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DEVELOPMENT OF THE CONCEPT OF THE PLASMA COATING FORMATION FROM PARTIALLY STABILIZED ZIRCONIUM DIOXIDE AND NICKEL CERMET ON THE FUEL CELL ELEMENT CONSIDERING FORECASTING AND THEIR EXPLOITATION PROPERTIES

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ABSTRACT
The concept of the plasma coatings forming from partially stabilized zirconium dioxide and nickel cermet on the element of a fuel cell has been developed on the base of the carried out analysis of works in this field for the period from 1988 to 2003. The given concept deter mines the aim, the main principles and directions of the work in this field considering the forecasting of exploitation properties of the fuel cell being formed. The aim of the concept is to spray plasma coatings from partially stabilized zirconium dioxide and nickel cermet on the fuel cell element – cathode on the LSM material base.

1. INTRODUCTION

The concept of the plasma coatings forming from partially stabilized zirconium dioxide and nickel cermet on the element of a fuel cell has been developed on the base of the carried out analysis of works in this field for the period from 1988 to 2003. The given concept deter mines the aim, the main principles and directions of the work in this field considering the forecasting of exploitation properties of the fuel cell being formed. The aim of the concept is to spray plasma coatings from partially stabilized zirconium dioxide and nickel cermet on the fuel cell element – cathode on the LSM material base with the following characteristics of layers:

- coating from partially stabilized zirconium dioxide: thickness of the coating is in the range of 50-100μm, porosity of the coating (overall) is 0.5% maximum, phase composition is >95% of cubic phase, tetragonal phase is 5% maximum, chemical composition is ZrO_2 – (8-12)% Y_2O_3;
- coating from nickel cermet: thickness of the coating is in the range of 100-200μm, porosity of the coating (overall) is 20-30%, Ni chemical composition is 40-50%, ZrO_2 – Y_2O_3 –50-60%.

It is necessary to solve the following main tests to achieve the said aim:

- to develop the technology of forming of the fuel cell element (cathode) which sustains thermal stress originating in the process of spraying a layer of the hard electrolyte and nickel cermet on it;
- to determine the chemical, granularity and phase compositions of the source powders of partially stabilized zirconium dioxide and nickel cermet effect on the structure and properties of the formed coatings;
- to determine the optimal parameters of spraying of the hard electrolyte layer from the powders of partially stabilized zirconium dioxide and the anode layer of the coating from the powders of nickel cermet using the technologies of plasma spraying under lower pressure (LPPS) and the air plasma spraying (APS);
- to determine the effect of the preliminary treating of the substrate on the properties of the formed layer coatings from partially stabilized zirconium;
- to determine the effect of the following thermal processing on the structure and properties change of the hard electrolyte layers on the base of partially stabilized zirconium dioxide and the hard electrolyte – cathode.

2. FORMATION OF PLASMA COATINGS ON THE BASE OF PARTIALLY STABILIZED ZIRCONIUM DIOXIDE AND NICKEL CERMET ON THE FUEL CELL ELEMENTS

Various methods of thermal spraying, depending on the material and the required properties of coatings are used now to obtain the fuel cell layers there. The following methods are used to spray the layers of the fuel cell: flame spraying (FS), air plasma spraying (APS), low pressure plasma spraying (LPPS), detonation spraying (DPS) and high velocity flame spraying (HVOF). High temperature of the gas jet, quick cooling of the melted ceramic particles on a cool substrate during deposition is a common phenomenon in the processes of the thermal spraying. In many cases investigators propose to carry out subsequent thermal processing to increase the electrolyte density due to the pores bulk decreasing, as well as to increase materials properties of the cathode and the anode. The subsequent thermal processing of the electrolyte layer may considerably influence the coating structure and enable to obtain electrolytic properties of the sprayed coatings which are similar to the coatings with sintered materials. Commercially available powders of partially stabilized zirconium oxide are mainly used to spray coatings. They are made using traditional technologies i.e.: joint melting with the following grinding and classification, joint grinding with the following granulation and sintering and drying by spraying [1-4].

The electrolyte layer must not be permeable, so that to separate fuel and oxidizer, and must be thin so that to decrease the inner resistance of the cell. Moreover it must be chemically resistant and thermally stable in the process of exploitation.

