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MAGNETRON DEPOSITION OF ANODE FUNCTIONAL LAYERS FOR SOLID OXIDE FUEL CELLS

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Abstract: *The proposed review is dedicated to the latest achievements in the field of magnetron deposition of thin-film anode functional layers (AFLs)for solid oxide fuel cells (SOFCs) of various designs (electrolyte-supported, anode-supported and micro-SOFC). Manufacturing of SOFCs components remains nowadays a key point for the industrial development of this electrochemical conversion device. Formation of thin nanostructured anodes by physical vapor deposition methodsallowsincreasing efficiency of SOFCs due to the reduction of polarization losses at the anode. The review discusses the use of thin-film anodes for different SOFC configurationsintended to work in low, intermediate and hightemperature ranges. The influence of the deposition parameters, microstructure and chemical composition of AFLs on SOFCperformance is analyzed.*

Keywords: *SOFC, anode functional layer, thin film, magnetron sputtering, polarization losses*

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Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that allow directly converting the chemical energy of fuel into electrical and thermal[1]. Due to the numerous advantages of SOFC, they are actively developing throughout the world. Within this topic, an urgent task is the development of medium-temperature, i.e. operating at 600–800 °C, anode-supported SOFC. The latter makes it possible to reduce internal losses in SOFC and increase the service life of power plants. Internal losses in SOFC consist mainly of ohmic losses in the electrolyte and activation losses in the electrodes.The former can be minimized by reducing the thickness of the electrolyte. Formation of nanostructured thin-film anodes with a developed three-phase boundary (TPB) "metal-ion conductor-fuel gas" allows reducing of activation losses in the anode [2,3].SOFC anodes are metal ceramic composites consisting of a phase with oxygenion conductivity (for example, yttria-stabilized zirconia (YSZ) or gadolinium doped ceria (GDC)) and a phase with electronic conductivity (metal or alloy). In anode-supported SOFC, the anode consists of at least two layers: a current collector layer (about 500 microns thick) and a thin functional electrochemically active layer (about 15 microns thick). The current collector layer should have a porous structure sufficient to supply the fuel to the TPB and remove the reaction products. Also it should ensure high mechanical strength and electrical conductivity.An electrochemical reaction takes place in the functional layer. Its intensity depends on the operating temperature and the density of the three-phase boundary. As the operating temperature decreases, the activation losses in the anode and their contribution to the total resistance of the SOFC increase.

For the manufacture of SOFC anodes, methods such as slip-casting and screen printing are widely used. However, they

require long stages of high-temperature sintering, which can cause undesirable reactions between the SOFC layers, deformations, cracks. These methods make it difficult to manufacture anode functional layers (AFLs) with a particle size of less than 1 micron even when using nanopowders, due to the coarsening of particles during high-temperature sintering [4]. A high surface energy of nanopowders contributes to their excessive agglomeration. The methods of physical vapor deposition (PVD) do not have these disadvantages [5]. They make it possible to reduce the temperature of the formation of functional layers and to implement structures that, in principle, cannot be created using powder sintering methods. PVD includes methods based on target evaporation, ion-beam sputtering and ion-plasma sputtering. For the manufacture of SOFC layers, the most frequently used methods are electron-beam [6, 7] and laser evaporation, magnetron sputtering. The laser evaporation method is used to form electrolytes [8, 9] and anode functional layers of the anode-supported SOFC [10].However, electron beam and laser evaporation do not allow the deposition of coatings on large area substrates. Among PVD methods, magnetron sputtering is the most promising method for SOFC fabrication.The advantages of this method are the possibility of independent regulation of the main parameters of the sputtering process, formation of uniform coatings with required characteristics, and the possibility of processing of large-area surfaces [11]. Regulating the process parameters such as particle energy, degree of ionization, substrate temperature, substrate bias voltage, deposition rate, gas pressure, discharge power and operating mode of the magnetron sputtering system makes it possible to produce dense or nanoporous coatings.

Deposition of anode functional layers for electrolyte-supported SOFC

When NiO/YSZ or NiO/GDC AFLsare formed by the reactive magnetron sputtering in the atmosphere of Ar + O_2, their microstructure, including porosity, can be regulated by the substrate temperature, deposition rate, particle angle of incidence, working pressure [12].The substrate temperature has the greatest influence on the structure of the material (amorphous or crystalline) and its phase composition. While the deposition rate, particle angle of incidence, working pressure, mainly affect the density of the coating (the presence of porosity).An important parameter is the ratio of Ar/O_2 in a vacuum chamber during reactive magnetron sputtering. The Ar/O_2 ratio of argon and oxygen affects the oxidation of the target during the sputtering process and, consequently, the target sputtering rate and film deposition rate. On the one hand, at low oxygen partial pressure, the film deposition rate is higher. However, the resulting film may have a lack of oxygen and then it will require high-temperature annealing in air. On the other hand, at high oxygen partial pressure, sputtering is carried out in the so-called "poisoned" mode. In this mode, the deposition rate of the film is minimal, but it has a stoichiometric composition.

NiO/YSZ AFL, for example, can be formed from two metal Ni and Zr/Y (86/14 at.%) targets by their joint sputtering, and one Ni/Zr/Y (68.8/26.6 /4.6 wt.%) target. The first method allows adjusting the content of Ni in the formed layer. But the second method is easier to implement.

