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MICROSTRUCTURE AND PROPERTIES OF PLASMA SPRAYED Al-DOPED YSZ COATINGS *

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The influence of alumina additive from 1 to 5 wt. % upon the microstructure and ionic conductivity of ZrO_2–8 mol % Y_2O_3 (YSZ) ceramics, deposited by means of plasma spray technology, was investigated. Plasma sprayed films have been analysed using scanning electron microscopy (SEM) and X-ray analysis (XRD). The microstructural examination reveals that alumina addition decreases the porosity and microcracks of plasma sprayed YSZ. Analysis of SEM micrographs shows that the amount of 5 wt. % alumina substantially improves the microstructure of plasma sprayed zirconia. The crystal structure of all plasma sprayed samples consists of cubic zirconia and α-alumina. By the data of ionic conductivity measurements, no significant influence of annealing at 1073 K for 10 h was noticed on characteristic temperature dependences of σ for plasma sprayed YSZ. Alumina doping from 2 to 5 wt. % considerably increases the ionic conductivity of plasma sprayed zirconia. The higher values of ionic conductivity were obtained when 5 wt. % of Al_2O_3 powder was added to YSZ.

Keywords: films, microstructure-final, ionic conductivity, ZrO_2, Al_2O_3

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1. Introduction

The development of solid oxide fuel cell (SOFC) component production by plasma spray technique is very attractive for several reasons. One of them is the cost of production. Most of technologies nowadays used for SOFC layer fabrication, such as chemical vapour deposition (CVD), electrochemical vapour deposition (EVD), sol–gel or spray pyrolysis methods, physical vapour deposition (PVD), type casting and others [1] are expensive, need further thermal treatment and sintering. Materials chosen as electrolytes have to be chemically stable, possess stable microstructure at the operating temperatures, thermal expansion coefficient of these materials must be compatible with electrode materials. Yttria-stabilized zirconia (YSZ) is one of the main materials used for SOFC electrolyte. The compound ZrO_2–8 mol % Y_2O_3 has maximum value of ionic conductivity, good chemical and thermal stability. SOFC elements prepared by techniques mentioned above are thick and an acceptable resistance for such SOFCs can be reached at very high operating temperatures, 1173–1273 K [2]. The reduction of SOFC operating temperatures down to 973–1073 K is another important problem, which determinates their practical use. The thin YSZ films is the way to do it.

Thin YSZ films could be deposited by plasma spray technology employing the DC plasma torch generated non-equilibrium plasma jet at atmospheric pressure. Manufacture of YSZ electrolyte for SOFC, with thickness less than 50 μm, by means of atmospheric pressure plasma spraying is a flexible, fast, and economic process [3]. On the other hand, the weakness of plasma sprayed YSZ films is porosity and large coefficient of thermal expansion, (10–11)$\cdot 10^{-6}$ K^{-1}. Pores and microcracks reduce the ionic conductivity of SOFC electrolyte layer.

At present, many investigations have been carried out to improve the microstructure and electrical properties of YSZ thin films by use of addition of alumina. Initial YSZ powder with 3–4 wt. % of Al_2O_3 addition allows one to produce SOFC electrolyte layer with higher value of bulk density [4] and with practically no open porosity. The experiments show [5] that the addition of 0.77–4 wt. % of alumina to 8YSZ – zirconia stabilized with 8 mol % yttria – increases the sinterability of the electrolyte material and reduces the sintering time.

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Table 1. Main operating parameters of plasma torch.

Power supply, kW	35–50
Total gas flow rate (air), $g\,s^{-1}$	3.5–5
$G(H_2)$, $g\,s^{-1}$	0.1–0.15
Temperature in the powder injection place, K	4000–3500
Outlet plasma jet temperature, K	3000–3600
Outlet plasma jet velocity, m/s	600–700

By their results, the performance of a cell with alumina added to the electrolyte is better than that of pure YSZ.

In this report we present results of ionic conductivity investigations of thin YSZ films doped with 1–5 wt. % of Al_2O_3 deposited using plasma spray technique in the frequency range from $2{\cdot}10^3$ to $1{\cdot}10^6$ Hz in the temperature range of 600–800 K.

2. Experimental procedure

YSZ thin films were deposited by means of linear single-chamber plasma torch [6]. The experimental procedure, equipment, and operating conditions have been described in detail elsewhere [7, 8]. Stainless steel substrates were used for microstructural investigation, and substrates of alloy-600 for ionic conductivity measurements.

