13

Electrophoretic deposition of YSZ coatings on Ni-metallized NiO−YSZ cermet substrates

© E.G. Kalinina,[1,2] A.V. Solovev,[2] S.S. Tulenin[2]

[1] Institute of Electrophysics, Ural Branch, Russian Academy of Sciences,
620016 Yekaterinburg, Russia
[2] Ural Federal University after the first President of Russia B.N. Yeltsin,
620002 Yekaterinburg, Russia
e-mail: jelen456@yandex.ru

Received October 11, 2025
Revised November 26, 2025
Accepted November 29, 2025

The possibility of electrophoretic deposition (EPD) of a yttria-stabilized zirconia (YSZ) coatings onto non-conducting NiO−YSZ porous cermet substrates was shown. Pre-metallization of NiO-YSZ substrates by thermal vacuum spraying of Ni ($0.14\,mg/cm^2$) was used. For the first time, the possibility of effectively carrying out the EPD process on thermal vacuum-coated metallized substrates has been shown. The feasibility of the EPD process at low voltages (40 V) was shown, with YSZ coating thicknesses of 85 and 44 μm before and after sintering (1400 °C), respectively. The proposed combination of EPD and thermal vacuum spraying technologies is promising in the field of forming ceramic coatings on porous non-conductive substrates and is relevant for applications in the field of creating solid oxide fuel cells.

Keywords: Electrophoretic deposition (EPD), solid oxide fuel cell (SOFC), YSZ coating, thermal vacuum spraying.

DOI: 10.61011/TP.2026.04.63276.285-25

Introduction

Hydrogen power engineering is one of the actively developing fields among systems of power generation and conversion due to high specific mass energy capacity of hydrogen, a capability of transition to renewable energy sources and arising environmental advantages [1]. Solid oxide fuel cells (SOFC) are designed to directly convert chemical energy of hydrogen of hydrocarbon fuel into electric energy as a result of an electrochemical reaction with an oxidizer. SOFC batteries can be applied as included in hybrid power units that comprise gas or vapor turbines [2,3]. It includes description of an approach to creating hybrid units that are highly-efficient in terms of power and combine the gas or vapor turbine, which functions to convert thermal energy into mechanical one when afterburning fuel components supplied into a combustion chamber after being transmitted through the SOFC battery.

Up to now, for a solid electrolyte of the SOFC cells the most widely used is yttrium-stabilized zirconium dioxide (YSZ). Advantages of this electrolyte material include high resistance to an oxidative and a reducing atmosphere within a wide temperature range, mechanical strength, a very low level of electron conduction. At the same time, SOFC efficiency with the YSZ electrolyte is achieved at quite high temperatures (800 °C−1000 °C), when a required level of ion conduction is provided (~ 0.1 S/cm).

Doping zirconium dioxide with 8 mol.% of yttrium oxide makes it possible to achieve a maximum value of ion conduction and to stabilize a high-temperature cubic phase [4]. At the same time, the high temperatures (~ 1000 °C) accelerate processes of degradation of all components of the SOFC cells, including reduction of conduction of the electrolyte due to microstructure changes [5]. Applying of a thin-film electrolyte membrane on a bearing porous anode makes it possible to reduce ohmic resistance of the solid electrolyte, thereby enabling reduction of a SOFC operating temperature. Various methods are applied for forming the thin-film layers, including electrophoretic deposition (EPD) [6,7], a method of dipping in combination with a sol-gel technology [8] and reactive magnetron sputtering [9].

EPD is one of the promising methods due to simplicity of technological implementation, scalability and high performance both in laboratory and industrial conditions. EPD of the film coating is performed to a conductive electrode that is placed in a liquid suspension of an applied powder material when the main electrode and the counter electrode are energized with a difference of potentials. The surface of the particles dispersed in the liquid medium has an excessive electric charge due to formation of a double electric layer thereon, thereby resulting in an effect of electrophoresis of particles, i.e. their motion in the external electric field and subsequent deposition to the electrode. During EPD, the charge is transferred from a region of forming of the coating on the substrate surface to the electrode. The best conditions for charge transfer occur when the substrates have their own conduction, for example, during EPD of the solid electrolyte layer to cathode substrates [10].

