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Effect of alumina addition on the microstructure of plasma sprayed YSZ

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Abstract

A plasma spray process for fabricating yttria-stabilized zirconia (YSZ) layers for SOFC was investigated. YSZ powders (CERAC, USA) <44 μm in diameter have been used to prepare plasma-sprayed ceramic films on the stainless steel sheets employing non-equilibrium plasma spray technology at atmospheric pressure. The effect of alumina addition from 1 to 5 wt.% on the properties of plasma sprayed YSZ films was investigated. Plasma sprayed zirconium oxide films have been characterized using scanning electron microscope (SEM) and X-ray diffractometer (XRD) for study of microstructure and phase analysis. The phase content and crystallite size of the films have been evaluated. The dependence of deposit characteristics on the concentration of additive was investigated and revealed that proper amount of alumina addition can improve the properties of plasma sprayed YSZ films. It was demonstrated how the started powder composition affects the density of the obtained films.

Keywords: Films; Microstructure-final; ZrO_2; Fuel cells; Plasma spraying

1. Introduction

For many years, zirconia has attracted the attention of scientists and technologists because of its superior properties, such as high heat resistance, high mechanical strength, and high ionic conductivity at high temperatures.[1] Yttria-stabilized zirconia (YSZ), which requires operating temperature of about 1000 °C, has been identified as the target electrolyte layer material for solid oxide fuel cells (SOFCs).[2]

However, its application is often limited by the high sintering temperature and poor toughness. Recently, many investigations on the improved mechanical and electrical properties of YSZ have been carried out by the use of the small additions of alumina. Hassan et al.[3] reported the performance of a cell with Al_2O_3 added to the electrolyte is better than that of a cell with pure 8YSZ, especially at operating temperatures between 800 and 900 °C. Ji et al.[4] found that doping Al_2O_3 to cubic YSZ can significantly increase the sinterability of the electrolyte layer and reduce the sintering temperature of YSZ. The highest values of grain boundary conductivity were achieved with 4 wt.% Al_2O_3. Feighery et al.[5] studied the effect of different alumina additions upon electrical properties of YSZ and found that the optimum composition for an improved Tosoh 8YSZ electrolyte material is between 5 and 10 wt.% Al_2O_3. Rizea et al.[6] investigated the influence of alumina additions on the grain boundary electrical conductivity of yttria-doped zirconia by impedance spectroscopy. By their results, alumina additions (≤2 wt.%) lead to an increase of conductivity of samples.

There are a variety of methods for making YSZ films and coatings. Plasma spraying is a popular and economical way to deposit ceramic coatings for electronics, semiconductors, and other technical applications at higher temperatures.[7–9] This process, which combines melting, rapid quenching, and consolidation into a single step, can be used for many ceramic materials that melt without decomposing. Low temperature plasma spraying is widely used in fundamental research and industry, especially for ceramic films deposition on various substrates.[7–11]

The objective of this work was to examine how secondary additive material influences the properties of plasma sprayed

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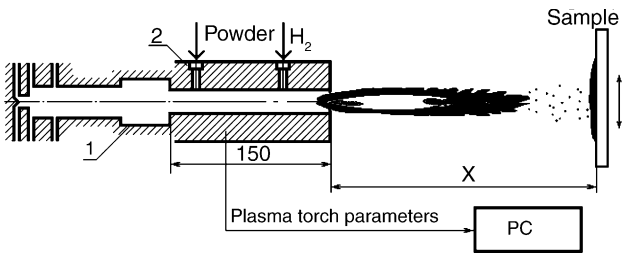

Fig. 1. Schematic view of experimental set-up: (1) plasma spray gun and (2) reactor.

Table 1
Plasma spraying parameters

Capacity of plasma torch P (kW)	49
Total mass flow of air G ($g\,s^{-1}$)	5.5
Total mass flow of hydrogen $G(H_2)$ ($g\,s^{-1}$)	0.1
Plasma jet temperature T (°C)	3130
Spray distance X (mm)	70
Flow velocity v ($m\,s^{-1}$)	1400

YSZ films. In this study, the effect of alumina addition on the formation of plasma sprayed films is related to the microstructure produced.

2. Experimental procedure

YSZ films were deposited on the stainless steel sheets employing non-equilibrium plasma spraying technology at atmospheric pressure DC plasma torch.[11] For this aim a special test bench with linear single-chamber plasma torch was built. Schematic view of the experimental set-up is shown in Fig. 1. Plasma spraying parameters are listed in Table 1.

Polished stainless steel sheets were used as the substrate material. Prior to plasma spray, the substrate surface was hand-polished to 0.05 μm finishing. All substrates were cleaned with acetone and dried in air before they were used. To obtain a uniform coating, the substrates were placed on a cylindrical fixture, which could rotate around its own axis during plasma spraying, 20–100 mm away from the exit of the torch. The thickness of the steel substrates was 100 μm.