In [13] Ni-YSZ films are deposited at room temperature by reactive magnetron sputtering from a single Ni/Zr/Y metallic target at rates ashigh as 4 μm h^{-1}. The bipolar pulsedvoltage with the pulse frequency 100 kHzwas used. The as-deposited film surface (Fig. 1,a,b) has granular morphology with small grains of 10 nm, and a cauliflower-like structure. The cross section shows that structure similar to cauliflower arises from a columnar structure, which is typical for magnetronsputteredfilms [14].

After annealingat 900 °C for 90 min NiO/YSZ film has a denser structure due to atomic reorganisation duringheat treatment(Fig. 1,c,d). The cross-section is no longer columnar and grainsand boundaries are less distinguished. According to X-Ray diffraction analysis, before annealing, the film exhibited a poorcrystalline quality. But after annealing at 900 °C, diffraction peaks

correspondingto the 8YSZ, NiO(200) and Ni(111) phases were detected. The microstructure of reduced thin-film anodes and their electrocatalytic properties were not studied.

Garcia-Garcia *et al.* [15] prepared highly porous, columnar NiO/YSZ thin films by reactive pulsed DC magnetron sputtering (200 W, 80 kHz) with deposition at glancing incidence. The pressure during deposition was maintained at 5×10^{-3} mbar in a process gas that consisted of 40 sccmAr and 2.5 sccm O^2.

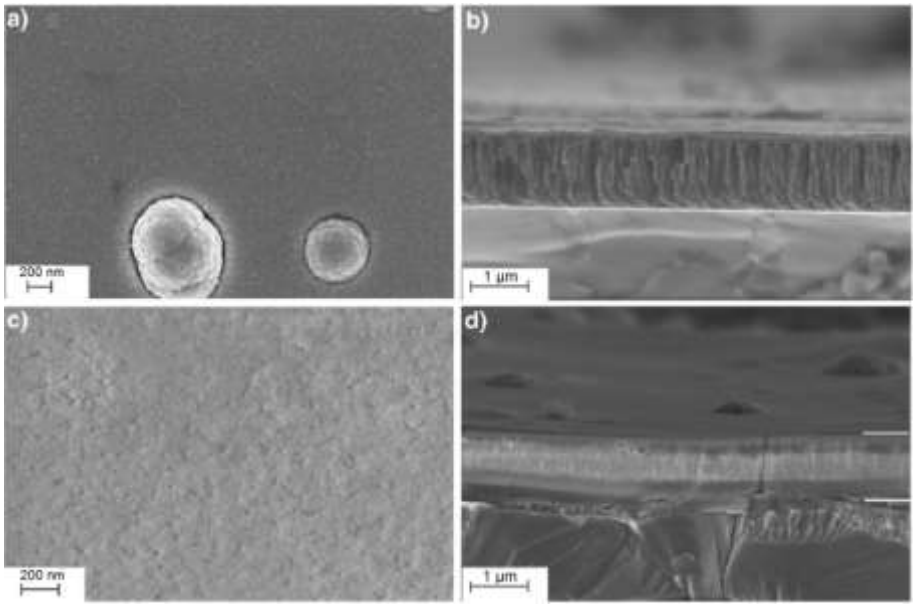

Fig. 1. SEM images of NiO/YSZ film as deposited (a, b) and after annealing at 900 °C for 90 min in air (c, d) [13].

The deposited at room temperature films were also essentially amorphous. Annealing such films at 850°C in hydrogen resulted in film crystallization withpreservation of the columnar structure.However, during the NiO reduction to metallic Ni latter was partially segregated to the film surface and formation of Ni agglomerates with a size of 0.7–2 µm (Fig. 2) was occurred.

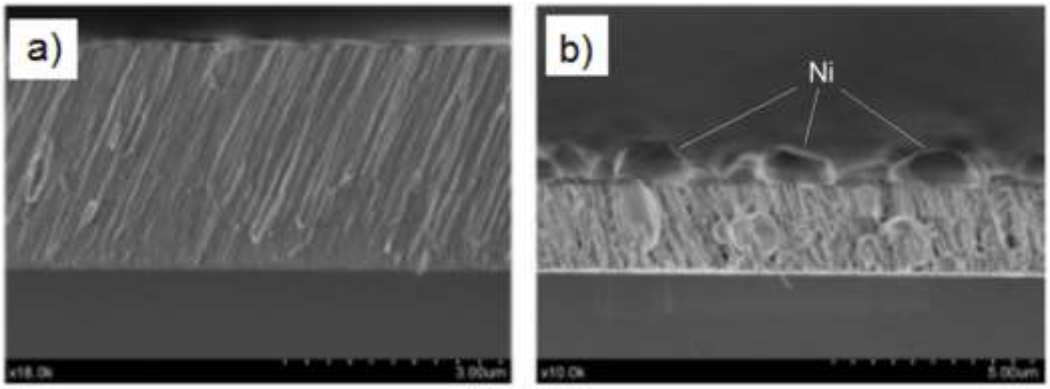

Fig. 2. Cross section of the as-deposited thin film(a) and after reduction in hydrogen (b). Siliconsubstrate [15].

Thus, themaindisadvantageofnickel-basedanodefunctionallayersformedbyPVDmethodsistheformationofnickelagglomeratesonanodesurfaceduringreductioninhydrogen [15]. The amount of agglomerates depends on the nickel content in the film. This phenomenon was also

observed for anodes formed by laser evaporation [10]. Ni agglomeration leads to a decrease in the three-phase boundary area at the anode [16] and can lead to the formation of cracks in the electrolyte film.

