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RESEARCH OF PLASMA SPRAYING OF THE $ZrO_2 - Y_2O_3$ ELECTROLYTE COATINGS

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Abstract. A quick cooling of coatings for the forming of the electrolyte layers with the given phase composition is widely used. In this work the preliminary heating of the specimens was applied instead of quick cooling technology. The influence of the substrate preliminary heating on the $ZrO_2 - Y_2O_3$ coatings structure and properties was investigated. The optimal of the spraying of coatings from the Ni and $ZrO_2 - Y_2O_3$ powders mechanical mix was determined. The research on the coating structure was carried out analysing the application of the optical metallography, scanning microscopy and X-ray method.

Keywords: fuel cells, electrolyte, zirconium dioxide, plasma spraying, phase composition, porosity.

Introduction

Phase diagram of the $ZrO_2 - Y_2O_3$ system (see Fig. 1) shows that the existence of all three basic phases (such as cubical, tetragonal and monoclinic) is possible in the ZrO_2 – 5–10% Y_2O_3 compositions range. So, at the plasma spraying of the heat-shielding ZrO_2 – 6–8% Y_2O_3 coatings, the coatings with the tetragonal phase content up to 99% are formed due to the specially used quick cooling of the coating deposit on the substrate (Ilyuschenko *et al*. 1998a, 1998b, 1997; Vityaz *et al*. 1997a, 1997b; Okovity 1998; Okovity *et al*. 1999).

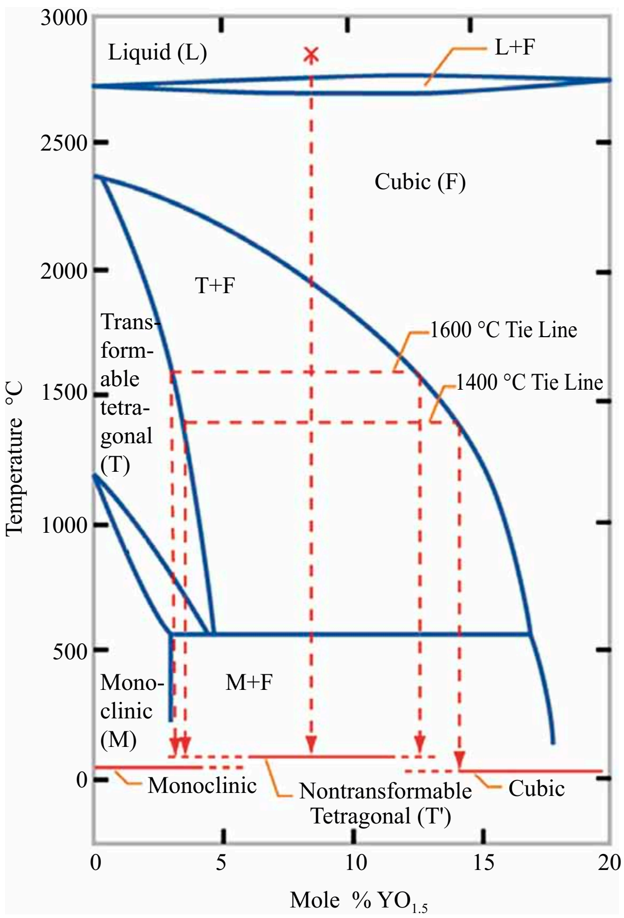

Fig. 1. Phase diagram of the $ZrO_2 - Y_2O_3$ system

The research of the influence of substrate preliminary heating temperature on the phase composition and structure of the solid electrolyte layers

The use of the $ZrO_2 - Y_2O_3$ compositions with the content of Y_2O_3 over 10% (stabilising the cubical phase in the wider range of temperatures at the quick cooling down from the flux) causes rising of the price of the initial powder materials for the coatings spraying. That's why the preliminary heating of the specimens from the room temperature to 700 °C was applied instead of the coating cooling for the forming of the electrolyte layers with the given phase composition. The optimization of the coatings' spraying parameters was carried out regarding the porosity and phase composition of the sprayed coatings. The optimized at the previous researches plasma generating gases and powder consumption has been kept up constant and came to: argon consumption – 40 L/min; hydrogen consumption – 10 L/min; powder consumption – 1.6 kg/h; spraying distance – 100 mm; arc current – 600 A. The ZrO_2 – 7% Y_2O_3 powder received upon applying the nitrate method was used for the coatings spraying. The size of the initial powder particles was less than 60 µm. The powder surface morphology research and the analysis of its structure have shown that the structure consists of the alloyed small initial components. The relief of the particles surface is typical for the processes of the mechanical grinding (see Fig. 2). The elements' content on the surface and in the section of the particles is given in the Table 1. The carried out X-ray investigations show (see Fig. 3) that the initial powder consists of tetragonal (94.7%) and monoclinic (5.3%) phases.