In order to deposit to non-conducting dense substrates, pre-formation of conductive layers, for example, plat-

inum [11] is applied on their surface and a conductive polymer layer of polypyrrole is synthesized as well [12,13]. EPD can be performed to non-conducting anode cermet substrates when their open porosity is enough - when the charge is transferred during EPD in a suspension-filled porous space of the substrate [14] under application of quite high voltage — up to 200 V [15]. In this case, nonuniformity of distribution of pores over the substrate surface directly affects nonuniformity of the coating being formed during EPD. In the study [16], Hosomi et al. applied a method of spraying a graphite layer of the thickness of up to 1 μm onto the surface of the cermet NiO–YSZ substrate. The authors applied graphite spraying both to a front and a reverse side of the cermet substrate with subsequent formation of the YSZ layer by the EPD method. Hosomi et al. noted nonuniformity of application of the YSZ layer in case of the front graphite sublayer; when placing the graphite layer at the reverse side they could produce the YSZ electrolyte layer of the 5 μm thickness with deposition voltage of 400 V. The above-described methods of forming surface electric conductivity of the substrates do not always allow achieving deposition of the solid-electrolyte uniform layer during subsequent EPD due to nonuniformity of the conductive layers, their porosity, an insufficient or excessive thickness, low conduction.

The present study is aimed at searching solutions to EPD on the SOFC cermet porous anode substrates, which are based on pre-formation of both surface and volume conduction of the porous substrates using the technology of thermal vacuum spraying. The present study has investigated structural and morphological differences of the electrophoretically-deposited YSZ layers on the non-conducting porous NiO–YSZ substrates using the nickel sublayer and the metal nickel electrode.

1. Experimental part

The YSZ coatings were formed by EPD by applying powders of two types, namely, a commercial YSZ powder of the DTsI-1 grade (OJSC ChMZ, Russia) designated as YSZ-1 and a YSZ-2 powder produced by controlled two-jet deposition by ammonia (the powder material is proved by M.A. Mashkovtsev, UrFU) [17]. Particles of the initial YSZ-1 powder had the average size of 80 μm. The YSZ-1 powder was ground in a planetary mill (Fritsch Pulverisette) at the rotational speed of 500 rpm for 4 h. The average size of the particles of the initial YSZ-2 powder was 15 μm and it was ground in the planetary mill at the rotational speed of 500 rpm for 5 h. An increased grinding time was applied for the YSZ-2 powder in order to increase its dispersity.

Suspensions of the powders YSZ-1 and YSZ-2 were prepared using a mixture of acetylacetone (AR) and isopropanol (CP) in a ratio of 1 : 1. A concentration of the prepared suspensions was 65 g/l. The suspensions YSZ-1 and YSZ-2 were supplemented with 0.6 vol.% of an aqueous solution of molecular iodine (the concentration of the iodine solution was 0.1 mol/l). Molecular iodine was introduced in order to improve deposition, since the effective charge of the particles increased due to generation of protons in the suspension during a reaction of iodine with acetylacetone. Originating protons specifically adsorbed on the particle surfaces, thereby contributing to an increase of their effective charge [11]. The suspensions were dispersed for 30 min in an ultrasound bath TDRFORCE Ultrasonic cleaner at power of 50 W and an emitter frequency of 22 kHz. EPD was performed in a deposition bath, which included a cassette with the cermet NiO–YSZ substrate fixed therein, with the conductive nickel sublayer or with a nickel plate. The cathode was the cermet substrate and the anode was a stainless steel plate. A distance between the electrodes was 10 mm, and the size of the electrodes was 10×10 mm.

The anode porous NiO–YSZ substrates were produced by joint rolling with the NiO/YSZ content-1 : 1 with addition of 10 mass.% of starch. The thickness of the NiO–YSZ substrates was $\sim 400\,\mu$m. They were sintered at the different temperatures — 1400 °C and 1500 °C in order to identify influence of porosity of the anode substrates on a morphology and the thickness of the applied YSZ layers.

Two deposition methods were applied, i.e. direct deposition of YSZ to the non-conducting porous NiO–YSZ substrate with arrangement of a Ni foil of the 100 μm thickness at the reverse side of the substrate; deposition by the second method included pre-application of the conductive nickel layer of a specific weight $\sim 100\,\mu$g/cm^2 by thermal vacuum spraying to the reverse side of the cermet substrate. Thermal vacuum spraying of Ni was made in a vacuum chamber at residual pressure of $5 \cdot 10^{-2}$ Pa, the spraying time of 1 min and a resistive tungsten evaporator's current of 140 A. The thickness of the sprayed nickel films was measured using a Linnik microinterferometer MII-4M („LOMO“, Russian) on model Sitall substrates.

EPD of the YSZ layers to the NiO–YSZ substrates was performed in a mode of constant voltage of 40 V for 5 min. The produced samples were dried in a Petri dish for 24 hours. The deposited YSZ layers were sintered in a furnace LHT-04/18 (Nabertherm, Germany) at the temperature 1300 °C and 1400 °C for 3 h.