Agglomeration of particles of the Ni phase is usually related to the Ostwald ripening process [17]. This process may be based on thetransport of Ni particles through the gas phase (evaporation and deposition) [18]. It is known that $Ni(OH)_2$ has a six-fold evaporation rate as compared to that of Ni. Transport of Ni atoms could occur from small granules to large ones byevaporation of $Ni(OH)_2$.

To solve the problem of nickel agglomeration, the influence of annealing in an air atmosphere at temperatures of 800–1200 °C on the microstructure of NiO/YSZ films formed by laser evaporation was studied in [10]. Annealing at 1200 °C has been shown to prevent nickel agglomeration, due to the formation of a strong YSZ matrix, which inhibits the enlargement of nickel granules (Fig. 3).

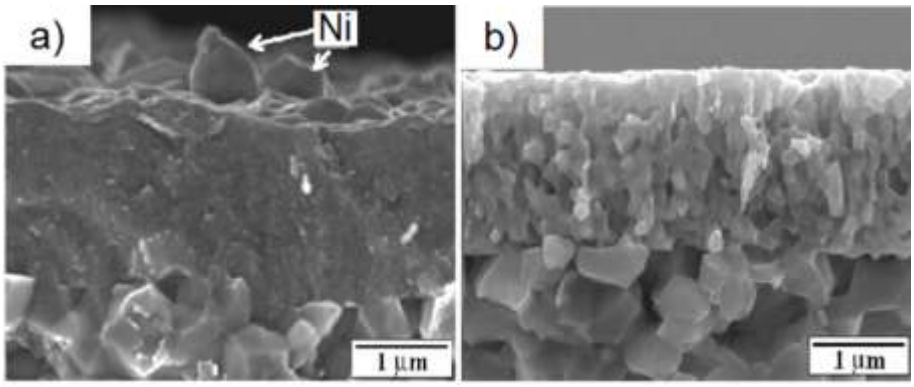

Fig. 3. Cross section of the PLD deposited NiO/YSZ films after reductionat 600 °C in 4% H_2. a) without post-annealing, b)annealed in air at1200 °C for 1 h [10].

In another work ofGarcia-Garcia *et al.*[19] ~5 µmNi/YSZanodewaspreparedonYSZelectrolyt ebyreactivepulsedmagnetronsputteringatanobli queangleofincidence.Target-substrate distance was 5 cm with an angle of 80° betweentarget and substrate normal. A 50 mm diameter Ni/Zr/Y alloy (68.8/26.6/4.6 wt.%) target was used to produce Ni(50 vol.%)/YSZ films at a discharge power of 200 W, 80 kHz frequency, working pressure of $5 \cdot 10^{-3}$ mbar and room temperature.

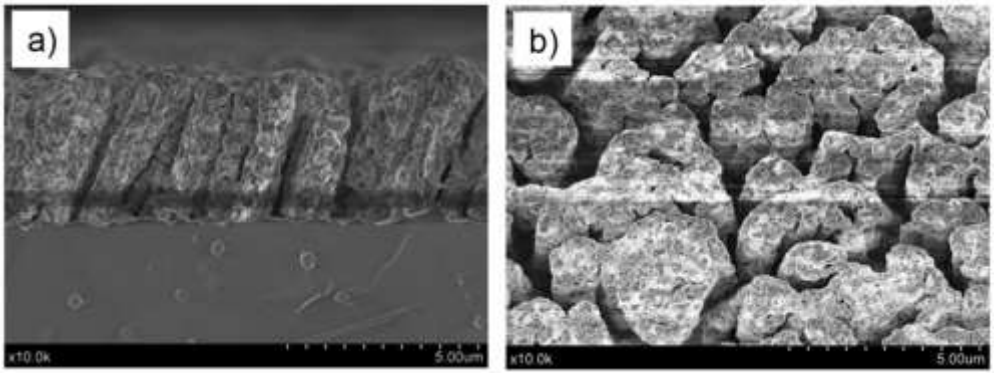

Fig. 4.SEMimages of the cross section (a) and the surface (b) of the Ni/YSZ anode, deposited by magnetron sputtering at an angle to the substrate, after preliminary annealing at a temperature of 1250 ºC in air and reduction in hydrogen at a temperature of 850 ºC [19].

Deposition rate of 1.5 μmh^{-1} was achieved. It was shown that pre-annealing of the amorphous as-deposited NiO/YSZ film at 1250 °Cwith the subsequent reduction produces a film consisting of uniformly distributed tiltedcolumnar grains having extensive three-phase boundaries (Fig. 4). The performance of thin film anode was comparable to thatof the commercial anode 50 μm thick (FuelCellMaterials (USA)), which was 10 times thicker and prepared by the doctor blade procedure. Single cell based on commercially available solid oxide half-cell comprising YSZ electrolyteand cathode (20 mm Single ElectrodeCell - Cathode Only, FuelCellMaterials, USA) with magnetron sputtered NiO/YSZ anode had maximum power density of about 450 mW cm^{-2} at 850 °C.

In order to increase the efficiency of thin-film anodes Garcia-Garcia *et al.* [20] suggested producing Ni-containing anodes comprising alternating layers of GDC and YSZ of 200 nm thickness.Also hybrid anode produced by co-deposition of Ni/YSZ and GDC were tested.The conditions for the deposition of layers did not change as compared with the previous works of the authors [15, 19]. In the as-deposited state, multi-layer anodes exhibited the highly porous columnar architecture, with well-definedboundaries between the NiO/YSZ and NiO/GDC layers (Fig. 5,a). The columnar structure was preserved after annealing in air (Fig. 5,b). As shown in Fig. 5,c,after the final reduction, highlyporous thin anodes with pronounced columnar architecture were obtained.