A commercial yttria stabilized zirconia powder (CERAC, USA, particle size <44 μm) typically 99% pure with 10–15 wt.% of yttria and aluminum oxide powder (Alfa Aesar, Johnson Matthey GmbH, 99.9% pure) with particle size <10 μm, as a source material for Al_2O_3 additive, were used as started powder for YSZ films deposition. The mixtures of started powder were prepared by ball milling for 8 h. The additive was doped into YSZ by the amount of 1–5 wt.% alumina. Started compositions of raw materials are listed in Table 2.

Scanning electron microscopy (SEM) was used to examine the microstructure evolution of the plasma sprayed films. Polished cross-sections of the samples were prepared for SEM analysis. The film thickness was evaluated by cross-sectional SEM observation. The specimens for cross-sectional microscopy were prepared by mounting the samples in epoxy resin, followed by polishing through 0.05 μm alumina.

Table 2
Characteristics of YSZ films vs. started powder composition

Sample	Initial powder composition		Crystallite size (nm)	Density (% theoretical)
	ZrO_2 (wt.%)	Al_2O_3 (wt.%)		
YSZ-0	100	0	98.2	73.8
YSZ-1A	99	1	93.3	75.5
YSZ-2A	98	2	80.1	78.8
YSZ-3A	97	3	74.7	86
YSZ-4A	96	4	64.1	87.2
YSZ-5A	95	5	60.9	85.9

The film density was measured using the Archimedes technique. Crystalline phases of started powders and plasma sprayed specimens were estimated by X-ray diffractometer (XRD). XRD technique was used to determine crystallite size of sprayed films.

3. Results and discussion

In this issue, we discuss the work done with two types of YSZ powder—pure YSZ and YSZ-doped with different amount of alumina towards the improvement of properties of plasma sprayed YSZ films. SEM observations of sprayed powders collected in flight have revealed some morphology differences between the powders sprayed. The illustrative SEM micrographs showing typical shape and size of powders sprayed are presented in Fig. 2.

The analysis of powders in the plasma jet showed that started powder composition has not a great influence on the melting state of powders used. From an examination of microstructures, all alumina-doped powders are completely melted and spheroidized. A ball-like microstructure is typical to all alumina-doped powders. From the data of SEM observations, the deposition temperature is the main parameter influencing the physical and chemical properties of the started powder and the film formation. The suitable temperature region for the deposition of YSZ films was found to be between 3000 and 3500 °C.

The influence of alumina addition on the densification of plasma sprayed YSZ films is shown in Fig. 3. Despite the different composition of initial powders, the morphology of all films is similar, as shown in Fig. 3. Typical lamellae structure is formed from deformed and solidified droplets. The unmelted particles are not dominated in the microstructure of sprayed films. Randomly distributed small pores of different sizes are observed in all coatings. The amount of pores in the microstructure of YSZ-3A, YSZ-4A and YSZ-5A is considerably less than in undoped samples or doped with 1–2 wt.% of alumina. The homogeneous distribution of particles and pores is typical over to the whole film thickness.

The density values of as-sprayed deposits compared with the theoretical density values of the actual composition

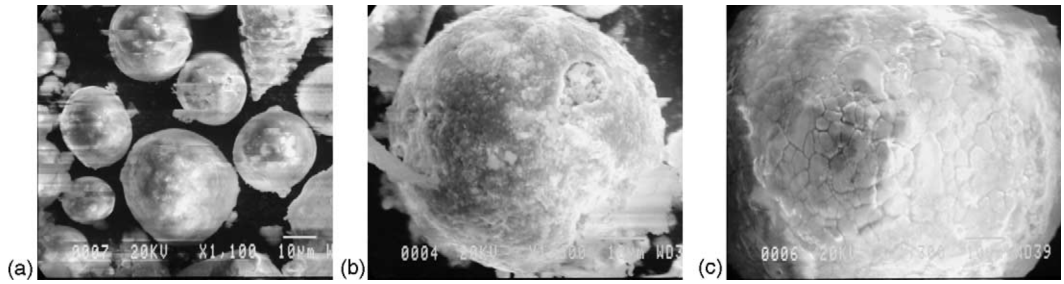

Fig. 2. SEM micrographs of pure YSZ (a) and alumina doped zirconia powder particles, (b) YSZ-2A and (c) YSZ-5A after passing through the plasma jet.

