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Author(s)	Chen, Yao; Kobayashi, Akira
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Bimodal Microstructural Samarium Doped Ceria with and without Carbon Nanotubes Fabricated through Plasma Spray[†]

CHEN Yao ** and KOBAYASHI Akira *

Abstract

With the aim of achieving a correlation between bimodal microstructure with the electrical conductivity of rare-earth-doped ionic conducting ceramics, spray dried samarium doped ceria (SDC) agglomerates with and without CNTs were employed as powder feedstock to synthesis SDC-based samples with bimodal microstructure through a plasma spray. Results showed that poor thermal conductivity of the powder-agglomerate porosity of spray dried powder feedstock coupled with optimized plasma processing parameters not only endowed the as-sprayed SDC and SDC-CNT samples with bimodal microstructures consisting of nanocrystalline grains and micronsized columnar grains, but also avoided damage of the CNTs from the harsh plasma environment.

KEY WORDS: (Bimodal microstructure), (Samarium doped ceria (SDC)), (Carbon nanotube), (Plasma spray)

1. Introduction

Solid oxide fuel cells (SOFCs) have been attracting attention due to their efficient conversion of electrochemical fuel to electricity with negligible pollution [1-2]. From the view of long-term durability and reliability, and cost efficiency, the current developmental target for SOFCs is to reduce the operating temperature into the intermediate temperature (IT) range (500–700 ºC), which requires increased electrolyte ionic conductivity and enhanced gas/electrode reaction kinetics [3]. However, it is found that Y_2O_3-stabilized ZrO_2 (YSZ), the most commonly used electrolyte in the high-temperature SOFCs, exhibits insufficient ionic conductivity at intermediate temperature (IT) ranges [4]. Much investigation reported that trivalent rare-earth-doped ceria such as Gadolinium and Samarium-doped ceria are promising electrolyte materials due to high ionic conductivity at low temperatures [5-6]. It is worth noting that rare-earth-doped ceria usually loses oxygen under reducing conditions and develops a mixed ionic/electronic conductor, which also makes it an anode candidate in SOFCs.

Nanocrystalline materials are well known to have high numbers of atoms residing at grain boundaries and surfaces that increase the surface area of the active sites for reactions[7]. It is reported that nanocrystalline YSZ exhibits an increase of about 2–3 orders of the magnitude in electrical conductivity as compared with microcrystalline specimens [3]. Activation energy for microcrystalline YSZ is ~1.24–1.30 eV, whereas this reduces to ~0.93 eV for nanocrystalline YSZ [3]. Nevertheless, a few researchers have also reported a decrease in the electrical conductivity with decreasing grain size (0.2–20 μm) for zirconia and ceria-based electrolytes [7-12]. These contradictory observations further motivate the authors' curiosity about the effect of bimodal microstructures on the electrical conductivity of rare-earth-doped ceria.

Moreover, a carbon nanotube (CNT) exhibits extremely high electronic conductivity, which is more than 1000 times greater than copper [13], and therefore introducing carbon nanotubes into rare-earth-doped ceria is expected to create potential anodes in SOFCs due to the improved mixed ionic and electronic conductivity. Also, it is noted that the addition of CNTs into doped ceria, acting as anodes, would be helpful to increase its mechanical properties and to reduce the mismatch of coefficient of thermal expansion between it and the ceria based electrolyte.

The aim of this research is to synthesise bimodal microstructure samarium-doped ceria (SDC) with and without carbon nanotubes (CNTs) through the plasma spray technique, and the SDC and SDC-CNT with bimodal microstructures are expected to create promising electrolytes and anodes for IT SOFCs.

2. Experimental Procedure

In the plasma spray, nanosized particles can not be directly sprayed using a regular powder feeder due to 1) tiny nanoparticles which clog the hoses and fittings that transport the particles to the plasma torch; 2) injection of these individual nanoparticles into plasma jet requires high level carrier gas, which destabilizes the plasma jet; and 3) individual nanoparticles usually exhibit lower inertial levels to penetrate the stagnation layer at the substrate, leading to lower deposition efficiency.

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* Associate Professor
** Foreign researcher

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Table 1 Representative plasma spraying processing parameters.