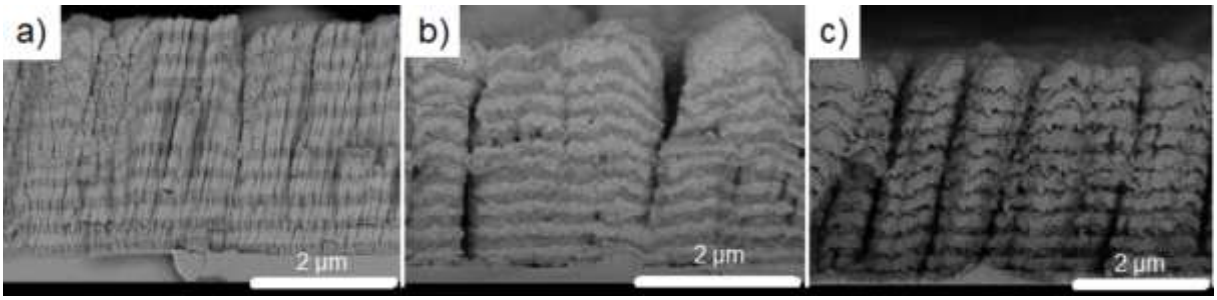

Fig. 5. SEM cross-section images of multi-layer thin-film anodes: a)as-deposited, b) annealed in air, c) reduced in hydrogen [20].

After subsequent fuelcell testing, the porous columnar architecture of the two-component layered thin film anodes wasmaintained and their resistance to delamination from the underlying YSZ electrolyte was superior to thatof corresponding single component Ni-YSZ and Ni-GDC thin films.The performances of the multi-layer and hybridanodes were almost the same and far superior to the single component YSZ and GDCanodesand also superior to theconventional commercially available thick anodes. Maximum power density of about 600 mW cm^{-2} at 850 °C is achievedwith hydrogen as fuel.

In another work Garcia-Garcia *et al.* [21] showed that thin Ni-GDC anodes exhibit excellent transport properties, robust under thermal cycling, and have good adhesion to the YSZ electrolyte.Similarly prepared Au-doped Ni-GDC anodesexhibited the same morphology, porosity, durability and electrochemical performance (power density of about 500 mW cm^{-2} at 850 °C in hydrogen). However, under steamreforming conditions with CH_4/H_2O mixtures the behaviour of the Au-doped Ni-GDC anodeswere far superior, exhibiting retention of good power density and dramaticallyimproved resistance to deactivation by carbon deposition (Fig. 6).

Tanveer*et al.* [22] suggested using thin nickel-samaria-doped-ceria (Ni-SDC) anodes prepared by magnetron sputtering forintermediate temperature electrolyte-supported solid oxide fuel cells. The anode was deposited by radio-frequencysputtering on a 150μmscandia-stabilized-zirconia (SSZ)substrate at room temperature.

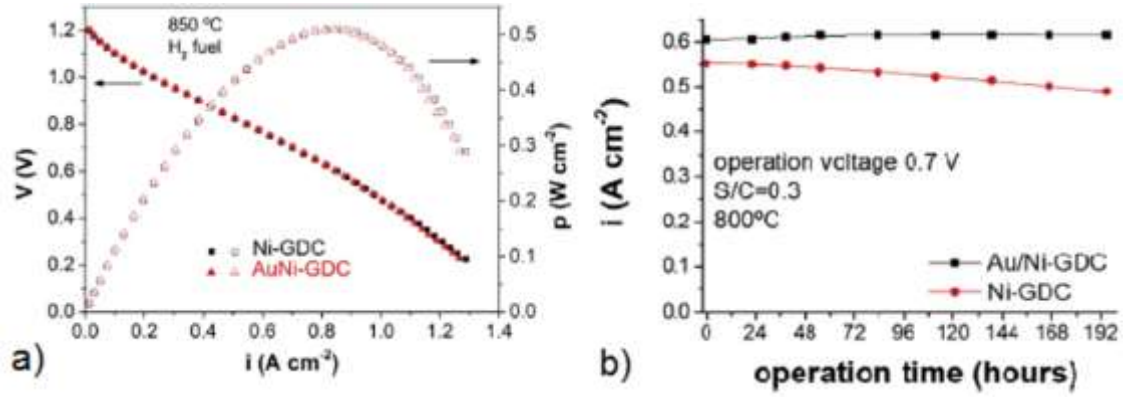

Fig. 6. The V–I and P–I characteristics of single cells with Ni-GDC and Au/Ni-GDC anodes obtained at 850°C withhydrogen as fuel (a).I-t behavior of single cells with Ni-GDC and Au/Ni-GDC anodes operated at 0.7 V polarization voltage, 800°C andsteam to carbon ratio S/C = 0.3 [21].

The deposition process lasted for 5 hrs at a constant power of 100 W, and pressure of 50 mTorr. To analyze the effect of reactive O_2 gas on the anode manufacturing process, two different background gases were used during deposition, mixture of Ar/O_2:8/2 and Ar. Both methods resulted in producing nano-porous Ni-SDC films after reduction in H_2. But the reactively sputtered anodes have a 20% slower growth rate than the non-reactively sputtered ones. Also, the presence of this amount of oxygen in the sputtering chamber resulted in producing lesser catalytic Ni in the anodes. This resulted in a poorer performance for the cells containing reactively sputtered anodes when compared to nonreactive ones. Anodes were not annealed in air after deposition; therefore, agglomeration of Ni was observed on the anode surface after cell testing.LSM/YSZ cathode was screenprinted on the other side of the electrolyte. Peak powerdensities for such cells were 240, 140and50mW cm^{-2} at 800, 700 and 600°C.