The microstructure and the morphology of the YSZ coatings were studied by Scanning Electron Microscopy (SEM) in a microscope VEGA Compact (TESCAN, Czech Republic). A specific surface of the powders was measured in the BET method using a TriStar 3000 unit (Micromeritics, Germany). X-ray diffraction analysis (XRD) was performed in a Miniflex 600 diffractometer (Rigaku, Japan).

2. Discussion of results

Grinding of the initial commercial YSZ-1 powder in the planetary mill for 4 h makes it possible to reduced the average particle size from 80 to 0.9 μm (Fig. 1, *a*). The specific surface of the YSZ-1 powder after grinding was 8.3 m^2/g. The YSZ-2 powder was ground in the planetary mill for 5 h. The increased grinding time and a finer average particle size of the initial YSZ-2 powder (15 μm) made it

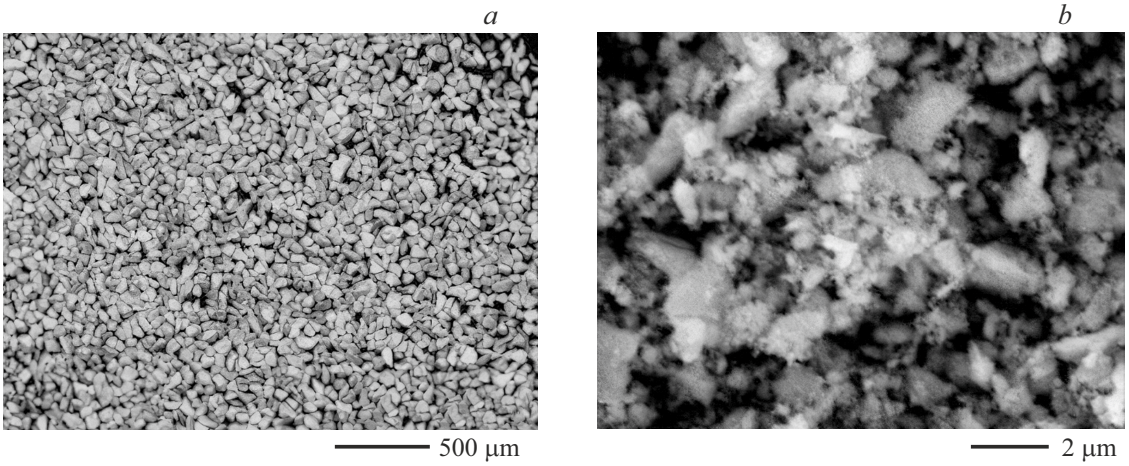

Figure 1. SEM images of the particles of the powders YSZ-1 (*a*) and YSZ-2 (*b*) after grinding.

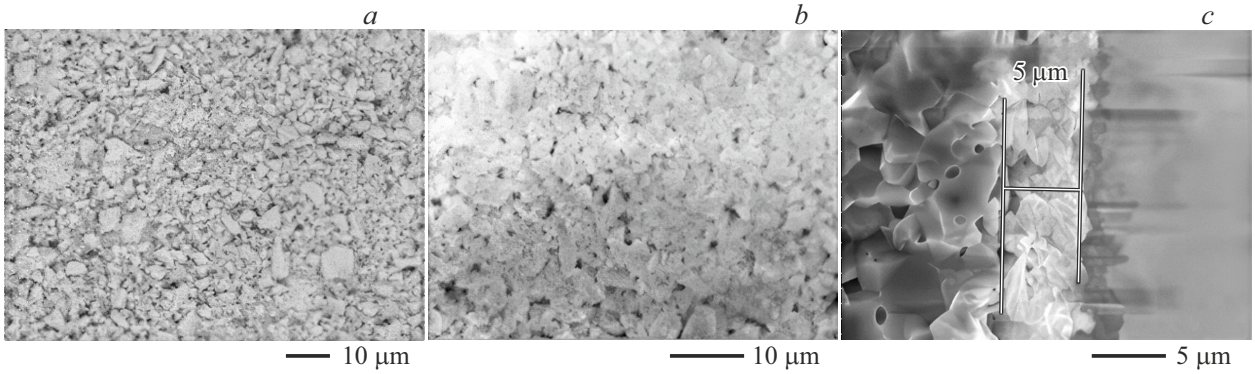

Figure 2. SEM images of the surface of the produced YSZ-1 layers on the NiO−YSZ substrate before (*a*) and after sintering at the temperature of 1300 °C, 3 h (*b*) as well as a transverse cleavage of the samples with the YSZ-1 coating on the cermet substrate after sintering at the temperature of 1300 °C (*c*).

possible to reduce the average particle size after grinding to 0.25 μm (Fig. 1, *b*). The specific surface of the YSZ-2 powder after grinding was 27.3 m^2/g.