During experiments the operating conditions of plasma torch were constant. The capacity of plasma torch, total mass flow of air, cooling water, and its temperature were measured and from these data plasma jet temperature was calculated. The main plasma spraying regimes for YSZ films deposition are presented in Table 1. The hydrogen gas was added to increase the heat content of the flame and thereby the power of the system.

Major characterization techniques included scanning electron microscopy (SEM) and X-ray diffraction (XRD). The microstructure was characterized using the SEM (JSM 5600). Phase composition of the initial powder as well as sprayed films was analysed by X-ray diffractometer (DRON-6) with Cu K_α radiation. The density and porosity of plasma sprayed films were evaluated from the data of SEM analysis. The film thickness was estimated from the cross-sectional scanning electron microscopy observations. Two-probe ac impedance measurements were performed in air using a computer-controlled HP Precision LCR meter 4284A for ionic conductivity data of plasma sprayed samples.

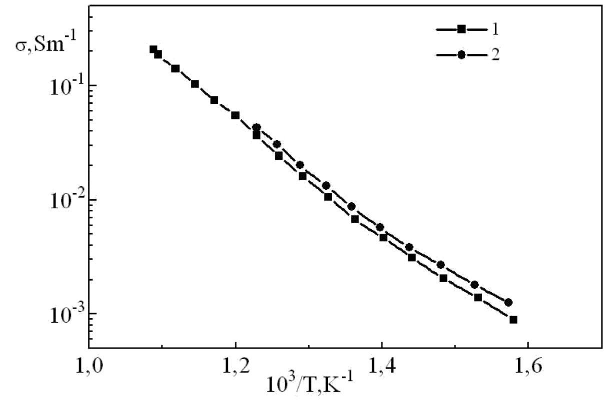


Fig. 1. Conductivity of as-sprayed YSZ film compared with the annealed YSZ. Heat treatment at 1073 K for 10 h.

Table 2. Plasma spraying regimes for YSZ film deposition.

P, kW	47.5
G, $g\,s^{-1}$	4.37
$G(H_2)$, $g\,s^{-1}$	0.1
T, K	3464
X, mm	70
Deposition time, s	30

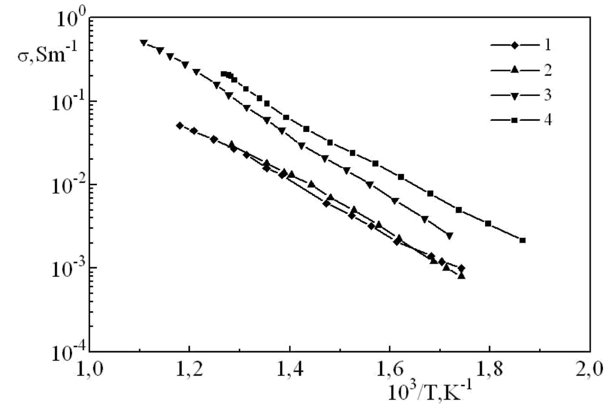


Fig. 2. Characteristic temperature dependences of σ for plasma sprayed 10–15 wt. % YSZ doped with Al_2O_3. The percentage of Al_2O_3 and value of activation energy respectively: *1* for 0%, 0.65 eV, *2* for 1%, 0.71 eV, *3* for 2%, 0.77 eV, *4* for 5%, 0.74 eV.

3. Results and discussion

Characteristic temperature dependences of ionic conductivity ($\lg\sigma = f(1/T)$) of plasma deposited YSZ films are presented in Fig. 1. For the deposition of YSZ thin films commercial (Russian) 8 mol % YSZ powders were used (particle size <50 μm). Plasma spray parameters are presented in Table 2. The film thickness is 35 μm.

The ionic conductivity and activation energy measurements confirm the conclusion that thin YSZ films deposited by plasma spray technology do not need further thermal treatment. No substantial changes were noticed in the microstructure of plasma sprayed YSZ samples after the thermal annealing at 1073 K from 1 to 10 h [8]. It has been observed that heat-treated films are qualified by finer and reduced porosity and increased density. Based on the results obtained, it can be deduced that the annealing of YSZ films at 1073 K for 10 hours has a marginal influence on the structural changes and conductivity of these films. No significant scattering of σ has been observed for this post-treatment of plasma sprayed YSZ. Ionic conductivity of YSZ thin films depends on the O_2 pressure, temperature, and thickness of the films [1]. Both groups of YSZ films – as-sprayed and annealed at 1073 K for 10 h – yielded an average ionic conductivity of 1.1 $\mathrm{S\,m^{-1}}$ at 1073 K respectively with the activation energy of 0.99 eV.