The researches on the properties of the coatings at the various levels of preliminary heating of the substrate have shown that the coating with the prevailing content of the tetragonal phase (99% – tetragonal phase, 1% – monoclinic, see Fig. 4) is formed on the substrate while heating it up to 500 °C. At the further increase of the substrates' preliminary heating temperature up to the 600 °C, the coating with the prevailing content of the cubic phase is formed on the substrate. The quantitative content of the cubic phase increases with the further rise of the substrates' heating temperature (see Table 2), at the same time the research of roentgenograms has shown the presence of the cubic phase of the $Y_{0.15}Zr_{0.85}O_{1.93}$ composition at the substrates, preliminary heating them up to 700 °C. The research of the coatings' structure carried out upon applying the optical metallography have shown that with the increase of the substrate preliminary warming temperature up to 700 °C, the general porosity of the coatings is reduced up to 2–3% at the formation of the precise coating boundary – a substrate without the presence of cracks on the coating boundary (see Fig. 5). Photos of the samples with the ZrO_2 – Y_2O_3 coatings on the substrates from $La_{0.5}Sr_{0.5}MnO_3$ are provided in the Figure 6.

Table 1. The element content in the ZrO_2 – Y_2O_3 powder particles

Number of measurement	Ratio of the elements and oxides, %				
	Y	Zr	O	Y_2O_3	Zr_2O_3
Particle surface					
1	3.97	70.3	25.73	5.04	94.96
2	4.47	69.83	25.7	5.67	94.33
3	4.72	69.59	25.69	6.0	94.0
4	5.6	68.8	25.6	7.06	92.4
5	5.82	68.56	25.62	7.4	92.6
In the particle's section					
1	3.6	70.7	25.73	4.5	95.5
2	3.8	70.5	25.7	4.82	95.18
3	3.91	70.4	25.69	4.96	95.04
4	3.97	70.3	25.73	5.04	94.96
5	4.1	70.19	25.71	5.2	94.8

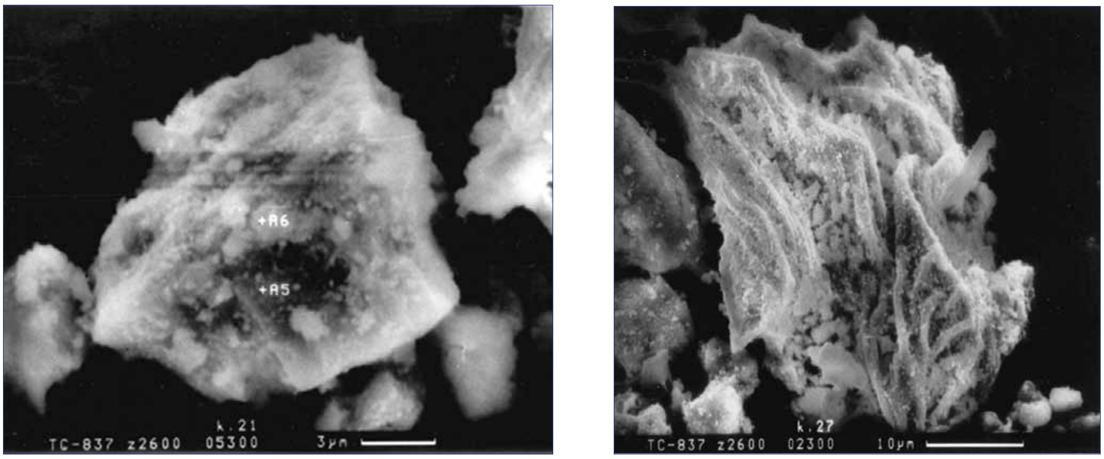

Fig. 2. Morphology of the ZrO_2 – Y_2O_3 powder particles (×1000)