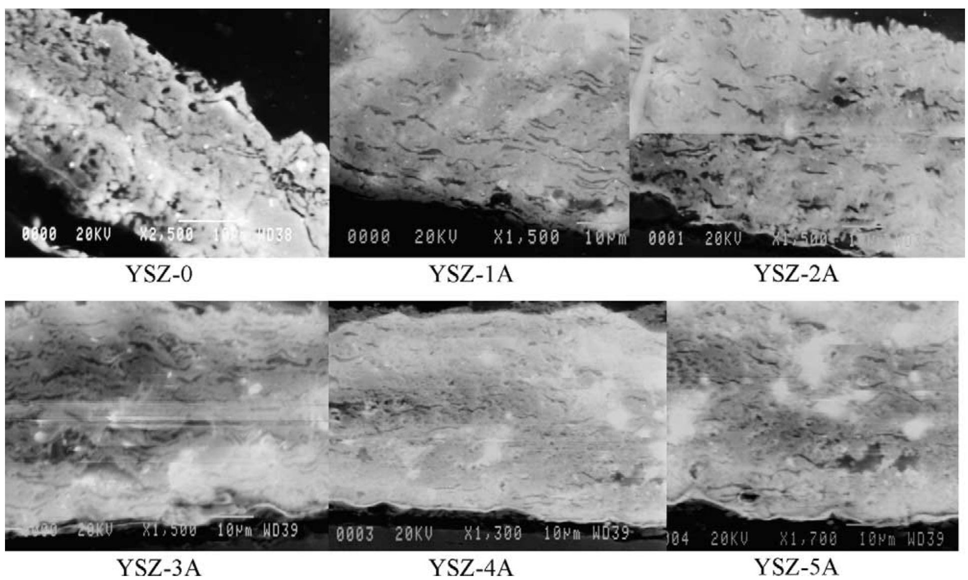

Fig. 3. SEM micrographs of the typical cross-sections of plasma sprayed YSZ films.

(taking account of the yttria and alumina) versus the composition of started powder are presented in Table 2. The influence of alumina additive on the microstructure of plasma sprayed films is noticeable for the YSZ doped with 3–4 wt.% of alumina. The YSZ-3A and YSZ-4A films are characterized by more dense structure and low porosity. The higher density of films means better sintering behaviour of ceramic.

The analysis of cross-sectional SEM micrographs showed that the thickness of all films was roughly between 25 and 60 μm subjected to the spray duration. The optimal spray duration is 60 s. The larger deviation in surface roughness is characteristic for plasma sprayed films YSZ-0 and YSZ-1A. It is determined, that the optimal spray distance for YSZ plasma deposition is 70 mm.

X-ray diffraction analysis of plasma sprayed films indicated the presence of two phases, α-Al_2O_3 and cubic ZrO_2 (Fig. 4). The main peaks of cubic zirconia and peaks of small intensity corresponding to (2 0 0) and (2 2 0) of alumina are identified in Fig. 4. The presence of corundum phase commonly improves the mechanical properties of zirconia. The sprayed films are nanocrystalline. The crystallite size of sprayed films has a tendency to decrease from 98.2 nm (YSZ-0) to 60.9 nm by increasing the alumina content in started powder to 5 wt.% (Table 2).

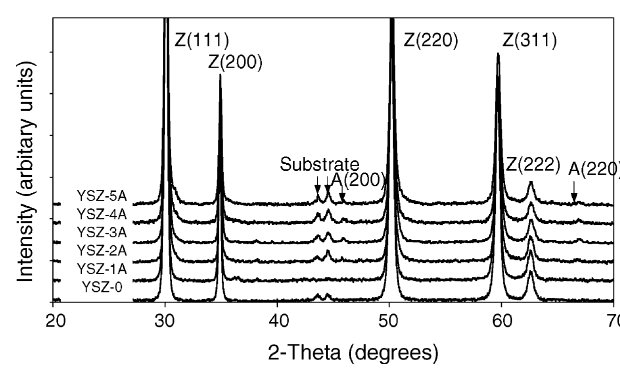

Fig. 4. XRD patterns of plasma sprayed pure YSZ (YSZ-0) film and alumina-doped YSZ films. Z, cubic ZrO_2; A, α-Al_2O_3.

4. Conclusions

Based on the results obtained, it can be deduced, that the variation of started powder properties by alumina addition has influence on the structure of plasma sprayed YSZ films. The properties of plasma sprayed YSZ films can be improved by a proper amount of alumina addition. A small amount of 3–4 wt.% alumina can be used as sintering additive for densification of plasma sprayed YSZ films. The deposition of powder with 3–4 wt.% alumina would produce films with improved structure and higher values of density. The investigations showed that the alumina-doped YSZ films are nanocrystalline, dense and homogeneous, with an average crystallite size of 60–93 nm. The crystallite size of alumina-doped YSZ films is less than undoped plasma sprayed YSZ.

Acknowledgment

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