Parameters	Volts (V)	Current (A)	Primary Gas, Ar (psi)	Secondary Gas, He (psi)	Carrier gas, Ar (psi)	TBD (inch)
Coatings	34	700	60	80	30	3.5-4.0

Hence, pre-treatment of these nanoparticles for plasma spray is necessary. In the research, a spray dry technique was employed to form microscopic agglomerates of nanosized SDC with or without carbon nanotubes (CNTs). As shown in **Fig. 1**, from the SEM images of spray dried SDC agglomerates and SDC-CNT agglomerates, it is clearly seen that microscopic agglomerates with a particle size distribution ranging from 15-40 μm were achieved via spray drying, and each agglomerate really consisted of fine SDC particles with a size range of 40-120 nm. Free-standing SDC-based samples were created using a Praxair SG 100 gun, and the plasma spray processing parameters are listed in **Table 1**.

Microstructure was characterized by field emission scanning electron microscopy (FE-SEM; Hitachi SU-70, Japan), and X-ray diffraction (XRD) patterns were obtained using a JEOL JDX-3530M X-ray diffractometer with Cu Kα radiation (λ= 1.54) at 40 kV and 40 mA.

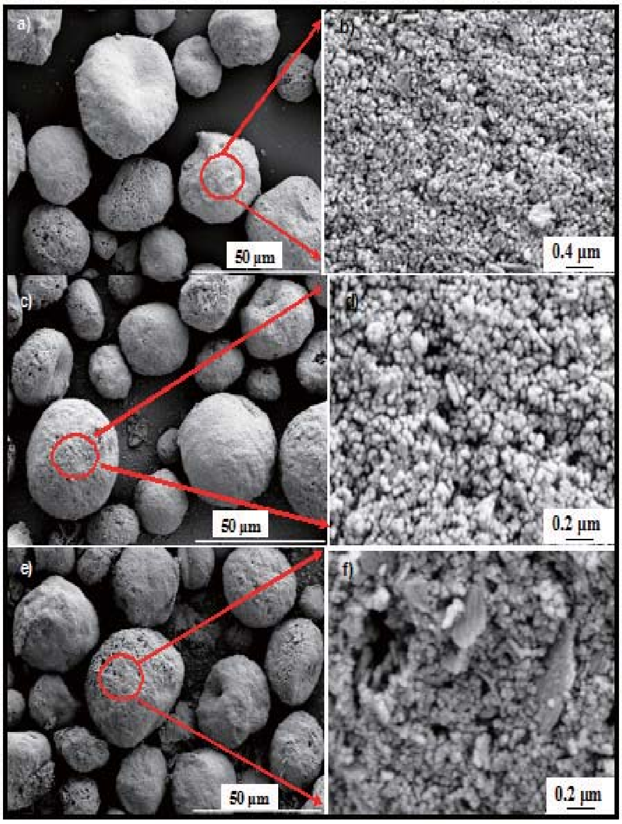

Fig. 1 SEM images of spray dried samarium doped ceria (SDC) agglomerates (a)-(b), spray dried SDC-5wt%CNT agglomerates (c)-(d), and spray dried SDC-10wt%CNT agglomerates (e)-(f).

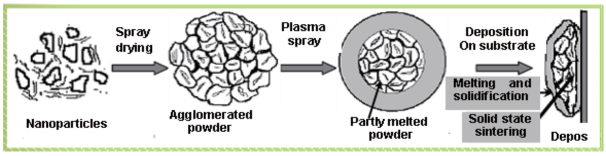

Fig. 2 Schematic diagram of plasma sprayed coatings with bimodal microstructure.

3. Results and Discussion

To ensure the final as-sprayed samples with bimodal microstructure, some degree of melting of feedstock agglomerates is necessary to guarantee both the existence of microscopic grains and a sufficient level of adhesion and cohesion between the splats. Furthermore, partially melting inside the agglomerates is to achieve the retain of nanocrystalline characteristics related to that of original feed stock agglomerates, as shown the schematic illustration of plasma sprayed coatings with bimodal microstructure, depicted in **Fig. 2**. For this purpose, plasma processing parameters should be carefully controlled by the direct measurement of the temperature (T) and velocity (v) of the in-flight particles within the plasma jet using an online process diagnostic technique such as Tecnar's Accuraspray G3 optical sensor.