The plasma spraying process is interesting because of high productivity of deposition and simplicity of making template structures using masks as compared with other processes of electrolyte layer deposition, e.g. such as electrochemical spraying of the coating by vapour deposition, chemical vapour spraying of the coating and sputtering. Moreover, some investigators suppose that the process of plasma spraying is perspec-

tive from the point of view of the total expenditures decreasing during the production of the fuel cells [1,2]. Now the investigations in this field are continued because of the advantages of the plasma spraying process. Now the main perspectives trends in the field of plasma spraying are the following:
production of the high-quality, dense layer of the electrolyte with thickness 100 µm maximum;
production of the gradient electrodes (cathodes and anodes).
Plasma ceramic coatings may have microcracks as the result of the thermal stress during shrinkage of the coating in the processes of spraying and the following cooling, as well as pores which are formed in places of the gases exhaust. These problems must be averted so that to obtain values of gaseous nonpermeability, electrical specific electric conductivity and coordination of coefficients of heat expansion which are needed for the fuel cell [1, 2].
The authors [1] investigated the process of the plasma spraying of the electrolyte layer from the powder of partially stabilized zirconium dioxide with the following thermal processing. Compositions of the used powders are shown in Table 1.

Table 1. Powder materials used for spraying

Coating	Powder composition
1	ZrO_2 – 8 mole % Y_2O_3
2	ZrO_2 – 8 mole % Y_2O_3, preliminary priming of the MnO_2 substrate (3 mg/cm^2)
3	ZrO_2 – 8 mole % Y_2O_3 with addition of 5 mass % of MnO_2
1-3 – fraction of the powder 10-45 µm	

The coatings are sprayed on the porous substrates from manganese-acid lanthanum. After spraying the electrolyte layer the thermal processing of the coatings is carried out in the air medium under the temperature from 1000 to 1500˚C within 3 hours. After sintering measurements of the nitrogen gaseous permeability through the electrolyte layer are carried out.
The maid investigations have shown, that the permeability decrease of the electrolyte layer was achieved under the temperature of 1730 K minimum and at 1780 K it reached the value $1x10^{-8}$.
$cm^4g^{-1}c^{-1}$ using ZrO_2 – 8mole% Y_2O_3 powders. It is determined that gaseous nonpermeability of the electrolyte layer may be improved by the process of the sprayed layer sintering.
When using the powder of ZrO_2-8 mole% Y_2O_3 with addition of 5 mass% MnO_2 for the coating spraying and when making a preliminary priming of the MnO_2 substrate surface, the analogous values of permeability are obtained under the lower temperature of sintering – 1630 K. Thus the effective temperature lowering when the sufficient gaseous nonpermeability is ensured is obtained by the MnO_2 presence in the sintering zone.
Investigations of the coatings microstructure before sintering and after it enabled to determine that there are multiple microcracks and pores in the sprayed layers of the coatings. During the sintering under the temperature of 1780 K the microcracks have disappeared and spherical closed pores have been formed. Considerable lowering of the layer permeability after thermal processing under 1780 K is the result of the pores shape changing after sintering from the open microcracks to the spherical closed pores.
Changing of the pores shape results in the required value of the gaseous nonpermeability. Therewith the total porosity value of the electrolyte layer (1.5-2%) does not practically change and as the result of it the compression and the peeling of the electrolyte layer does not take place.
During the investigation of the effect of the electrolyte layer thickness on the gaseous permeability it is determined that the velocity of leaking is very small for the thickness exceeding 60 µm but for thickness the of 60 µm maximum the velocity of leaking quickly increases that is probably caused by nonuniformity of deposition (an incomplete overlap).
The properties of the layer which is made using the process of spraying-sintering are compared with the properties of the layer made by the compaction technology with the following sintering.
The properties of the layer you can see in Table 2.

Table 2. Chemical composition, crystalline phase and properties of the layers of the levels of zirconium dioxide

Process	Granulometric powder composition, µm	Chemical composition mass, % ZrO_2 Y_2O_3 MnO_2	Crystalline phase	Coefficient of thermal expansion	Ion conductivity
Compaction-sintering	0.3	83.2 13.9 0	C	10.4	0.14
Spraying - sintering	10-45	81.1 14.5 3.8	C	9.9	0.12

Investigation of the characteristics: the voltage density and the current density, the capacity density of the cell of the size of 50x21x6 with the active electrode area of 10.8 cm^2 has been carried out under the temperature of 1270 K. The 1060 mV voltage has been obtained in the electric circuit that is the value very similar to the theoretical one calculated from the used gaseous composition. This result has been obtained on the 60µm thickness of the electrolyte layer, ensuring sufficient gaseous nonpermeability of the electrolyte produced by the process of spraying – sintering. The maximum density of capacity – 0.73 W/cm^2 has been obtained under 0.49 V and 1.50 A/cm^2. Such result has been achieved because of the low inner resistance of the thin electrolyte level [1].
The authors [2] investigated the possibility of the cathode losses decreasing due to the application of the constituted cathode from (La0,8Sr0,2) 0.98 MnO_3 (LSM) and ZrO_2-12% Y_2O_3 (YSZ) materials. The technologies of vacuum – plasma spraying (VPS) and flame spraying (FS) on the preliminary made anodes of flat hard-fuel cells with the 60 mm diameter are used to produce the cathode. The carried out microstructure investigations showed the presence of the open porosity of the cathode coatings and a compositional gradient from YSZ-LSM constituted cathode to a pure LSM.
As the authors [2] consider, the main reason of the necessity of the constituted cathode forming is the difference of the of thermal expansion coefficients of the cathode and the electrolyte layer that may differ from 30 to 50% in the range of working temperatures from 800 to 1000 C.
The constituted cathodes are produced using the LSM and YSZ powders as well as the composite powders from the both powders. The composite powder is made of joint milling of the LSM and YSZ powders to the size less than
1 micron with the following drying by sputtering and sintering. The sizes of particles are from 20 to 50 micron.