According to the XRD data, the initial commercial YSZ-1 powder contained three phases: 73 weight% — a cubic structure of the solid solution $(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$ with the space group Fm3m (225) and the lattice parameter $a = 5.131$ Å; 20 weight% — a tetragonal structure of the solid solution $(ZrO_2)_{0.972}(Y_2O_3)_{0.028}$ with the space group P42/nmc (137) and the lattice parameters $a = b = 3.607$ Å, $c = 5.182$ Å; 7 weight% ZrO_2 — a monoclinic structure with the space group P121/c1 (14) and the lattice parameters $a = 5.143$ Å, $b = 5.213$ Å and $c = 5.300$ Å. According to the XRD data, the initial YSZ-2 powder was a single-phase one and characterized by the cubic structure with the space group Fm3m (225) and the lattice parameter $a = 5.138$ Å.

Direct EPD from the YSZ-1 suspension to the porous cermet NiO−YSZ substrate during its arrangement onto the electrode (Ni-foil) made it possible to produced the deposited YSZ layer of the 5 μm thickness (Fig. 2). The deposited YSZ-1 layer was sintered at the temperature of 1300 °C for 3 h. Fig. 2 shows SEM images of the surface and the transverse cleavage of the YSZ-1 coating after sintering. According to the SEM data (Fig. 2), the YSZ particles exhibit partial sintering with each other.

According to the XRD data, the formed ceramic YSZ-1 coating consists of two phases. The main phase (96 mass%) — zirconium dioxide stabilized by yttrium oxide has a tetragonal structures with the crystal lattice parameters $a = 3.624$ Å and $c = 5.127$ Å. The secondary phase (4 mass%) — zirconium dioxide; it has a cubic lattice with the parameter $a = 5.152$ Å.

In order to prepare the second sample for EPD, the substrate was metallized by spraying Ni to the reverse side. The nickel layer was sprayed in vacuum (the residual vapor pressure in the chamber was 10^{-2} Pa) by thermal vacuum spraying. During spraying, the evaporated vapor of the metal condense on the substrate surface in the form of a uniform layer, thereby providing electric conductivity of the surface of the porous NiO−YSZ cermet.

Preliminary experiments were performed to determine a dependence of the thickness of the sprayed nickel coating on the charge mass in the evaporator of the thermal vacuum spraying unit (Fig. 3). The obtained dependence was linear, on its base we selected a value of the charge

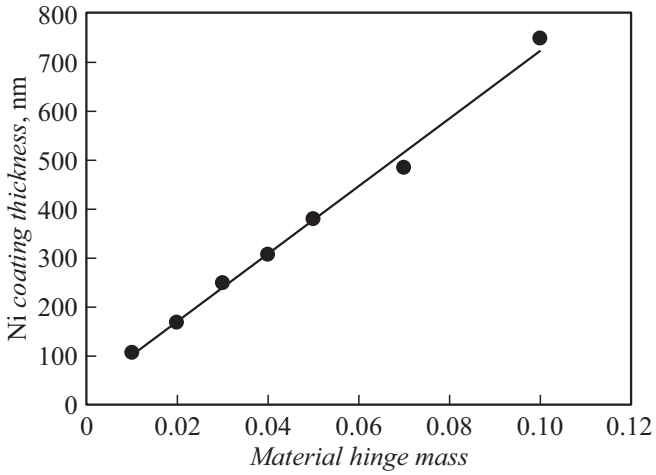

Figure 3. Dependence of the nickel coating thickness on a material charge mass in the evaporator of the thermal vacuum spraying unit.

mass for obtaining the minimum required thickness of the coating in terms of obtaining a solid nickel layer on the model substrate (Sitall), which provided conduction of the substrate surface. It was determined that the required thickness of the nickel coating was ~ 110 nm at the charge mass of 0.01 g with the fixed spraying time of 1 min. It was experimentally found that an increase of the spraying time resulted in formation of thicker conducting layers that demonstrated susceptibility to delamination.

The SEM data (Fig. 4) of the surface of the NiO–YSZ samples with the sprayed conducting nickel coating demonstrated that fine Ni particles with the average size ~ 200 nm were formed on the surface of the substrates.