Jou and Wu [23] investigated thin Ni/YSZ anodes fabricated by reactive co-sputtering of a Ni and a Zr–Y target, followed by sequentially annealing in air at 900°C, as part of an YSZ electrolyte-supported SOFC.A distinctive feature of the study was conducting test inasingle-chamberconfiguration,inamixtureofCH_4 and air(CH_4:O_2 volume ratio = 2:1) at700 °C.Themaximumpowerdensityofthe SOFCusingthe triple-layered Ni–YSZ thin film astheanodewas1.14mWcm^{-2}, whichwaslarger thanthatof0.76mWcm^{-2}, obtainedusingascreen-printed20-mm-thick Ni/YSZanode.

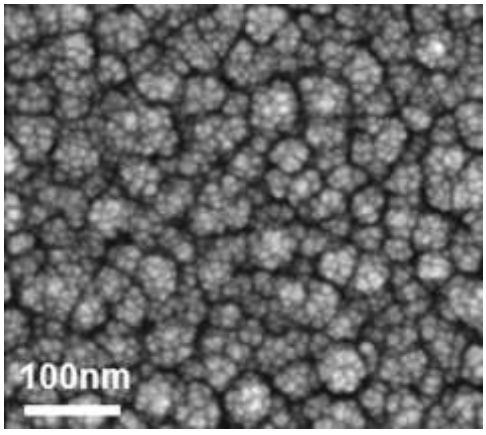

Fig. 7. Surface SEM image of Ru/CGO film deposited on YSZ/Si_3N_4/Si substrate (nominal volumetric ratio of Ru/CGO = 7/3) [24].

Deposition of anode functional layers formicro-SOFC

Takagi*et al.* [24] demonstrated that magnetron sputtered anodes could be used in micro-solid oxide fuel cells (μSOFCs) also. Rutheniumand gadolinia-doped ceria (Ru/CGO) composite nano-crystalline thin film anodes were synthesized by co-sputtering from Rumetal (DC power) and CGO oxide (RF power) targets without substrate heating. Ru/CGO composite films on YSZ/Si_3N_4/Si substrate showed highly granular morphology with primary grain sizes of ~10 nm andsecondary particles or pillars as large as 70-100 nm as shown inFig. 7.

Stress-relaxed composite thin film anodes were developed on self-supported μSOFCs with YSZ thin film electrolytes and porous platinum cathodes. μSOFCs were tested with roomtemperature humidified methane as fuel and air as the oxidant. They exhibited an open circuit voltage of0.97 V and a peak power density of 275 $mWcm^{-2}$ at 485 °C.

Deposition of anode functional layers for anode-supportedSOFC

In the works described above, thin-film anodes were mainly deposited on the electrolyte discs for the use in electrolyte-supported SOFCs. However, as was shown by us, thin-film anodes can also be used in anode-supported SOFC to reduce the polarization resistance at the anode [25]. The idea is to increase the characteristics of the anode-supported cells (ASC) by forming a thin-film anode functional layer between the thin-film electrolyte and commercial tape casted anode, as shown in Fig. 8.

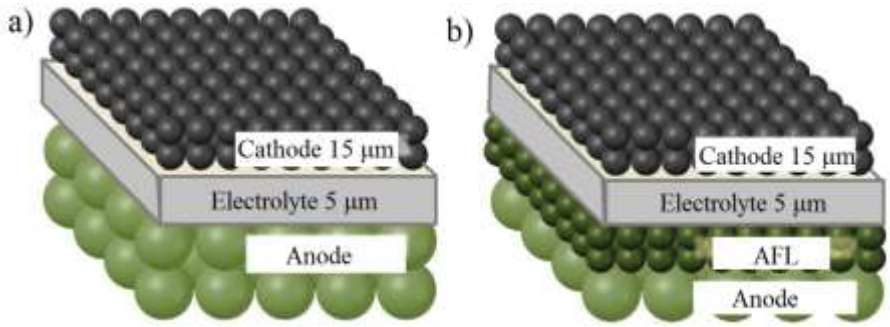

Fig. 8. The schematicof anode-supported cell configuration: a) conventional, b) with thin anode functional layer.

To study the influence of thin AFL on SOFCs'performance, single cells with and without AFL werefabricated. A 2 cm in diameter and 0.4-mm-thick NiO/YSZanode supports cut out by laser from commercial anodesheets (Ningbo SOFCMAN Energy Technology, China) were usedas substrates for magnetron deposition of both NiO/GDC and NiO/YSZ anode functional layers. AFLs were depositedby reactive co-sputtering of Ni,$Zr_{0.86}Y_{0.14}$ and $Ce_{0.9}Gd_{0.1}$ targets with diameter of 75mm. The distance between the magnetron target center andsubstrate was 80 mm. Prior to film deposition, the substrateswere heated to 400 °C.The deposited AFL samples were annealed in air atmosphereat different temperatures (600–1200 °C) for 1 h. For a good thermo-mechanical compatibility with theelectrolyte, the cells with NiO/GDC AFL were tested withGDC electrolyte, while cells with NiO/YSZ AFLs weretested with YSZ electrolyte. Electrolyte layers4-μm-thick were also deposited by reactive magnetron sputtering. Thedetails of this process were described in our previous work [26].The LSCF/GDC cathode layer was prepared on all cellsby a screen-printing method using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3/Ce_{0.9}Gd_{0.1}O_2$ paste (CERA-FC, Korea). The cathode area was 1 cm^2.Cathode sintering was performed at a temperature of 800 °Cfor 1 h before the fuel cell electrochemical test.

