Thin film of Yttria stabilised zirconia on NiO using vacuum cold spraying process for solid oxide fuel cell

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Abstract: Yttria stabilised zirconia (YSZ) was fabricated on a glass and NiO-YSZ anode support substrate using the vacuum cold spraying (VCS) technique at room temperature. The field emission scanning electron microscope (FESEM) analysis revealed a dense microstructure and several vertical cracks within 0.1 μm width of the YSZ film. The transmission electron microscopy (TEM) was used to analyse the grain size and it was found to be 20 nm which was finer size compared to the average particle size of the starting YSZ powder. The x-ray diffraction (XRD) analysis showed lacking of phase transformation during the VCS process. The YSZ film fabricated by VCS technique showed better gas tightness compared to that fabricated by atmospheric plasma spray process. The Young’s modulus of the YSZ film was found to be 172 GPa.

Keywords: Yttria stabilised zirconia; YSZ; vacuum cold spraying; VCS; solid oxide fuel cell; thin film; gas permeability; conductivity; mechanical properties.


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1 Introduction

Solid oxide fuel cell (SOFC) is the most efficient device invented for the conversion of chemical fuels to electrical power. This class of fuel cell has numerous advantages such as high ionic conductivity, better stability, chemical and thermal compatibility, high strength and toughness, and relatively low cost (Han and Peng, 2004). Fuel cells are characterised by different components and most importantly the electrolyte. Yttria stabilised zirconia (YSZ) is a common electrolyte used in the SOFC. YSZ as electrolyte in the SOFC is an oxygen ion conductor and operate at the temperature ranging between 800–1,000°C. The characteristics, like high thermal stability, high ionic conductivity, and good thermal expansion compatibility with the electrodes materials, together make the YSZ as electrolyte suitable for the SOFC (Basu et al., 2005; Chen et al., 2002; Lang et al., 2002; Li et al., 2004, 2005).

YSZ thin films have been fabricated by different deposition techniques, such as sol–gel processes, physical sputtering techniques, and chemical gas phase techniques i.e., electrochemical vapor deposition, spray pyrolysis and chemical vapour deposition (Chour et al., 1997; Choy, 1995; Dekker et al., 1992; Nakagawa et al., 1989; Negishi et al., 1981; Peshev and Slavova, 1992; Sakurai et al., 1993). But these techniques have several drawbacks as some of them are being conducted at high temperature which is not suitable for the low melting point substrate materials like glass and plastic (Akedo, 2006). Also they use time intensive chemical processes leading to diffusion of the substrates. A number of studies have been reported the use of reduced sintering temperature for the purpose of low energy consumption and implementing innovative functional components (Imanaka et al., 2007).

Vacuum cold spraying (VCS) technique has been explored as a potential alternative to the above conventional processes for the formation of dense and thick ceramic layer at room temperature. This technique is based on the impact adhesion of fine particles for forming and micro-patterning of thick ceramic layers. The VCS technique emerges as a novel and attractive coating method for ceramic integration (Maki et al., 2006). In the VCS process an aerosol of fine powder is accelerated near to the substrate by a high speed carrier gas system. The speed of the carrier gas is controlled by the pressure gradient and the gas flow rate. The accelerated aerosol particles are finally ejected through a fine nozzle and impact onto a fixed substrate. During the impaction and interaction with the substrate, the ceramic aerosol particles form a thick, dense, and hard
ceramic layers. The overall process is conducted at room temperature (Akedo et al., 2003).

In this work, an YSZ ceramic powder was coated on the glass and NiO-YSZ anode support substrate using a manually designed VCS apparatus that constitutes an aerosol and a deposition chamber. The overall process of coating was conducted at ambient temperature. The cost of coating can be reduced dramatically compared to the conventional sputtering technique as the VCS is a room temperature process. The main purpose of this study is to apply a thin film of YSZ as the electrolyte in the SOFC. To fulfil the application, the mechanical and electrical properties such as microstructure, grain size, crystallinity, density, ionic conductivity, hardness and Young’s modulus were analysed using different instruments.