We use Medicoat AG (Magenwie) (CH) 50 kW DC-VPS equipment with four tank powder feeder for different powders for the VPS process. The spraying parameters are varied in the following range: the pressure 100-120 mBar, the distance of spraying is from 275 to 350 mm, argon consumption is from 40 to 50 l/min, hydrogen consumption is from 5 to 8 l/min, electric arc power is from 16 to 25 kW. The substrate is heated up to 570 K before the spraying of the first layer.

We use the burner CastoDyn DS 8000 by the firm Castolin SA for gas flame spraying. We use four tank feeder of Sulzer Metco AG system which enables to supply two powders simultaneously and to change the consumption of powders being supplied for the deposition of the graduated coatings.

Composite cathodes with the thickness of 80µm are sprayed in the vacuum by the plasma spraying. The first layer is the layer of solid electrolyte with the thickness of 10 µm, the content of YSZ is 100%. In the following layers the content of YSZ is decreased to zero at the increasing of LSM up to 100%. We spray the layer of LSM by the gas flame spraying after the composite cathode has been sprayed in vacuum. Bench tests of cathode characteristics carried out at the temperatures of 1020-1270 K have shown that the optimal thickness of the cathode is up to 40 µm with the presence of interlayer with the following content: 50:50 YSZ-LSM.

The authors [4] have investigated the process of the cell forming using the processes of the gas flame and the plasma spraying. The three-layer nickel separators are used as the substrate for the coatings spraying. They are made of wire and sintered in vacuum. The anode material layer is sprayed on these substrates by gas flame spraying. This material consists of NiO mole% YSZ, particles size is from 45 to 106 µm, C_2H_2 and O_2 are used as the combustible gases the distance of spraying is 100 mm. The penetrability to gas of the anode layer is $8.34x10^{-2}$ $cm^4g^{-1}s^{-1}$. Electrolyte layer is sprayed in the air by the gas flame method using the powder YSZ with the fraction from 5 to 25 µm, the mixture of argon, hydrogen and nitrogen is used as the plasma creating gase, the distance of spraying is 50 mm.

The penetrability to gas of the electrolyte layer amounts to $7.79x10^{-8}cm4g^{-1}s^{-1}$. The cathode layer is sprayed using the material (LaSr)MnO_3 when the electrolyte layer is sprayed by the gas flame spraying. So we have produced 30 fuel cells collected in two blocks, each of them has 15 pieces. The 300 hours' investigations have shown that the utilization factor is 50% at the temperature of 1240 K, at the power of 3.3 kW, when the density of the current is 0.3 Acm2. At the decreasing of the current density up to 0.5 Acm2 the power is 5 kW.

The authors [5] have carried out investigations to produce a fuel cell by the layer-to-layer plasma spraying.

The installation "Metco-9Mb" is used for the air spraying. We use argon-hydrogen mixture As the plasma creating gases. Spraying parameters:

anode layer - the current is 500 A, the voltage is 65V, the distance of spraying is 150 mm, powder consumption is 2268 g/hour;

electrolyte layer - the current is 650 A, the voltage is 55V, the distance of spraying is 64 mm, powder consumption is 907 g/hour;

cathode layer – the current is 700 A, the voltage is 32 V, the distance of spraying is 150 mm, powder consumption is 907 g/hour;

A single fuel cell with the electrolyte layer thickness of 50-80µm has been tested at the temperature of 770-1070 K. As the result of the tests at the temperature of 870 K the voltage in the circuit is 0.95 V, at 970 K the voltage is 1.045 V. The range of the cell power density is 80-150 mV/cm^2 [5].

The authors [6] have proposed to decrease the size of the particles supplied by the plasma jet in order to increase the quality of the solid electrolyte layer formed on the base of partially-stabilized zirconium dioxide. For this purpose they have proposed the technology similar to the one being used in printers for the ink supply. Water suspension of small disperse particles of ZrO_2-Y_2O_3, with the size of 0.1µm and specific surface of 7 m^2/g is used to get "ink". Ceramic "ink" from cartridge is introduced to the plasma jet under the pressure of 0.5 MPa through a nozzle with inner 50 µm hole. The regime of spraying: the current is 600 A, the voltage is 5 7V, the distance of spraying is 40-55 mm, argon consumption is 45 l/min, hydrogen consumption is 10 l/min, substrate heating is from 493 to 803 K. The carried out tests have shown that the porosity of coatings accounts to 0.5% at the preliminary heating of the substrate up to 733 K from the distance of 55 mm.