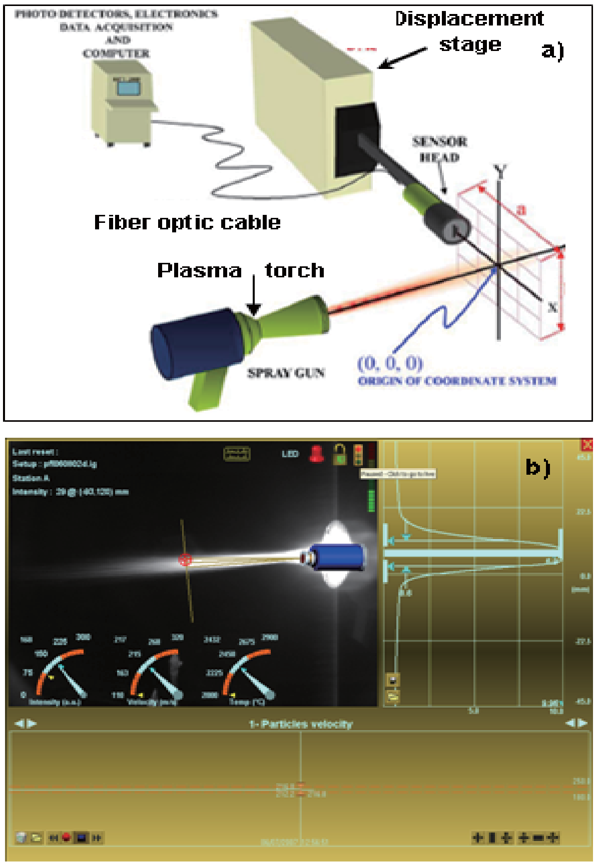

Fig. 3 Schematic diagram of online process diagnostic technique employed in this research to optimize processing parameters.

Table 2 On-line measurement results of the average surface temperature and velocity of the in-flight particles

	Average surface temperature	Average velocity
Samarium doped Ceria (SDC)	3050 °C	283 m/s
SDC-5wt%CNT	2920 °C	272 m/s
SDC-10wt%CNT	2845 °C	255 m/s

This sensor can measure the average surface temperature, velocity and flow rate of the individual in-flight particle, providing a continuous view of processing conditions through the particle stream, as shown **Fig. 3**, and the measured average surface temperature and velocity of these in-flight agglomerates in plasma jet using Tecnar's Accuraspray G3 optical sensor are found in Table 2.

It is clear that the measured average surface temperature of the in-flight agglomerates is relatively higher that the melting point of ceria (~2500 °C). It is also indicated that temperature variation of different powders owing to CNT dispersion is clearly evinced in **Table 2**. Contrasting difference is attributed to the role of high thermal conductivity of CNTs in the spray dried agglomerates.

As compared with that of spray dried SDC agglomerates, it is evidenced from the XRD results of plasma sprayed SDC samples with and without CNTs (**Fig. 4**), only single cubic ceria phase appears after plasma spraying of SDC agglomerates with and without CNTs, and no monoclinic and other metastable phases are found in the as-sprayed SDC samples.

As clearly seen in **Fig. 5(a)**, the SEM image of the cross-section of an as-sprayed SDC sample, few cracks can be found due to the residual thermal stress. The typical microstructure of the plasma-sprayed SDC and SDC-CNT samples are bimodal in nature, consisting of

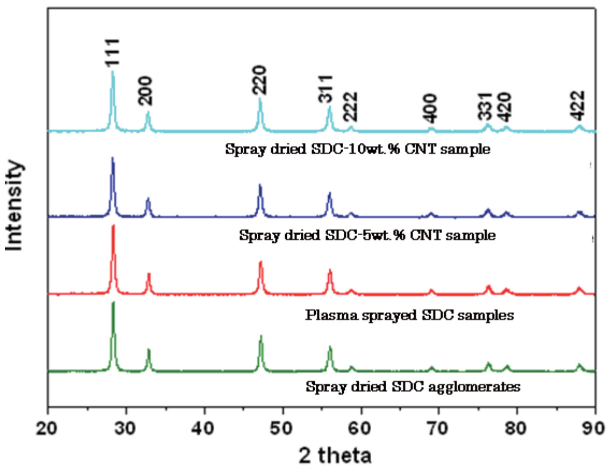

Fig. 4 XRD results of spray dried SDC agglomerates ands plasma sprayed SDC sample with and without CNTs.