2 Experimental

2.1 VCS apparatus

The principle of VCS process was followed to produce a thin YSZ film as a result of aerosol particle densification. The VCS apparatus constituted two vacuum chambers and were connected by a gas pipe. The first chamber was the deposition chamber where the film formed. The deposition chamber was evacuated using a rotary vacuum pump followed by a mechanical booster pump during the deposition process. The second chamber was the aerosol chamber that generated the ceramic aerosol. The aerosol chamber consisted of a carrier gas system and a vibration system to prepare ceramic aerosol. The ceramic aerosol accelerated from the aerosol chamber to the deposition chamber through the gas pipe due to the flow of high speed carrier gas. Nitrogen gas was used as the carrier gas. High speed of the carrier gas was achieved by the pressure difference between two chambers and monitoring the flow of gas from the nitrogen gas cylinder. A fine nozzle was used to eject the fine ceramic particles in the form of aerosol and spray on to the substrate fixed in deposition chamber. The particle velocities were controlled by a mass flow controller. The typical deposition parameters used for the VCS process are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental parameter</th>
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</thead>
<tbody>
<tr>
<td>Pressure in deposition chamber</td>
<td>0.01–0.1 MPa</td>
</tr>
<tr>
<td>Pressure in aerosol chamber</td>
<td>~0.3 MPa</td>
</tr>
<tr>
<td>Size of nozzle</td>
<td>10mm × 0.4 mm</td>
</tr>
<tr>
<td>Accelerating gas</td>
<td>He</td>
</tr>
<tr>
<td>Flow rate</td>
<td>5–30 L/min</td>
</tr>
<tr>
<td>Speed of the substrate</td>
<td>30–100 mm/sec</td>
</tr>
<tr>
<td>Distance between the nozzle and substrate</td>
<td>1–20 mm</td>
</tr>
</tbody>
</table>

2.2 Substrate and starting powder

A reagent grade YSZ (8 mol% Y₂O₃ and 92 mol% ZrO₂) powder was used as starting materials for the thin film. A glass or NiO-YSZ was used as substrate for the VCS process thin film. Nitrogen gas was used for the formation of aerosol as well as carrier
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2.3 Characterisations of YSZ film

During the VCS process, a thickness of about 5 μm YSZ film was prepared on NiO-YSZ substrate. Thereafter the film along with the substrate was sealed in an epoxy resin. The composition and phase of the both starting powder and fabricated film was analysed by x-ray diffraction (XRD) technique. The microstructure of the YSZ film was analysed using an field emission scanning electrode microscope (FESEM) instrument. The final grain size was confirmed using a transmission electron microscopy (TEM). Home-made equipment was used to measure the gas tightness of the YSZ film. The gas permeation volume rate through YSZ film was measured using an electromagnetic flow-meter after achieving a steady pressure in the equipment. To measure the ionic conductivity of the film, an additional YSZ film was prepared on aluminium oxide bar as substrate. During the ionic conductivity measurement platinum wires were attached to the YSZ film with help of the platinum paste. A thermocouple was kept in close proximity to the specimen in order to minimise the temperature measurement errors during the ionic conductivity measurement. The complex impedance (Z) of the YSZ film was measured in the air within a temperature range between 500–900°C using a four point probe AC impedance spectroscopy technique. The nanoindentation analysis was performed using a nano-indenter XP (Nano Instruments, MTS systems corporation, USA). The indentation was made with the help of a Berkovich indenter. The indenter was calibrated with a standard silica specimen following a standard continuous stiffness measurement (CSM) method. The standard CSM measures the stiffness, and determines the hardness and elastic modulus continuously as a function of penetration depth. The load was held at 70% of the maximum load for 60 s to correct the thermal drift during the penetration. The tip geometry and machine compliance were calibrated prior to analysis. In every test the indenter was driven at the above indicated rate into the specimen until the load reach the preset peak level load and then unloaded gradually to zero. For each peak load five tests were conducted at different locations in the sample. The hardness and Young’s modulus of the YSZ film were determined using the Oliver and Pharr analysis method (Oliver and Pharr, 1992).

3 Results and discussion

The ceramic film of 8 mol% YSZ was fabricated successfully on the both glass and NiO-YSZ substrate using VCS technique at room temperature. The thickness of the YSZ film varied from 5 to 10 μm. The deposition rate for YSZ aerosol ranged from 0.5 to 2 μm/min. The substrate temperature never exceeded the room temperature during the deposition process.

Crystal structure of the thin film was characterised using the XRD technique. Standard XRD scan was performed using Cu Kα radiation for both the starting powder and the fabricated YSZ films. The XRD patterns are shown in Figure 1. From the XRD analysis the structures were found to be cubic for the both starting powder and YSZ
films. This indicates that there was no phase transformation occurred in the YSZ materials during the VCS process. However, the XRD patterns (Figure 1) of the VCS fabricated YSZ film are broader and smaller when compared to that of starting YSZ powder. This may be due to either of finer grain size of the YSZ film than the starting powder, stress inside the YSZ film, and poor crystallinity in the film, or combination of all.