According to the results of Ivers-Tiffée et al. [9], 8 mol % YSZ bulk ceramic shows ionic conductivity at 1073 K from 3 to 4.2 $\mathrm{S\,m^{-1}}$, while 3 mol % YSZ bulk ceramic is of 1.1 $\mathrm{S\,m^{-1}}$ at the same temperature. Compared with these ionic conductivity measurements' data, plasma sprayed YSZ thin films show a high potential for SOFC element production. Investigations by Zhang et al. [10] indicate that ionic conductivity of YSZ coatings deposited by APS has been one-fifth to one-third of corresponding bulk materials.

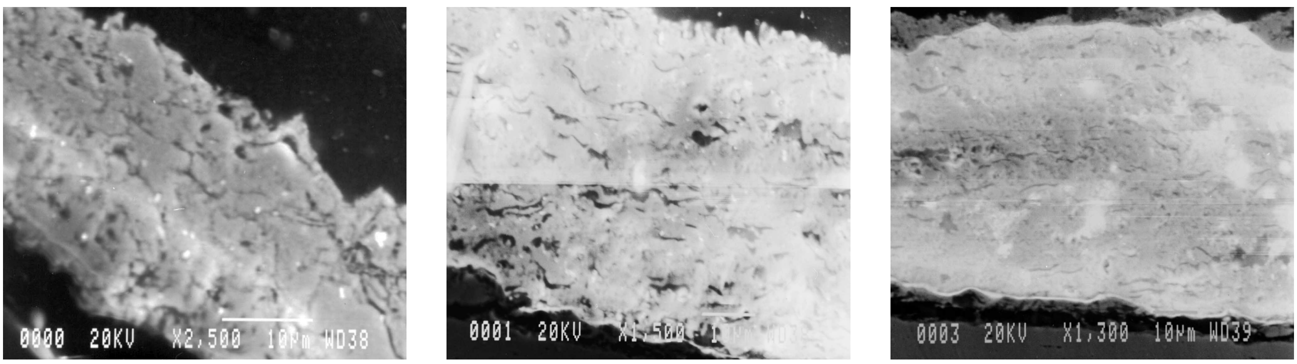
As mentioned above, the weakness of plasma sprayed YSZ films is their porosity and presence of microcracks [3, 5]. Pores and microcracks reduce the ionic conductivity of SOFC electrolyte layer. The abovementioned defects could be decreased by densification of microstructure. Some investigations have been carried out in order to improve the structural characteristics and electrical properties of YSZ by use of small amount of α-Al_2O_3 [5]. For this aim the stabilized zirconia powder (CERAC, particle size 0–50 μm, 99% pure)

Table 3. Plasma spraying regimes for YSZ film formation.

Regime	1	2	3	4
P, kW	48.8	48.5	48.5	48.5
G, $\mathrm{g\,s^{-1}}$	4.21	4.29	4.29	4.45
$G(H_2)$, $\mathrm{g\,s^{-1}}$	0.15	0	0	0.15
T, K	3350	3503	3507	3358
X, mm	70	70	70	70
Al_2O_3, %	0	1	2	5

with 10–15 wt. % of yttria and aluminium oxide powder (Alfa Aesar, 99.9% pure with particle size <10 μm) were used for plasma spray deposition. α-Al_2O_3 addition from 1 to 5 wt. % to YSZ powder was used. The results of ionic conductivity measurements of alumina doped plasma sprayed YSZ thin films are presented in Fig. 2, where the data are plotted as a function of doping concentration. Plasma spray parameters are listed in Table 3. An increase of the conductivity of YSZ with increasing the doping level has been found. The small amount of additive (1 wt. % of alumina) has insignificant influence on the conductivity of plasma sprayed YSZ. The impact of alumina on conductivity increases when the concentration of alumina is more than 2 wt. %. The highest values of temperature dependence of conductivity were found for YSZ doped with 5 wt. % of alumina. We suspect this is closely related with the microstructural evolution during doping.

The influence of alumina addition on the microstructure of plasma sprayed YSZ was studied by analysing SEM views of deposited layers. SEM micrographs of the fracture surfaces are presented in Fig. 3. Examination of microstructures revealed the decreased amount of pores and voids with increasing percentage of alumina doping. YSZ doped with 5 wt. % is characterized by more dense structure. Obviously, the



(a) (b) (c)

Fig. 3. The cross-sectional SEM views of plasma sprayed YSZ thin films with different amount of alumina dopant: (a) 0 wt. % of Al_2O_3, (b) 2 wt. % of Al_2O_3, (c) 5 wt.% of Al_2O_3.

sinterability of plasma sprayed YSZ material is increased with the addition of 5 wt. % of alumina.