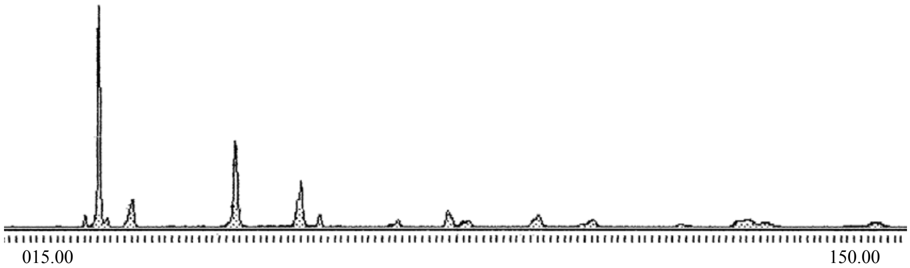

Fig. 3. X-ray photograph of the $ZrO_2 - Y_2O_3$ powder

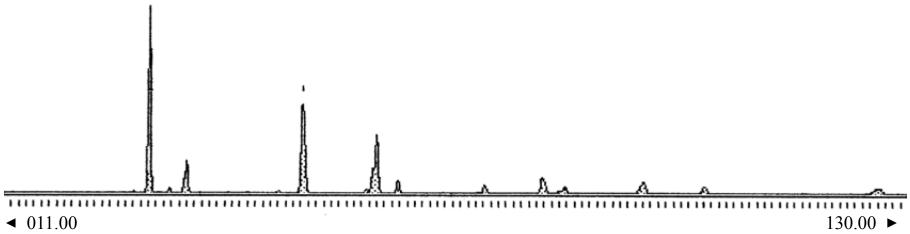

Fig. 4. X-ray photograph of the $ZrO_2 - Y_2O_3$ powder, substrate heating – 500 °C

Table 2. Phase composition of the $ZrO_2 - Y_2O_3$ coating depending on the preliminary warming temperature of the substrate

Substrate temperature, °C	Phase composition, %		
	Tetragonal	Cubic	Monoclinic
500 °C	99.0	–	1.0
600 °C	–	95.6	4.4
700 °C	–	96.8	3.2

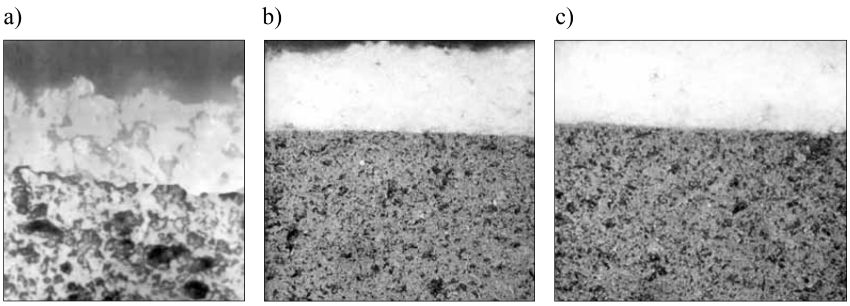

Fig. 5. Structure of the $ZrO_2 - Y_2O_3$ coating. Preliminary heating temperature of the substrate: a – 500 °C; b – 600 °C; c – 700 °C

Fig. 6. $La_{0.5}Sr_{0.5}MnO_3$ samples (black color) with the $ZrO_2 - Y_2O_3$ coatings (white color)

The research of the structure and properties of the anodic coating deposition by the plasma spraying