Figure 1  XRD of YSZ film and YSZ primary powder (see online version for colours)

Figure 2  Fracture image of YSZ film
Figure 3  Gas tightness of YSZ film (see online version for colours)

![Graph showing gas permeability vs. gas pressure]

Figure 4  TEM image of YSZ film

![TEM image of YSZ film]

Figure 2 shows a typical cross sectional SEM image of the YSZ film. From the figure it can be observed that the thickness of the non-bonded interface was varied within 0.5 μm due to different spraying distances. Several vertical cracks were observed within the film. The width of the cracks was found to be 0.1 μm. The top-coat of the film shows a dense microstructure. This may be due to continual bombardment of the growing film by energetic aerosol flow. The continual bombardment serves to increase the surface
mobility of adsorbed atoms on the substrate surface resulting more compact microstructures.

**Figure 5** Arrhenius relation of lnσT and 1000/T for the YSZ film (see online version for colours)

The gas tightness test was performed for the YSZ films fabricated by both VCS process and atmospheric plasma spray process. The result is shown in Figure 3. From the figure it can be observed that the gas permeability was unchanged with the increase of gas pressure from 1,000 to 2,000 mbar for the YSZ film fabricated by VCS process. However, the YSZ film fabricated by plasma spray process failed the gas tightness test as the gas permeability increased with the increase of gas pressure. Therefore, the YSZ film fabricated by VCS process can be used successfully as the solid electrolyte in the SOFC.

Figure 4 shows the TEM image of the YSZ film fabricated by VCS process. From the TEM analysis the final grain size of the film was found to be 20 nm which was finer size than the average particle size of the starting YSZ powder. Additionally, the TEM results showed that the coating layer was crystallised during the deposition process. The dense microstructure was formed by either the reduction of grain size, or the fracture or plastic deformation at room temperature during the VCS process.

The Arrhenius equation (Lin et al., 1983) has been used to analyse the ionic conductivity data. The Arrhenius equation can be written as:

$$
\sigma = \sigma_0 e^{-\frac{E_a}{R T}}
$$

where $\sigma$ is conductivity, $\sigma_0$ is pre-exponential factor, $E_a$ is activation energy and $T$ is absolute temperature. Therefore, a plot was drawn between logσT versus 1/T and is shown in Figure 5. The activation energy was calculated from the slope of the plot and found to
be 1.12 eV which was similar to that of the starting materials. It indicates that the ionic transport mechanism of the YSZ was unchanged during the VCS process. The activation energy calculated for the YSZ film fabricated by atmospheric plasma spray process was found to be 1.14 eV. In the comparison of activation energies, the ionic conductivity of the YSZ film fabricated by VCS process proved more suitable than that of the atmospheric plasma spray process at whole range of temperature. The difference of activation energy of the YSZ film fabricated by the two different processes may be attributed by the different microstructures and the existence of defects. In case of the YSZ film fabricated by atmospheric plasma spray process, the amount of oxygen vacancies and defects are large enough to generate the dopant-vacancy associated over whole temperature range, and the activation energy would be $E_a + E_m$. However, in case of the YSZ film fabricated by VCS process, the amount of oxygen vacancies was not significant for the concentration of complex defects and the activation energy would be only $E_m$. Also the ionic conductivity of the YSZ film fabricated by VCS process was more than that of atmospheric plasma spray process at all range of temperature due to the reduction of grain-boundary resistance through the formation of nanocrystalline grains. (Aoki et al., 1996).

Figure 6  Young’s modulus of YSZ film (see online version for colours)

The Young’s modulus and hardness of the YSZ films was calculated from the results of nanoindentation experiments using the Oliver and Pharr method. (Oliver and Pharr, 1992) The above physical parameters were determined separately in case of perfectly elastic and elasto-plastic nanoindentation. The hardness and elastic modulus were determined as the function of penetration depth. The Young’s modulus was plotted versus the penetration depth and the plot is shown in Figure 6. It can be observed that Young’s modulus of the YSZ film increased sharply with the increase of penetration up to 75 nm.
into the surface and it remain unchanged on further increase of the penetration. The Young’s modulus found to be 172 GPa when the penetration depth was 75 nm.

4 Conclusions

The VCS technique was used to fabricate YSZ on the NiO-YSZ anode support substrate at room temperature. The microstructure of the YSZ film was analysed using FESEM which revealed the non-bonded interface within 0.5 μm due to different spraying distance. Also the FESEM result showed vertical cracks inside the film. No phase transformation of the YSZ film occurred during the VCS process as the XRD peaks of the starting powder and film were similar. However, the peaks of the film were broader and smaller due to finer grain size and stress inside the film. TEM results revealed the grain size of the YSZ film was 20 nm. The YSZ film fabricated by VCS process showed better result towards the gas tightness test compared to the YSZ film fabricated by atmospheric plasma spraying process. The Young’s Modulus of the YSZ film increased with the increase of penetration depth up to 75 nm and on a further increase it remained unchanged. The Young’s Modulus of the YSZ film found to be 172 GPa.

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