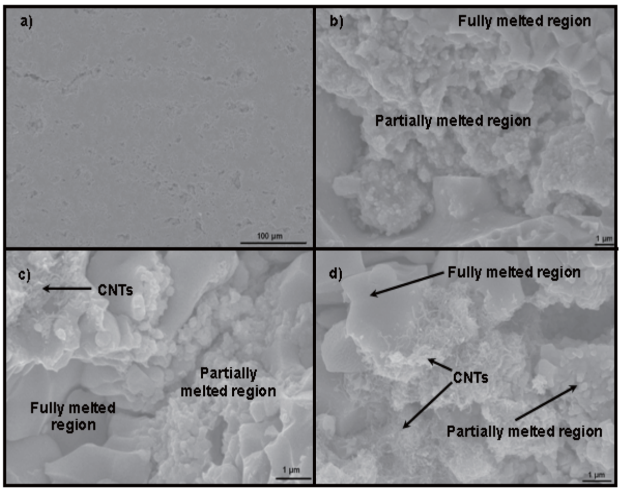

Fig. 5 SEM micrographs showing the cross-section of plasma sprayed SDC sample (a), and typical microstructure of plasma sprayed SDC sample (b), plasma sprayed SDC-5wt.%CNT sample (c), plasma sprayed SDC-10wt.%CNT sample (d), respectively.

nanocrystalline grains and micronsized columnar grains, in which microscopic grains exist in fully melted region, whereas nanocrystalline grains are found in partially melted/sintered regions (Fig. 5(b)-(d)).

Agglomerated powder feedstock through spray drying and careful control of plasma parameters contributes to two distinct regions within as-sprayed coatings, viz. partially melted /solid-state sintered (PM) and fully melted and resolidified (FM) structure. Owing to the poor thermal conductivity of porous spray dried agglomerates, around 30-45 percent porosity, partial melting is sustained in the core whereas a fully melted region is obtained on the surface. The surface-melting of powder particles results in fully melted and re-solidified regions whereas the core of the powder agglomerate gets sintered in the solid state. Hence, solid state sintering of the SDC nano-particles occurs in the core region without destroying the nano nature of the starting powders. Thus, the matrix results in a bimodal grain structure, i.e. fully melted and resolidified outer region and partially melted/solid-state sintered core region. The partially melted/sintered region helps in distributing the shock energy experienced during an impact, and helps deflecting crack resisting its propagation. Fully melted regions impart strength and binding integrity to the composite coating. Moreover, velocity (v) and temperature (T) are the controlling parameters strongly affecting the microstructure of the sprayed coatings. Velocity corresponds to the kinetic energy attained by in-flight particle. This in turn decides the degree of flattening and subsequent densification of the powder particle upon impact. The degree of melting is decided by the temperature attained by in-flight particles. Thus the interplay of kinetic (through velocity) and thermal-energy (via temperature) is critical in the generation of the microstructure. Thereby, in-flight sensor monitoring of velocity and temperature (of the in-flight powders) serve as controlling factors in optimizing the plasma processing parameters.

To preserve the advantages of CNTs in the SDC matrix, it is necessary for CNTs to survive with their original morphology and structure in the harsh environment of the plasma plume. Controlled plasma processing parameters, especially partial melting of the core of these agglomerated feedstocks, mainly contributes to the survival and distribution of CNTs. Additionally, poor thermal conductivity of powder-agglomerate porosity and subsequently limited melting of the agglomerate's surface and core also avoid damage of CNTs from the harsh plasma environment. Therefore, as seen in Fig. 5(c) and Fig. 5(d), interlinked-CNTs are distributed, undamaged and retained in the plasma sprayed samples.

4. Conclusions

Spray dried SDC agglomerates with and without CNTs were employed as powder feedstock to synthesise SDC-based samples with bimodal microstructure through the plasma spray. Poor thermal conductivity of powder-agglomerate porosity of spray dried powder feedstock coupled with optimized plasma processing parameters not only endow the as-sprayed SDC and SDC-CNT samples bimodal microstructure in nature consisting of nanocrystalline grains and micronsized columnar grains, but also avoid damage of the CNTs from the harsh plasma environment. The measurement of electrical conductivity of SDC and SDC-CNT samples with bimodal microstructure are ongoing.

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