4. Conclusions

Thin (30–45 μm) YSZ films (ZrO_2–8 mol % Y_2O_3) were deposited by means of plasma spray technology and the influence of alumina dopant, from 1 to 5 wt. %, on the microstructure and ionic conductivity of sprayed samples was investigated. A slight increase of conductivity values was observed after annealing of sprayed samples at 1073 K for 10 h. The higher values of conductivity were found for YSZ with a higher content of doping – 5 wt. % of alumina. Examination of microstructures revealed the densification of plasma sprayed YSZ material with the increase of percentage of alumina doping. The ionic conductivity was determined by material composition and coating microstructure.

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References

[1] J. Will, A. Mittendorfer, C. Kleinlogel, D. Perednis, and L.J. Gauckler, Fabrication of thin electrolytes for second-generation solid oxide fuel cells, Solid State Ionics **131**, 79–96 (2000).

[2] P. Bohas, A. Orliukas, and L.J. Gauckler, in: *Proceedings of the 1st European Solid Oxide Fuel Cells Forum* (Lucerne, Switzerland), Vol. 2, 651 (1994).

[3] R.H. Henne, M. Lang, M. Müller, R. Ruckdäschel, and G. Schiller, Manufacturing of solid oxide fuel cells – a challenge for DC and RF plasma deposition process, Ann. New York Acad. Sci., Heat and mass transfer under plasma conditions **891**, 124–136 (1999).

[4] K. Brinkiene and R. Kezelis, Effect of alumina addition on the microstructure of the plasma sprayed YSZ, J. Eur. Ceram. Soc. **25**, 2181–2184 (2005).

[5] A.A.E. Hassan, N.H. Menzler, G. Blass, M.E. Ali, H.P. Buchkremer, and D. Stöver, Influence of alumina dopant on the properties of yttria-stabilised zirconia for SOFC applications, J. Mater. Sci. **37**, 3467–3475 (2002).

[6] V. Valinčius, V. Krušinskaite, P. Valatkevičius, V. Valinčiūte, and L. Marcinauskas, Electric and thermal characteristics of the linear, sectional dc plasma generator, Plasma Sources Sci. Technol. **13**, 199–206 (2004).

[7] K. Brinkiene and R. Kezelis, Correlations between processing parameters and microstructure for YSZ films produced by plasma spray technique, J. Eur. Ceram. Soc. **24**, 1095–1099 (2004).

[8] K. Brinkienė, R. Kėželis, A. Baltušnikas, and V. Mėčius, Thermal treatment influence on microstructure of plasma sprayed zirconia thin films, Mater. Sci. (Medžiagotyra) **9**, 387–390 (2003).

[9] E. Ivers-Tiffée, A. Weber, and D. Herbstritt, Materials and technologies for SOFC-components, J. Eur. Ceram. Soc. **21**, 1805–1811 (2001).

[10] C. Zhang, C.-J. Li, G. Zhang, X.-J. Ning, C.-X Li, H. Liao, and C. Coddet, Ionic conductivity and its temperature dependence of atmospheric plasma-sprayed yttria stabilized zirconia electrolyte, Mater. Sci. Eng. B **137**, 24–30 (2007).

PLAZMA FORMUOTŲ YSZ DANGŲ SU Al PRIEMAIŠA MIKROSTRUKTŪRA IR SAVYBĖS

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Santrauka

Tirta aliuminio oksido priemaišų (1–5 masės %) įtaka YSZ – itrio oksidu (8 mol %) stabilizuoto cirkonio oksido – keramikų mikrostruktūrai ir joniniam laidumui. YSZ keramikos buvo pagamintos plazminio nusodinimo metodu. Dangos tirtos rentgeno spindulių difrakcijos (XRD) ir skenuojančios elektroninės mikroskopijos (SEM) metodais. Eksperimentai parodė, kad Al_2O_3 priedai (2–5 masės %) žymai sumažina dangos porėtumą, jose sumažėja mikroįtrūkimų. Visų plazminiu purškimu gautų bandinių kristalinės sandaros pagrindas – kubinės gardelės cirkonio dioksidas ir α aliuminio oksidas. Ištirtas gautų dangų joninis laidumas. Nustatyta, kad papildomas plazminių dangų kaitinimas esant 1073 K temperatūrai 10 h neturi didelės įtakos jų joniniam laidumui. 2–5 masės % aliuminio oksido priedas pagerina YSZ dangų laidumą. Didžiausios YSZ joninio laidumo vertės gautos naudojant 5% Al_2O_3 priedą.