The Ni particles form a coating on the surface of the NiO–YSZ substrate and penetrate its volume via a pore system, thereby providing origination of conduction of the substrate for subsequent EPD of the main layer of the solid YSZ-2 electrolyte. Experiments were taken to determine the dependence of the thickness of the YSZ coating on the EPD time (voltage of 40 V) on the nickel-metallized NiO–YSZ substrate that was pre-sintered at the temperature of 1400 °C (Fig. 5).

For subsequent deposition of the YSZ-2 layer, the mode of constant voltage of 40 V, 5 min was selected. The YSZ-2 layer was applied in the above-said method to the anode substrates that were preliminarily heat-treated at the temperatures 1400 °C and 1500 °C (2 h). The YSZ-2 layer was sintered at the temperature of 1400 °C, 3 h. An applied experimental diagram with combination of the technology of Ni-layer thermal vacuum spraying and EPD of the YSZ coating on the cermet NiO–YSZ substrate is shown in Fig. 6.

According to the SEM data (Fig. 7), the particle size of the deposited YSZ-2 layer before sintering was ~ 0.5 μm, while sintering at 1400 °C exhibited grain enlargement and partial sintering of the coating that remained porous.

It was detected based on the XRD results that the formed ceramic coating had a single-phase structure of zirconium dioxide stabilized with yttrium oxide, with the cubic structure and the lattice parameter $a = 5.146$ Å. Based on the SEM results, the thickness of the ceramic YSZ-2 coating was determined on the transverse cleavages of the samples produced on the substrates with the pre-sintering temperatures 1400 °C and 1500 °C (Fig. 8). It was detected that the thickness of the YSZ-2 coating significantly depended on the pre-sintering temperature of the initial cermet NiO–YSZ substrate. With the increase of the substrate pre-sintering temperature, the thickness of the deposited coating decreases (see Table).

It was found that the thickness of the YSZ-2 coating produced by the EPD method was determined by the cermet substrate pre-sintering temperature and a pore morphology within its volume, which is due to a different

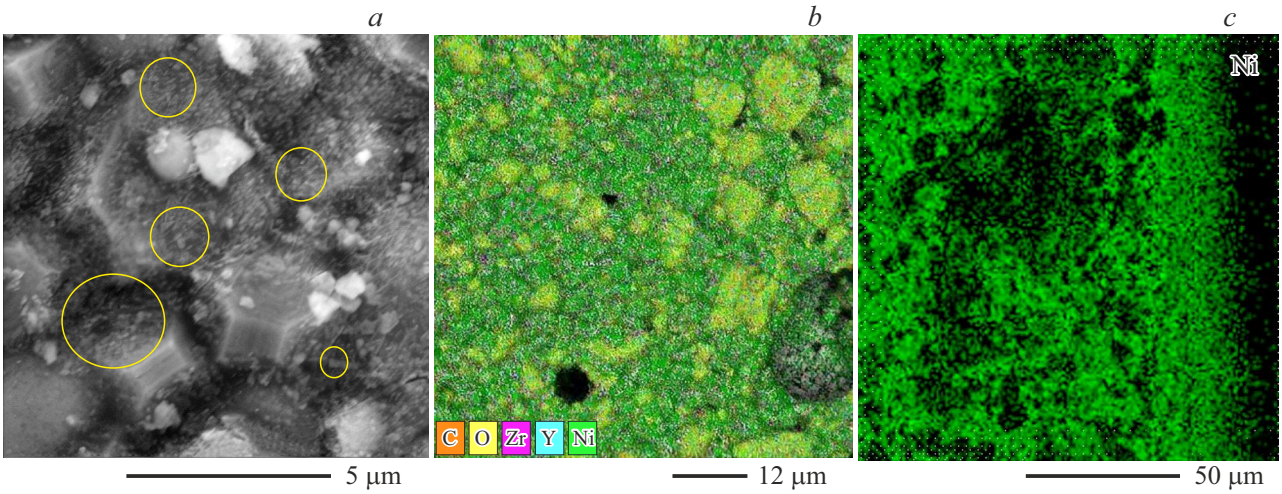

Figure 4. SEM images of the sample of the NiO–YSZ substrate with the sprayed conducting nickel coating: *a* — the substrate surface; *b* — the map of Ni distribution over the substrate surface; *c* — the map of Ni distribution over the transverse cleavage of the substrate.

