SPS temperature, prolonging the soak duration will eventually decrease the micro-hardness and Young's modulus. This is because, for short treatment time (3 min), increasing temperature and number of SPS cycle can help the densification of the samples without severe grain growth, while prolonging the soak time to 9 min in a single SPS cycle can exaggerate grain growth, and consequently, the micro-hardness and Young's modulus values decrease as the densification of the sample is suppressed.

The thermal conductivity of as-sprayed sample and SPS samples B, D, and H show that the thermal conductivity of plasma sprayed YSZ discs is greatly enhanced by SPS post-spray treatment temperature (Fig. 6). The elimination of porosity and sealing of the micro-cracks induced by plasma spray is believed to be the dominant cause for the improvement of thermal conductivity of the sample. The thermal conductivity results for SPS samples F, G, H and I indicate that the SPS sample G (1500 °C/3 min/2 cycles) gives the highest thermal conductivity, denoting there is an optimum of number of SPS cycle (Fig. 7). And the decrease of thermal conductivity for the SPS sample I (1500 °C/9 min) can attribute to the coarsening of voids at the grain boundaries.

Fig. 8(a) shows the effect of SPS treatment temperature on the ionic resistivity of PS YSZ electrolytes when the measurement is taken at 1000 °C. The data for YSZ samples compacted by SPS directly from YSZ powder is also shown in Fig. 8. It can be seen that YSZ samples compacted from YSZ powder by SPS shows markedly lower ionic conductivity than PS YSZ treated by SPS under same SPS conditions, especially for the YSZ powder sample compacted directly by triple cycle SPS at 1200 °C for 3 min per cycle (Sample C). This is because plasma spray YSZ samples post-spray treated by SPS have a higher density compare to the powder samples directly compacted by SPS at the same conditions. It is obvious that with the increase of SPS temperature, the ion conducting resistivity of PS YSZ electrolyte decreases.

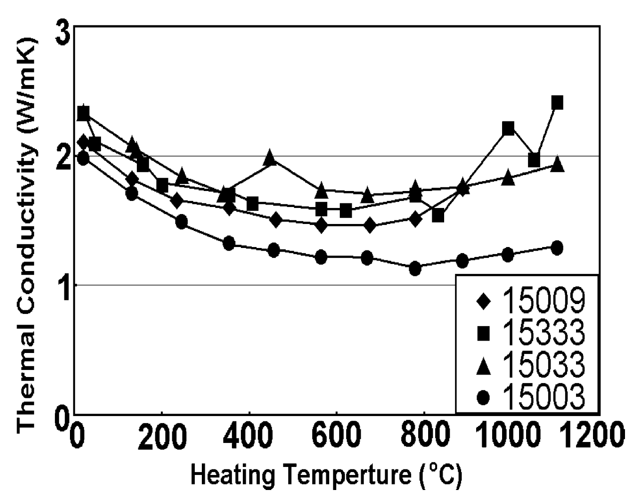
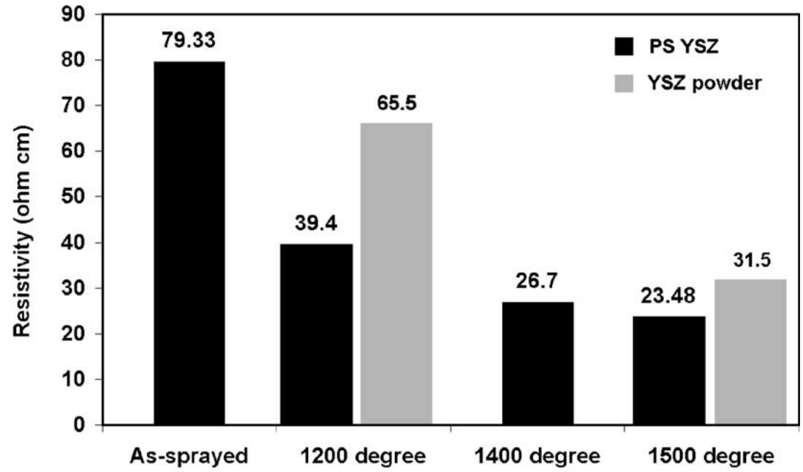
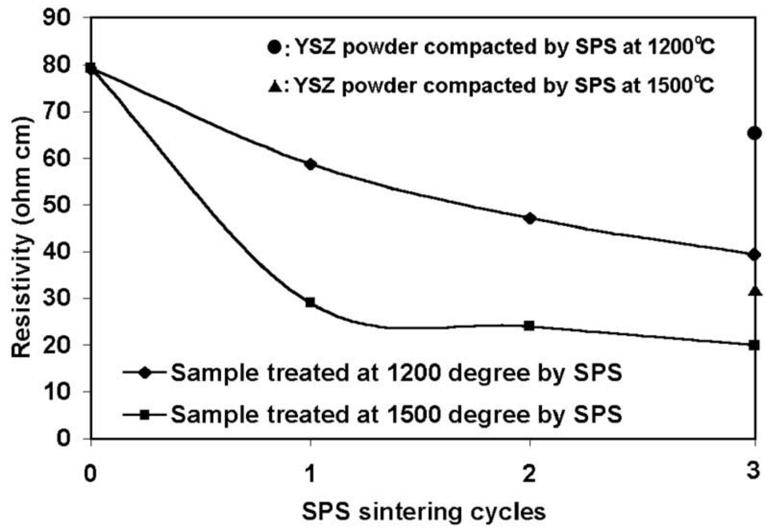