The powder mixes of the electrolyte material and nickel are used as the anodic materials (Eguchi *et al*. 1998). The use of nickel is proved by its high specific electric conductivity and chemical stability at high temperatures. The presence of nickel in the anodic material provides additional catalytic effect on the process of the fuel oxidation on the anode. The Ni-YSZ anodic material is most frequently used for the fuel cells with the YSZ electrolyte material while the Ni-SDC and Ni-GDC anodic materials better satisfy the characteristics of the cells with the electrolytes on the cerium dioxide basis. Standard anodic materials contain the amount of nickel up to 43% of volume. Composite powders for the formation of the anodes are made with the specific area of surface according to the requirements of the methods of manufacture of the anodes for the fuel cells. For example, the composite powders for the “screen printing” process have the specific area of 15–20 m^2/g, and for the “tape casting” process – 5–10 m^2/g. The anode is made with the high porosity (20–40%) for effective interaction of the fuel gas with the cathode material, carrying out the oxidizing reactions and the reagent bulk removal. The mechanical mix of the nickel powder (electrolytic nickel) – 45 weight % and the ZrO_2 – 7% Y_2O_3 powder – 55 weight % was used in the given work for the anodic layer spraying. The mixing of the powders with fractions less than 60 microns was carried out according to the "drunken barrel" technology during 2 hours at the rotation speed of 30 rpm, in ceramic bank. Anodic coatings were sprayed on the surface of the already sprayed layer of the solid electrolyte. Samples were cooled by the compressed air while the spraying of the coatings. The conditions of the spraying of the anodic coating are: arc current (350, 400, 450) A; voltage – 60 V; the powder consumption – 2.0 kg/h; the argon consumption – 40 L/h; the hydrogen consumption – 6 L/h; the consumption of the transporting gas argon – 5 L/h; spraying distance – 150 mm. The structures of the samples with the sprayed layers of solid electrolyte and the anodic coating are provided in the Figures 7–9.

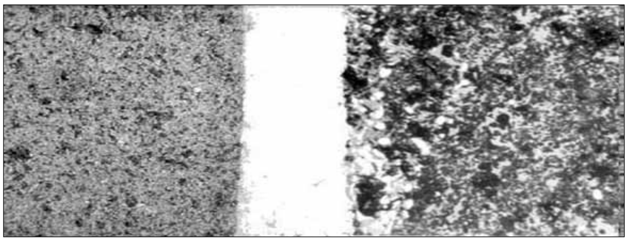

Fig. 7. The anodic coating structure at the arc current of 350 A: 1 – a cathode material; 2 – the layer of solid electrolyte deposit by the plasma spraying; 3 – the anodic coating deposit by the plasma spraying

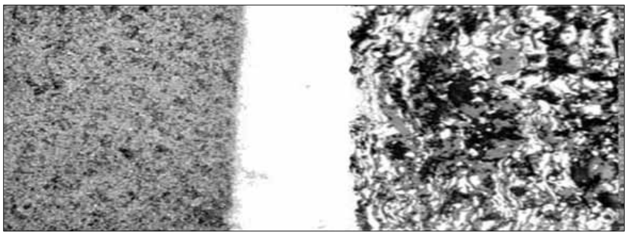

Fig. 8. The anodic coating structure at the arc current of 400 A: 1 – a cathode material; 2 – the layer of solid electrolyte deposit by the plasma spraying; 3 – the anodic coating deposit by the plasma spraying

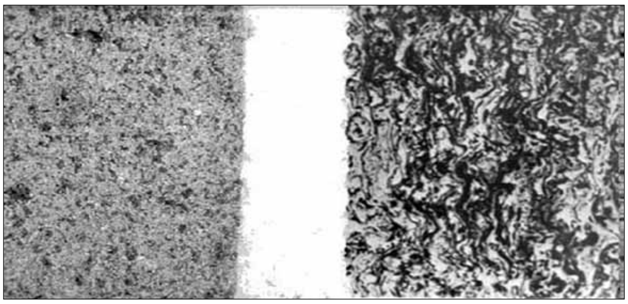

Fig. 9. The anodic coating structure at the arc current of 450 A: 1 – a cathode material; 2 – the layer of solid electrolyte deposit by the plasma spraying; 3 – the anodic coating deposit by the plasma spraying