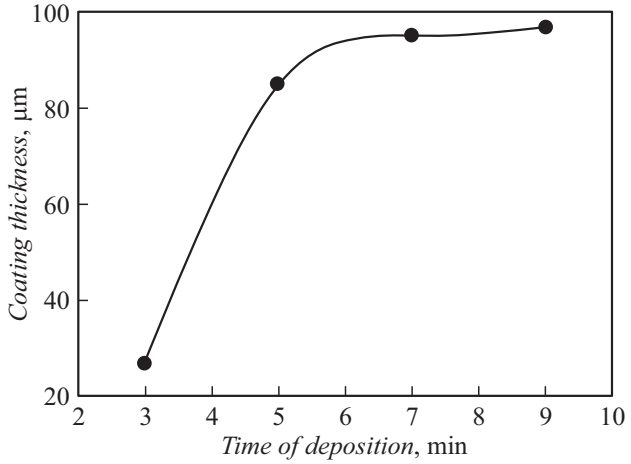

Figure 5. Dependence of the thickness of the YSZ-2 layer on the deposition time at constant voltage of 40 V on the nickel-metallized NiO−YSZ substrate that was pre-sintered at the temperature of 1400 °C.

nature of current-carrying paths within the substrate volume. With the increase of the substrate pre-sintering temperature, its porosity decreases and a port shape changes, i.e. a predominantly spherical pore shape is replaced by a slit-like one, thereby complicating transfer of the electric charge during EPD. The more developed pore system in the substrate also contributes to better penetration of Ni vapor into the substrate volume when it is metallized by thermal vacuum spraying. As can be seen from Table, the thickness of the YSZ coating was 85 and 44 μm before and after sintering in case of deposition of the film to the substrate with the pre-sintering temperature of 1400 °C.

In this case, the film shrank in its thickness in 1.9 times. On the other hand, for the substrate with the pre-sintering temperature of 1500 °C the thickness of the YSZ coating was 66 and 17 μm before and after sintering at 1400 °C, thereby corresponding to shrinkage of the coating in the thickness in 3.9 times. The noted difference of a shrinkage degree of the YSZ coating can be related to more favorable conditions in case of the substrate with the pre-sintering temperature of 1400 °C, for which the more developed pore system improved both a deposition rate as well as a packing density of the particles in the coating, which was matched with reduction of shrinkage of the coating during sintering. We should note an advantage in terms of the deposition rate in the proposed method of EPD to the Ni-pre-metallized substrate as compared to the method of direct EPD done without metallization. For the metallized substrate, the deposition rate reached 17 μm/min, whereas during direct EPD the deposition rate was 1 μm/min.

Thickness before and after sintering of the YSZ-2 coating on the Ni-pre-metallized NiO−YSZ substrate

Sintering temperature of the cermet NiO−YSZ, °C	Thickness of the formed coating YSZ-2, μm	
	Before sintering	After sintering
1400	85	44
1500	66	17

Conclusion

The study has demonstrated that EPD of the YSZ coating can be performed on the porous cermet Ni-metallized NiO−YSZ substrate. The substrate was metallized by

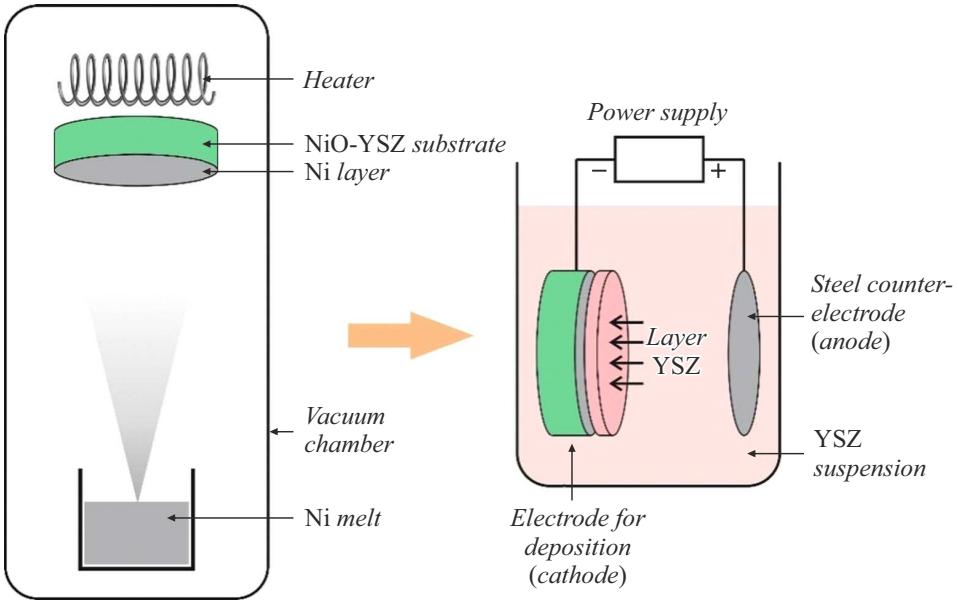

Figure 6. Experimental diagram with combination of the technology of Ni-layer thermal vacuum spraying and EPD of the YSZ coating on the cermet NiO−YSZ substrate.

