Mechanical properties of plasma sprayed boron nitride nanoplatelet reinforced gadolinium-doped ceria (GDC) coating for intermediate temperature solid electrolyte

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Abstract. Boron nitride nanoplatelet (BNNP) reinforced gadolinia-doped ceria (GDC) electrolyte was successfully fabricated by plasma spray. Phase constitution by X-ray Diffraction revealed that ceria was the dominating phase, and Raman spectra showed that the added BNNPs retained their original structure after harsh plasma spray process. Meanwhile, microstructure observations of the as-sprayed samples indicated that the addition of BNNPs had a significant influence on the reduction of porosity. Compared to GDC electrolyte, hardness and elastic modulus of the BNNP/GDC electrolytes were improved by ~ 15.7% and ~ 41.6%, respectively. More importantly, fracture toughness of as-sprayed BNNP/GDC electrolyte increased by ~45.6%. These results illustrated that BNNPs had a positive influence on the mechanical properties. BNNP pullout, crack bridging by anchored BNNPs are the dominate toughening mechanisms for GDC composites electrolyte through SEM observing the fractured surfaces and development of indentation-induced cracks.

1. Introduction
Solid oxide fuel cell (SOFC) migrates oxygen ion-conducting electrolyte from an air electrode (cathode) to a fuel electrode (anode) where it reacts with a fuel (H₂, CO, etc.). Efficient and clean energy conversion can be provided in a variety of applications ranging from small auxiliary power unit to large scale power plants [1].

Due to the increasing requirements for long-term durability, reliability and cost efficiency [2], the current development goal of SOFC is to reduce the operating temperature in the medium temperature (IT) range (500-800 °C) [3], which requires an increase in electrolytes. Ionic conductivity and enhanced gas/electrode reaction kinetics [4]. As compared with Yttria (Y₂O₃) stabilized ZrO₂ (YSZ) electrolyte widely used in the SOFC which operates at elevated temperature between 800-1000°C, ceria-based solid electrolyte doped with Gd³⁺ and/or Sm³⁺ has been widely recognized as the more promising candidate. The gadolinia-doped ceria (GDC) was observed to be two to three orders of magnitude higher oxygen ion conductivity than YSZ due to the fact that oxygen ion conductivity of GDC at temperatures below 600 °C [5].

During intentional or accidental shut-down events, the elements of SOFCs undergo thermal shocks. Additionally, components of SOFCs should also match their thermal expansion to ensure the operation reliability of SOFCs [6]. A significant degree of mismatch in thermal expansion coefficients can result in large stresses, causing cracking or delamination during operation [7, 8], leading to decrease in the operation reliability of SOFCs. Hence, an effective method was employed to tolerate and minimize the
thermal expansion mismatch, i.e., the fracture toughness of the electrolyte should be significantly improved to tolerate these stresses generated by thermal expansion mismatch\cite{9}.

Recently, boron nitride nanoplatelets (BNNPs), a structural analogue of graphene, have comparable mechanical properties (e.g. tensile strength ~ 35 GPa and elastic modulus ~ 700-900 (GPa)\cite{10}. Moreover, unlike carbonaceous nanomaterials, BNNPs are chemically inert up to 950°C\cite{11}. More importantly, BN with electric insulation has a consistent gap of 5.5–6.0 eV\cite{10}. Therefore, above unique mechanical properties, electric insulation and antioxidation capacity associated with BN nanoplatelets are expected to be suitable reinforcing nanofillers in GDC.

It is well known that several methods of making SOFC electrolytes include chemical vapor deposition (CVD), electrochemical vapor deposition (EVD), sol-gel methods, ribbon casting, screen printing, physical vapor deposition (PVD), and plasma spraying. Among them, plasma spraying has many advantages over the above techniques in terms of ease of processing, significantly higher deposition rate and control of composition, porosity and microstructure\cite{12}.

In this research, BNNP reinforced GDC composite electrolyte was fabricated using plasma spray, the microstructure and mechanical properties of the as-sprayed electrolytes with and without BNNPs were analyzed and evaluated.