Analysis of cross-sections of Ni/YSZ and Ni/GDC AFLs (Fig. 9) showed that the composite films acquire a finely

porousstructure after reduction in hydrogen. For all samples, a good contact of the AFL layer was observed.

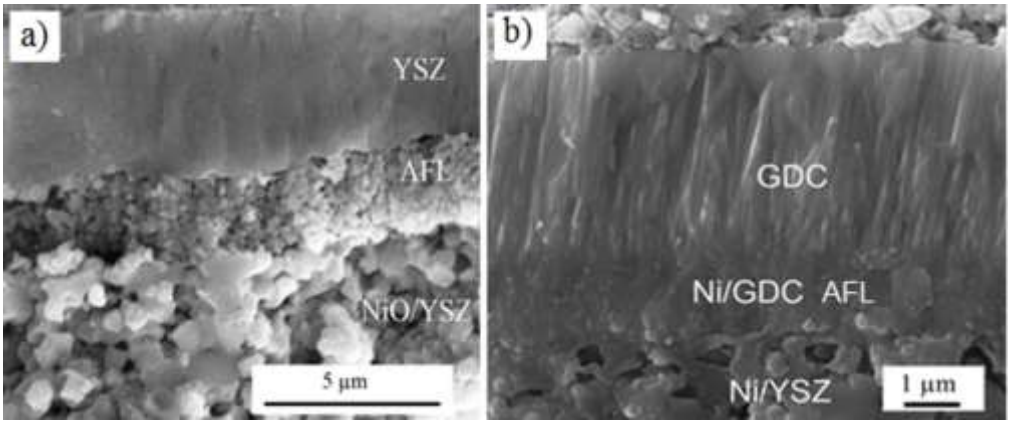

Fig. 9. Cross sectional SEM images of the SOFCs with nanostructuredanode functional layers: a)Ni/YSZ AFL (NiO 60 vol.%.),b)Ni/GDC AFL (Ni 40 at. %). SEM images were obtainedafter cells testing [25].

The grain size and pore size of AFLsare hundreds of nanometers, in contrast to the substratehaving micron-sized grains and pores. AFLs have arelatively smooth and uniform surface that facilitates depositionof a high quality dense and thin electrolyte layer leading to reduction in resistive losses. Theelectrochemical activity of a cermet anode with the givenmicrostructure and materials depends on the volume and onthe grain size [27]. Smaller grains increase the triple phaseboundary length and, as a result, the polarization resistancedecreases.

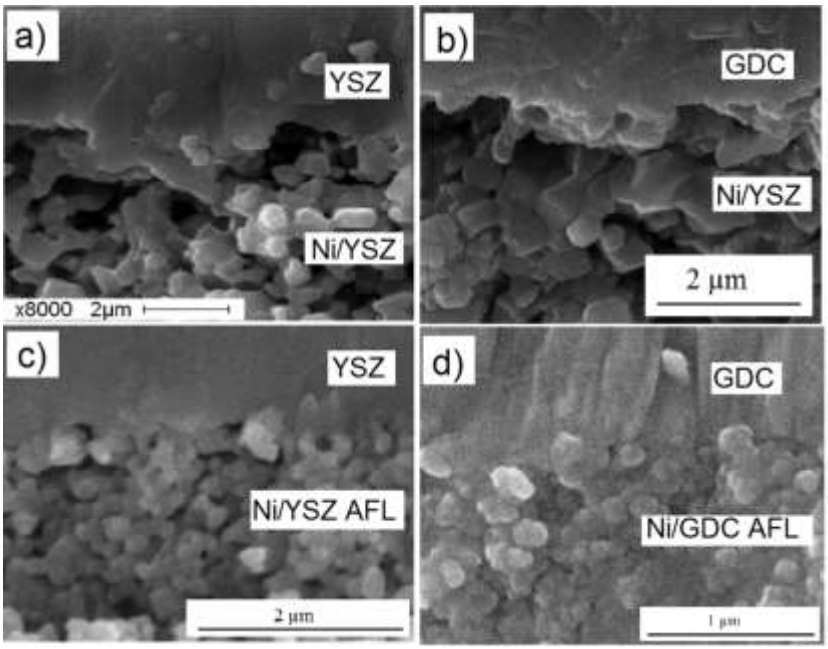

Fig. 10. Cross-sectional SEM images focused on the interface anode-electrolyte of the YSZ-based SOFCs without AFL (a), with AFL (c), andGDC-based SOFCs without AFL (b), with AFL (d) [25].

Figure 10 shows cross-sectional SEM images focused onthe anode-electrolyte interface of the YSZ- and GDC-basedSOFCs without and with anode functional layers. The fineand homogeneous microstructure of the AFLs enhances thecontinuity of the interface that should reduce interfacepolarization resistance.In order to estimate the impact of the NiO/YSZ and Ni/GDC AFL anodefunctional layers on the fuel cell performance, the current–voltage (I–V) and current–power (I–P) curves of the anode-supportedcells with and without AFL were compared atdifferent temperatures, as shown in Figs. 11 and 12.