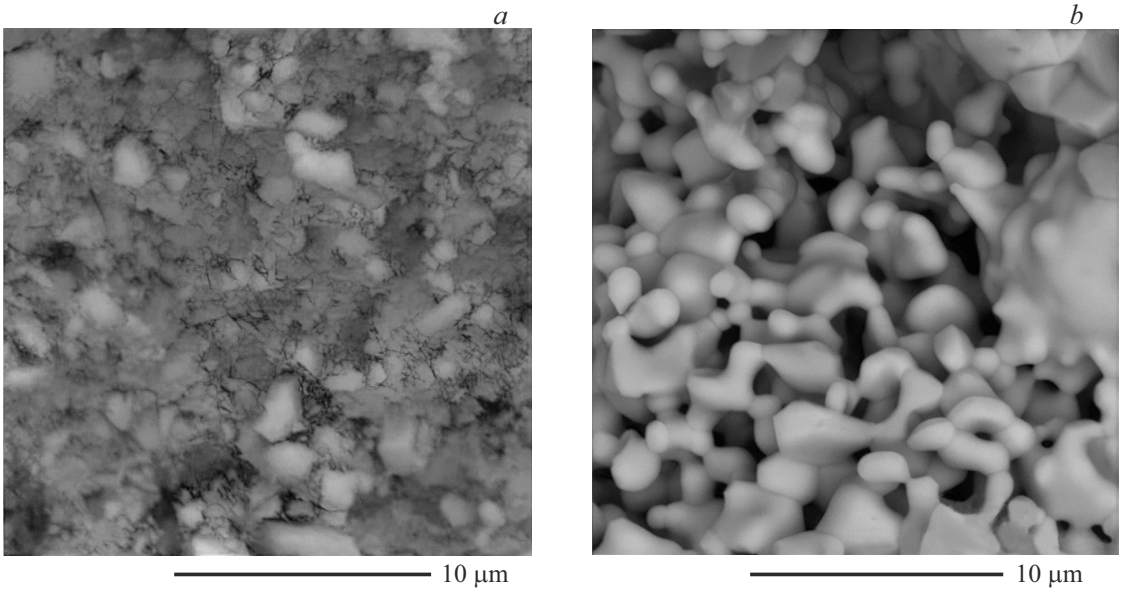

Figure 7. SEM images of the surface of the YSZ-2 coating deposited onto the nickel-metallized NiO–YSZ substrate, before (*a*) and after sintering at 1400 °C, 3 h (*b*).

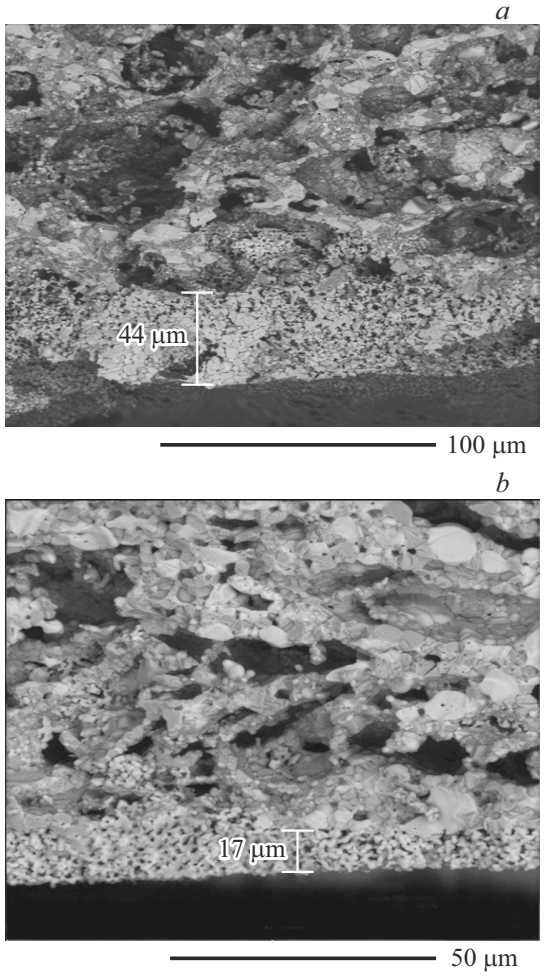

Figure 8. SEM images of the YSZ-2 layer (1400 °C) on the Ni-metallized NiO–YSZ substrate with the pre-sintering temperature of 1400 °C (*a*) and 1500 °C (*b*).