Fig. 7. Thermal conductivity of plasma sprayed YSZ discs SPS-treated at 1500 °C for different soak time and SPS cycles: (15009: 1500 °C/9 min for one cycle; 15333: 1500 °C/3 min for three cycles; 15033: 1500 °C/3 min for two cycles; and 15003: 1500 °C/3 min for one cycle).



(a)



(b)

Fig. 8. Effect of (a) SPS treatment temperature and (b) SPS multiple cycles on the ion conducting resistivity of PS YSZ electrolytes.

Fig. 8(b) shows the effect of SPS cycles on the ion conducting resistivity of YSZ electrolyte, the measurement is also taken at the temperature of 1000 °C. The ion conducting resistivity of PS YSZ electrolyte decreases from about 80 ohm·cm to around 20 ohm·cm. This result is compatable to the result in previous work.[21] It can be found that for a certain SPS temperature, multiple-cycle treatment can yield a lower ion conducting resistance of the PS YSZ electrolyte. This is because multiple-cycle SPS can provide further densification of the electrolyte.

4. Conclusions

Spark plasma sintering (SPS) is found to be an effective method for densifying plasma sprayed yttria stabilized zirconia (PS YSZ) discs for solid oxide fuel cell (SOFC) application. Beyond 1200 °C, the lamella microstructure of PS YSZ transformed completely to granular structure. This is brought about by active atomic diffusion among the YSZ grains. Consequently, the porosity of the PS YSZ electrolyte is significantly reduced, and the micro-hardness and Young's modulus increased. However, the phase composition remained intact. Multiple SPS cycles, with relatively short soak duration for each 3-min cycle was found to greatly densify the sample without severe grain growth. Hence, increasing the number of SPS cycles per specimen, with a relatively short soak time, has a more positive influence on the improvement of mechanical properties of the PS YSZ discs than single SPS cycle, albeit with longer exposure. The thermal conductivity of the PS YSZ is greatly improved (up to two times) by the SPS post-spray heat treatment, and there is an optimum multiple SPS cycles for the improvement of thermal conductivity. SPS samples F and G give the highest thermal conductivity. The ion conducting resistivity is reduced drastically with an increase of SPS temperature and SPS multiple cycles.

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