The open circuit voltages (OCV) of cellswith YSZ electrolytewere 1.08–1.17 V, depending on the temperature, that is closeto the theoretical value of the SOFC.The peak power densities of the cell without AFL were 132, 469, and950mWcm^{-2} at 600, 700, and 800 °C, respectively. Singlecell with magnetron sputtered NiO/YSZ AFL (NiO 60 vol. %)has peak power densities of 222, 675, and 1240mWcm^{-2} atthe same temperatures. Thus, the peak power density of fuelcells with the AFL is 30% higher at 800 °C and 68% higherat 600 °C than that of the cell without AFL. That is, the effectof AFL on the fuel cell performance is more pronounced atlow temperatures.

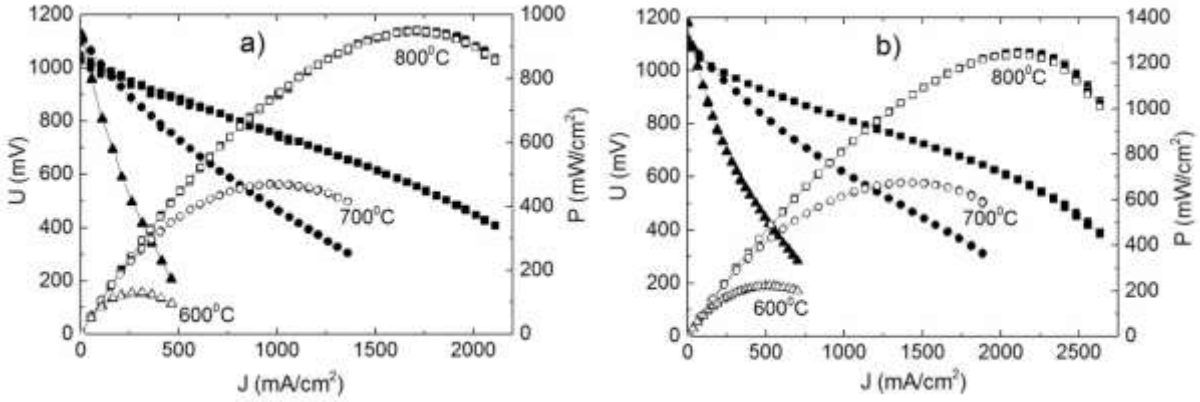

Fig. 11.I–V and I–P characteristics of the anode-supported SOFC withYSZ electrolyte and LSCF/GDC cathode without (a) and with (b) magnetronsputtered NiO/YSZ AFL (NiO 60 vol. %) measured at temperatures of600–800 °C [25].

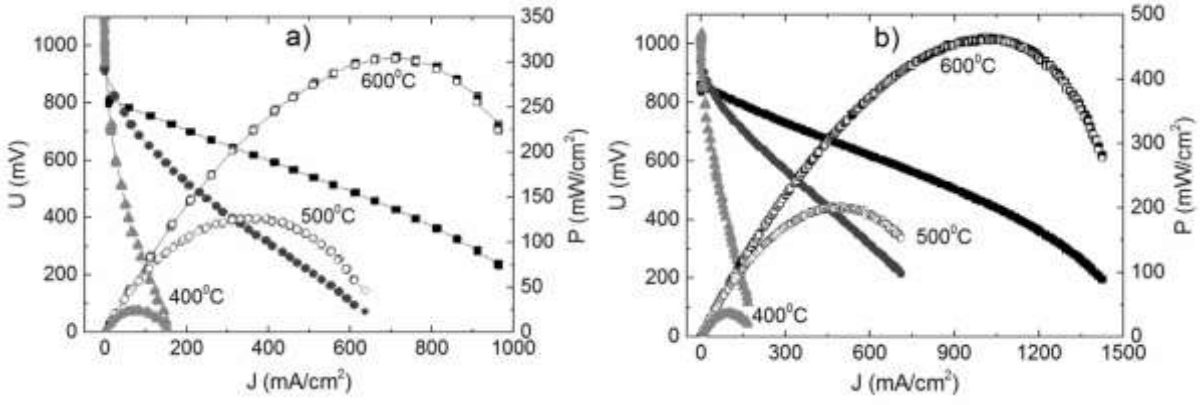

Fig. 12.I–V and I–P characteristics of the anode-supported SOFC withGDC electrolyte and LSCF/GDC cathode without (a) and with (b)magnetron sputtered NiO/GDC AFL (Ni 40 at. %) measured at temperaturesof 400–600 °C [25].

The OCV values of the cells with GDC electrolyte were 1.134, 0.920,and 0.811V at 400, 500, and 600 °C, respectively. Thereduction of ceria from Ce^{4+} to Ce^{3+} in a

reducingatmosphere increases electronic conductivity, which decreasesthe open-circuit voltage of the cell. But at atemperature below 500 °C the electronic conductivity ofGDC becomes negligible and OCV reaches high valuescomparable with YSZ electrolyte. The maximum powerdensities of cell without AFL were 25, 125, and 305mWcm^{-2} at 400, 500, and600 °C, respectively. The OCV and maximum powerdensities of the cell with AFL were 1.037, 0.940, 0.861Vand 40, 200, 460mWcm^{-2} at 400, 500, and 600 °C,respectively. The increase in power density due to theformation of AFL is about 60% depending on the temperature.

The total area-specific resistance (ASR) of YSZ-based cellwithout AFL calculated from linear fit of I–V curve measuredat 800 °C was 0.27Ωcm^2. When AFL is applied, the ASRdecreased to 0.2Ωcm^2. The same dependence is observedwhen using NiO/GDC AFL. At 600 °C AFL depositionresults in reduction of ASR from 0.54 to 0.38Ωcm^2. Thisimplies that a deposited NiO/YSZ and NiO/GDC AFLsreduced the total cell ASR by 26–30%.