thermal vacuum spraying of Ni, which contributed both to surface and volume conduction of the porous substrate due to deposition of Ni vapor and their penetration into the substrate volume. It was demonstrated that the process of EPD on the nickel-metallized substrate has high performance, i.e. the YSZ coating of the 85 μm thickness (before sintering) was produced during deposition in the mode of constant voltage of 40 V, 5 min on the NiO–YSZ substrate with the pre-sintering temperature of 1400 °C. After sintering the YSZ electrolyte layer at the temperature of 1400 °C the coating thickness was 44 μm. It is demonstrated that the substrate pre-sintering mode directly affects the thickness of the deposited YSZ layer due to change of substrate porosity and the pore morphology during heat treatment. In particular, an increase of the substrate pre-sintering temperature to 1500 °C results in change of the coating thickness, which was 66 and 17 μm before and after sintering, respectively. This is the first time when a modification of the EPD method on the non-conducting porous substrates is developed with application of the technology of metallization of their surface by thermal vacuum spraying, which can be applied in a wide field of applications, including the SOFC technology.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J.O. Abe, A.P.I. Popoola, E. Ajenifuja, O.M. Popoola. Int. J. Hydrog. Energy, **44** (29), 15072 (2019). DOI: 10.1016/j.ijhydene.2019.04.068

[2] A. Choudhury, H. Chandra, A. Arora. Renew. Sustain. Energy Rev., **20**, 430 (2013). DOI: 10.1016/j.rser.2012.11.031

[3] A. Ashar, R.J. Braun, G. Jackson. ESC Meet. Abstr., MA2022-01 (38), 1676 (2022). DOI: 10.1149/MA2022-01381676mtgabs
[4] H.G. Scott. J. Mater. Sci., **10**, 1527 (1975). DOI: 10.1007/BF01031853
[5] S.Z. Golkhatmi, M.I. Asghar, P.D. Lund. Renew. Sustain. Energy Rev., **161**, 112339 (2022). DOI: 10.1016/j.rser.2022.112339
[6] L. Besra, M. Liu. Prog. Mater. Sci., **52**, 1 (2007). DOI: 10.1016/j.pmatsci.2006.07.001
[7] I. Corni, M.P. Ryan, A.R. Boccaccini. J. Eur. Ceram. Soc., **28**, 1353 (2008). DOI: 10.1016/j.jeurceramsoc.2007.12.011
[8] M. Niazmand, A. Maghsoudipour, M. Alizadeh, B. Raoufi, M. Ghorbanzadeh. Ceram. Int., **48** (13), 18030 (2022). DOI: 10.1016/j.ceramint.2022.02.155
[9] A.A. Solov'ev, A.V. Shipilova, A.N. Koval'chuk, I.V. Ionov, S.V. Rabotkin. Russ. J. Electrochem., **52** (7), 662 (2016). DOI: 10.1134/S1023193516070161
[10] [E.G. Kalinina, A.P. Safronov, Yu.A. Kotov. Russ. J. Electrochem., **47** (6), 671 (2011). DOI: 10.1134/S1023193511060036
[11] E. Kalinina, K. Shubin, E. Pikalova. Membranes, **12** (3), 308 (2022). DOI: 10.3390/membranes12030308
[12] E.G. Kalinina, E.Yu. Pikalova. Int. J. Hydrog. Energy, **48** (59), 22610 (2023). DOI: 10.1016/j.ijhydene.2022.12.328
[13] S. Hu, W. Li, W. Li, N. Zhang, H. Qi, H. Finklea, X. Liu. J. Colloid Interface Sci., **555**, 115 (2019). DOI: 10.1016/j.jcis.2019.07.094
[14] L. Besra, C. Compson, M. Liu. J. Am. Ceram. Soc., **89**, 3003 (2006). DOI: 10.1111/j.1551-2916.2006.01015.x
[15] E. Pikalova, D. Osinkin, E. Kalinina. Membranes, **12** (7), 682 (2022). DOI: 10.3390/membranes12070682
[16] T. Hosomi, M. Matsuda, M. Miyake. J. Eur. Ceram. Soc., **27** (1), 173 (2007). DOI: 10.1016/j.jeurceramsoc.2006.04.079
[17] S. Buinachev, M.A. Mashkovtsev, N. Zhirenkina, D. Aleshin, A. Dankova. Int. J. Hydrog. Energy, **46** (32), 16878 (2021). DOI: 10.1016/j.ijhydene.2021.02.131

Translated by M.Shevelev