2. Experimentals

2.1. Materials and coating fabrication
GDC powders with a diameter of ~0.5-1.0 μm and a length of ~100 nm (Ningbo SOFC MAN Energy Technology Co., Ltd, China) and BNNPs with a thickness of ~20-30 nm and a diameter of ~0.5-5μm (Nanjing Xian Feng Nano Material Company, China) were employed as precursor materials. To ensure uniform distribution of BNNPs in the GDC composite coatings, the intact BNNPs were sonicated in ethanol for 3 h at a concentration of about 0.1mg/ml. Subsequently, GDC was added to the BNNP suspension followed by ultrasonic treatment for 1 h and magnetic stirring for 3 h, respectively. Finally, the obtained powder was dried in an oven at 80°C for 24 h. The compositions chosen here were pure GDC, 0.5wt.%BNNP/GDC and 1.0wt.%BNNP/GDC. In order to ensure good fluidity of the raw material powder and uniform distribution of BNNP in the spray electrolyte, spray drying was used to obtain micronized agglomerates having good fluidity for plasma spraying. These GDC powders and BNNP-GDC composite powders are dispersed in a water-soluble organic binder (Polyvinyl Alcohol), and the suspension was sprayed in a spray chamber of a spray dryer (LGZ-8, Wuxi Dongsheng Spray Granulation Drying Equipment Plant, China), and then dried to obtain porous spherical nanostructure agglomerates with a diameter of 40-75 μm (Fig. 1a). Moreover, it can be seen from Figure 1b. that BNNPs is uniformly distributed on the surface of the spray-dried agglomerated composite powder.

![Fig 1. SEM images showing (a) spray-dried agglomerated BNNP/GDC composite powders and (b) distribution of BNNPs on the surface of the spray-dried composite agglomerate.](image-url)

304 stainless steel (100 mm×15 mm×5 mm) was selected as substrates. Prior to plasma spray, the
substrate was sandblasted using Al_2O_3 particles with an average size of ~1 mm and then washed with acetone. These spherical spray-dried agglomerates were plasma sprayed on a Ti-6Al-4V substrate using a SG 100 gun (Praxair Surface Technology, Danbury, CT) using a plasma power of 36-40 kW and 800 A plasma gun current and powder feed. The speed is 2.5 g / min and the gap distance is 60 mm. Argon gas was used as the main gas (flow rate: 28 slpm), and helium gas was used as the auxiliary gas (35 slpm). Argon was also used as a powder carrier gas (8 slpm).

2.2 Microstructure and mechanical characterizations

The cross sections of the sprayed GDC and BNNP/GDC electrolytes were metallurgically polished for microstructural characterization and instrument microindentation. X-ray diffraction (XRD, X’Pert-ProMRD, Holland) was performed using Cu Kα radiation to analyze the phase composition of the spray coating using a scanning rate of 5°/min. The presence of BNNP in the sprayed coating was confirmed using a micro-Raman spectroscopy (Renishaw, UK) with an argon ion laser with a wavelength of 633 nm and an acquisition time of 10 seconds. Cross-sectional and cross-sectional observations of the spray coating were characterized using a scanning electron microscope (SEM, Hitachi S-4700, Japan).

Instrument microindentation experiments were performed on the polished cross sections of the polished coating using an MCT tester (Swiss CSM) with a maximum load of 500 mN at the Vickers tip (1 N/min ramp load and 10 s dwell time). Ten tests at intervals of 500 μm were performed at different locations of each sample. The elastic modulus and hardness were calculated from the load-displacement curve using the Olive-Pharr method [13]. The fracture toughness is then calculated using the following equation [14]:

\[ K_{IC} = 0.016 \left( \frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}} \]  \hspace{1cm} (1)

Where \( H \) is the Vickers hardness, \( E \) is the modulus of elasticity, \( P \) is the applied load, \( 2c \) is the total length of the indentation-induced crack (\( 2c = 2l + 2a \)), where \( l \) is the crack length of the indentation angle \( 2a \) is the indentation pair Corner line. A radial crack was obtained using a microhardness tester (HXD-1000 TMC, Shanghai Taiming Optical Instrument Co., Ltd., 15 seconds residence time) with a Vickers probe and a 0.49 N load applied.

3. Results and discussion

Fig 2. SEM images of (a) as-sprayed GDC, (b) as-sprayed 0.5wt.%BNNP/GDC and (c) as-sprayed 1.0wt.%BNNP/GDC electrolytes.
The deposited coatings had a uniform thickness of ~160 μm, all the as-sprayed GDC electrolytes were free of cracks, and the as-sprayed electrolytes exhibited fully melted zone, partially melted zone and some pores, in which fully melted zone acted as binder to maintain the as-sprayed coating integrity, as shown in Fig 2. Moreover, it should be noted that the propensity for pore and partially melted zone significantly decreased with increasing of BNNP addition content.