3. THE CONCEPT OF THE PLASMA COATINGS FORMING FROM PARTIALLY STABILIZED ZIRCONIUM DIOXIDE AND NICKEL CERMET ON THE FUEL CELL ELEMENT

The concept of the plasma coatings forming from partially stabilized zirconium dioxide and nickel cermet on the element of a fuel cell has been developed on the base of the carried out analysis of works in this field for the period from 1988 to 2003. The given concept deter mines the aim, the main principles and directions of the work in this field considering the forecasting of exploitation properties of the fuel cell being formed. The aim of the concept is to spray plasma coatings from partially stabilized zirconium dioxide and nickel cermet on the fuel cell element – cathode on the LSM material base with the following characteristics of layers:

coating from partially stabilized zirconium dioxide: thickness of the coating is in the range of 50-100µm, porosity of the coating (overall) is 0.5% maximum, phase composition is >95% of cubic phase, tetragonal phase is 5% maximum, chemical composition is ZrO_2 – (8-12)% Y_2O_3;

coating from nickel cermet: thickness of the coating is in the range of 100-200 µm, porosity of the coating (overall) is 20-30%, Ni chemical composition is 40-50%, ZrO_2 – Y_2O_3 –50-60%.

It is necessary to solve the following main tests to achieve the said aim:

to develop the technology of forming of the fuel cell element (cathode) which sustains thermal stress originating in the process of spraying a layer of the hard electrolyte and nickel cermet on it;

to determine the chemical, granularity and phase compositions of the source powders of partially stabilized zirconium dioxide and nickel cermet effect on the structure and properties of the formed coatings;

to determine the optimal parameters of spraying of the hard electrolyte layer from the powders of partially stabilized zirconium dioxide and the anode layer of the coating from the powders of nickel cermet using the technologies of plasma spraying under lower pressure (LPPS) and the air plasma spraying (APS);

to determine the effect of the preliminary treating of the substrate on the properties of the formed layer coatings from partially stabilized zirconium;

to determine the effect of the following thermal processing on the structure and properties change of the hard electrolyte layers on the base of partially stabilized zirconium dioxide and the hard electrolyte – cathode.

For the realization of the Concept it is necessary to carry out a number of metallographic and technical investigations aimed at:

the determining of the structure and the properties of the initial powders;

the determining of the structure and the properties of the fuel cell element (cathode) which is applied as the substrate for the plasma coatings form partially stabilized zirconium dioxide and nickel cermet spraying;

the determining of the structure and the properties of the sprayed plasma coatings from partially stabilized zirconium dioxide and nickel cermet, with the following determining of the interconnections between the parameters of the coatings spraying, powder materials and thermal treatment;

the determining of the influence of the optimal regimes of the coatings spraying and the following thermal treatment on the permeability to gas of the coatings layers.

4. CONCLUSION

It is shown on the base of the main technologies of the production of the solid electrolyte layer based on zirconium oxide that the technology of the solid electrolyte layer forming by plasma spraying is the most perspective owing to a number of advantages:

high rate of deposition

possibilities to regulate density, chemical and phase composition of electrolyte layer

It is determined on the base of the analysis of the data about the influence of the regimes of spraying of the plasma coatings based on partially stabilized dioxide that the most optimal spraying regimes by LPPS and APS methods are the following:

the most optimal spraying regimes for LPPS method are the following: the preliminary heating of the substrate is up to 570 K; the pressure in the camera is 100 mBar; the spraying distance is 250-270 mm; consumption of Ar is from 40 to 50 l/min; consumption of H_2 is from 6 to 8 l/min; the capacity of electric arc is 18-20 kW;

the most optimal spraying regimes for the APS method are the following: the distance of spraying is 60-65 mm; the current is 650 A, the voltage is 55 V, consumption of powder is 1 kg/hour; consumption of Ar is from 40 to 50 l/min; consumption of H_2 is from 6 to 8 l/min.

It is determined on the base of the analysis of the data of the chemical composition of nickel cermet that the amount of nickel in the material of cermet must be not less than 40%. It is shown that the most optimal regime of spraying of the plasma coatings made of cermet is the following: the current is 500 A; the voltage is 65 V, the distance of spraying is 150 mm, powder consumption 2.3 kg/hour.

The concept of the plasma coatings forming from partially stabilized zirconium dioxide and nickel cermet on the fuel cell element is proposed. The aim, the basic principles and the direction of the work in this field is determined taking into account the prediction of the exploitation properties of the fuel cell being formed and taking into account their exploitation properties.

5. REFERENCES

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