The metallographic researches of the anodic coatings structures have shown that at the arc current of 350 A (see Fig. 7) the contents of ZrO_2 – 7% Y_2O_3 in the coating is at the level of 20–25 weight %, at the porosity of the coating of 15–20%. It is obvious that at the given mode of the coating spraying due to the insufficient capacity of the plasma jet for the heating of the ceramics (ZrO_2 – 7% Y_2O_3) particles, there is their insufficient concretion in the coating and the coating is formed basically due to the particles of the nickel powder. At the arc current of 400 A (see Fig. 8), the content of ZrO_2 – 7% Y_2O_3 in the coating is at the level of 40–45 weight %, at the porosity of the coating of 30–35%. At the arc current of 450 A (see Fig. 9), the content of ZrO_2 – 7% Y_2O_3 in the coating is at the level of 45–50 weight %, at the porosity of the coating of 20–25%. Thus the most optimal mode of spraying of the anodic layer of the coating from the mechanical mix of the nickel and ZO_2 – 7% Y_2O_3 powders is the following mode: current 400 A, voltage – 60 V, the powder consumption – 2.0 kg/h; the argon consumption – 40 L/h; the hydrogen consumption – 6 L/h; the consumption of the transporting gas argon – 5 L/h; spraying distance – 150 mm. Samples from $La_{0.5}Sr_{0.5}MnO_3$ with the ZrO_2 – Y_2O_3 coating (white color) and the anodic coating (dark grey color) are provided in the Figure 10.

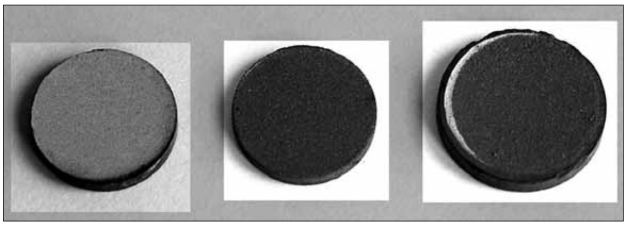

Fig. 10. The samples from $La_{0.5}Sr_{0.5}MnO_3$ with the ZrO_2 – Y_2O_3 coating (white color) and the anodic coating (dark grey color)

Conclusions

As a result of the research of the influence of the substrate preliminary heating on the ZrO_2 – Y_2O_3 coatings structure and properties, it has been established that the coatings with the content of the ZrO_2 cubic phase not less than 95.6% are formed on the substrates from $La_{0.5}Sr_{0.5}MnO_3$ when the substrate heating temperature is higher than 600 °C. The further increase of the temperature at the substrate preliminary heating results in the increase of the percentage of the ZrO_2 cubic phase – 96.8% at 700 °C, with the formation of the cubic phase of the $Y_{0.15}Zr_{0.85}O_{1.93}$ structure. Increasing the temperature of the substrate preliminary heating up to

700 °C allows forming of the coatings with the precise coating-substrate boundary, at the general porosity of the coating of 2–3%. The further optimization of the coatings depositing, with the purpose of the reduction the porosity, is possible due to the application of the smaller fraction of the initial powder of the 20 +/– 5 μm size for the coatings depositing, decreasing of the spraying distance and the introduction of the more fusible oxides (Al_2O_3, MgO) having high isolating properties and lower, in comparison with ZrO_2, temperatures of melting, into the composition of the initial powder. The optimal regime of the spraying of the anodic coating from the mechanical mix of the nickel and $ZrO_2 – Y_2O_3$ powders has been determined. The increase of the uniformity of the distribution of the anodic coatings components may be improved due to the development and use of the composite material for the depositing of the coating anodic layer.

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$ZRO_2 – Y_2O_3$ ELEKTROLITINIŲ DANGŲ PLAZMINIO PURŠKIMO TYRIMAS

O. Devoino, V. Okovity

Santrauka

Greitas dangų aušinimas siekiant suformuoti tam tikros fazinės sudėties elektrolito sluoksnį yra plačiai taikoma technologija. Šiame darbe vietoj greito aušinimo technologijos buvo taikomas išankstinis substrato pakaitinimas. Nustatyta $ZrO_2 – Y_2O_3$ dangų struktūros ir savybių priklausomybė nuo substrato pakaitinimo temperatūros ir parinkti optimalūs dangų iš Ni ir $ZrO_2 – Y_2O_3$ miltelių mišinio purškimo parametrai. Taikant optinę metalografiją, skenuojančią mikroskopiją ir rentgenografinę analizę atlikti užpurkštų dangų struktūros tyrimai.

Reikšminiai žodžiai: kuro elementai, elektrolitas, cirkonio dioksidas, plazminis purškimas, fazinė sudėtis, porėtumas.