This can be clearly seen from Fig 3a. that the main phase of all sprayed electrolytes is cerium oxide with a phase change during plasma spraying. The Raman spectra of the received BNNP powders and the sprayed BNNP/GDC coating are shown in Fig 3b. In general, the Raman spectrum of BNNPs only shows the Raman G band associated with the E_{2g} vibration mode [14]. It can be clearly seen that the characteristic G-band frequency of the sprayed composite is ~1366 cm^{-1}, which is slightly blue-shifted compared to the BNNP received as it is. The above results strongly suggest that these added BNNPs can withstand harsh high temperature processing.

Fig 3. (a) XRD results of as-sprayed GDC electrolytes with and without BNNPs, (b) Raman spectra of as-received BNNP powders and as-sprayed BNNP/GDC electrolytes.

Table 1. Mechanical properties of as-sprayed GDC and BNNP/GDC electrolytes

|               | E (GPa) | H (GPa) | K_{IC} (MPa m^{1/2}) |
|---------------|---------|---------|-----------------------|
| GDC           | 126.4±13.9 | 5.46±0.31 | 1.16±0.11             |
| 0.5wt.%BNNP/GDC | 162.8±14.6 | 6.06±0.28  | 1.53±0.26             |
| 1.0wt.%BNNP/GDC | 179.1±16.7 | 6.32±0.33  | 1.69±0.22             |

The measured mechanical properties of pure GDC and BNNP/GDC electrolytes were listed in Table 1. Compared to the pure GDC electrolyte, the indentation hardness and elastic modulus of a 0.5wt.%BNNP/GDC electrolyte increased. Nevertheless, as the amount of BNNPs increased further, the hardness and elastic modulus decreased slightly. The fracture toughness of as-sprayed BNNP/GDC coating showed a ~31.9% improvement (from 1.16±0.11 to 1.53±0.26 MPam^{1/2}) at 0.5% BNNP weight fraction, while it increased up to ~45.6% (1.69±0.22 MPam^{1/2}) at 1.0% BNNP weight fraction. The presented results strongly imply that BNNPs are more promising potential in toughening GDC composite coatings.

Based on the SEM observation of the fracture surface and the indentation induced crack, several kinds of strengthening toughness which enhance the toughness of the sprayed BNNP/GDC electrolyte were analyzed. As shown in Fig 4a, it is clearly seen that the embedded BNNP is pulled out. When the BNNP pull-out operation, friction between the BNNP and the substrate is produced, which alleviates the stress concentration in the front working zone (FPZ) in front of the crack tip. It is worth noting that the BNNP pulled out without damage experienced this deformation (as indicated by the arrow in Fig 4a) may be due to the flexibility of BNNP. The special surface texture of the embedded BNNP and higher specific surface area are expected to contribute to a stronger interface bond through mechanical locking between a BNNP and GDC grains. Furthermore, observing the propagation of cracks on the
surface of the crack indicates that the crack is blocked by the embedded BNNP (Fig. 4b). It is believed that BNNP can wrap more intergranular regions due to its two-dimensional nature. Therefore, cracks along the grain boundaries must propagate over a greater distance and consume more energy, causing cracks to be prevented or arrested.

Fig 4. SEM images of fractured surfaces of the BNNP/GDC electrolyte showing (a) the pullout of BNNP (b) crack arrested by the embeded BNNP.

4. Conclusions
In summary, a boron nitride nanosheet (BNNP)-enhanced yttria-doped yttria (GDC) electrolyte is produced by plasma spraying, where in BNNP maintains its original structure even after a harsh process and is relatively uniform in the sprayed coating. Ground distribution. Compared to a single piece of GDC electrolyte, results showed that fracture toughness of a 1.0wt.%BNNP/GDC coating were improved by up to ~45.6%, and hardness and elastic modulus of the BNNP/GDC electrolytes were improved by ~15.7% and ~41.6%, respectively. Above results illustrated that the embedded BNNPs can endow GDC with significant improvement in fracture toughness and moderate enhancement in strength.

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