Deposition of Cu-based SOFC anode functional layers

Ni-based anodes are usually used in solid oxide fuel cells when fuel is hydrogen. In this case anodes experience relatively low degradation rates and fast electrochemical kinetics. But if synthesis gas is used as fuel, Ni could be easily poisoned by contaminants like sulfur or carbon [28, 29]. Carbon deposition reduces the cell performance by blocking the anode reaction sites and damaging the microstructure of Ni in the anode. In recent studies [30, 31], Cu has been suggested as an alternative to Ni as the electronic conductor in SOFC anodes. Recently, Cu/yttria stabilized zirconia (YSZ), Cu/samaria-doped ceria (SDC) and Cu/gadolinia-doped ceria (GDC) anodes [32–36] have been developed and tested, showing good electronic conductivity and tolerance towards sulfur-containing fuels. However, Cu has a low catalytic activity for hydrogen or hydrocarbon electrochemical oxidation, and so doped ceria should be used instead of YSZ in order to improve the cell performance.

Despite the advantages of Cu-based composite anodes, it is difficult to apply conventional ceramic processing methods to fabricate Cu-containing SOFCs due to the low melting point of Cu (that is 1085 °C). Presently they are manufactured using a multi-step wet ceramic technique that requires more processing and firing steps and not attractive for mass production. Furthermore, high sintering temperatures increase interdiffusion of elements between adjacent cell layers.To avoid the sintering of copper oxide at high temperatures, we proposed using magnetron sputtering for thin CuO/GDC anodes deposition.

CuO/GDC thin films were deposited by reactive magnetron co-sputtering of Cu and $Ce_{0.9}Gd_{0.1}$ targets with diameter of 75 mm. Sputtering was carried out in oxygen-argon atmosphere at working pressure of 0.2 Pa in pulse bipolar mode at pulse repetition frequency of 80 kHz and positive pulse duration of 4 μs. The argon and oxygen flow rates were fixed at 26 and 33 sccm, respectively.

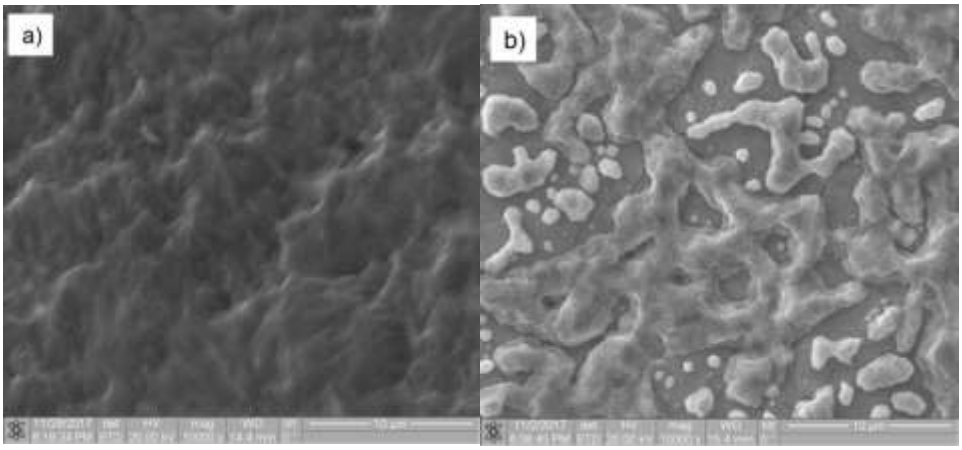

Fig. 13. Surface morphology of Cu/GDC film deposited on porous NiO/YSZ substrate (after reduction in hydrogen).

Targets were positioned at 45° to the fixed substrate holder. The distance between the magnetron target center and substrate was 80 mm. Prior to film deposition, the substrates were heated to 450 °C. The porous commercial NiO/YSZ anodes (SOFCMAN, China) with a thickness of 0.4 mm were used as substrates. The discharge power of a Ce-Gd magnetron was 1 kW. The discharge power of the Cu magnetron ranged from 100 to 700 W to control the volume content of CuO in the film. The copper content in the films was determined after films reduction in hydrogen. For example, at 500 W power of the Cu magnetron, the film contained 42 at. % of Cu.

Surface morphology of 2 μm thick Cu/GDC film (42 at.% of Cu) after reduction in H_2at a temperature of 750 °C for 2 hours is shown in Fig. 13. As can be seen from the SEM image, Cu agglomeration occurs on the surface of the film, in analogy with what happens when nickel-containing thin films are reduced at high temperature. In order to solve this problem, preliminary annealing of the films in air at 800and 1000 °C was carried out, by analogy with Ni-based anodes.

Figures 14 and 15 show surface and cross-sectional images of thin-film CuO/GDC anodes deposited at power of Cu magnetron 500 W and annealed at a temperature of 800 and 1000 °C, respectively. After annealing, the samples were reduced in hydrogen. Both films formed intimate contact across the interface between the film and the substrate. Moreover, film/substrate interfaces are homogeneous. At an annealing temperature of 800 °C, agglomeration of copper into isolated particles having characteristic dimensions of less than 1 μm occurs on the surface of the film (Fig. 14,a). After annealing at 1000 °C,the absence of Cu agglomerates on the surface of the film and formation of a more porous structure of the film with local cracks of micron width on the surface is observed (Fig. 15,a).

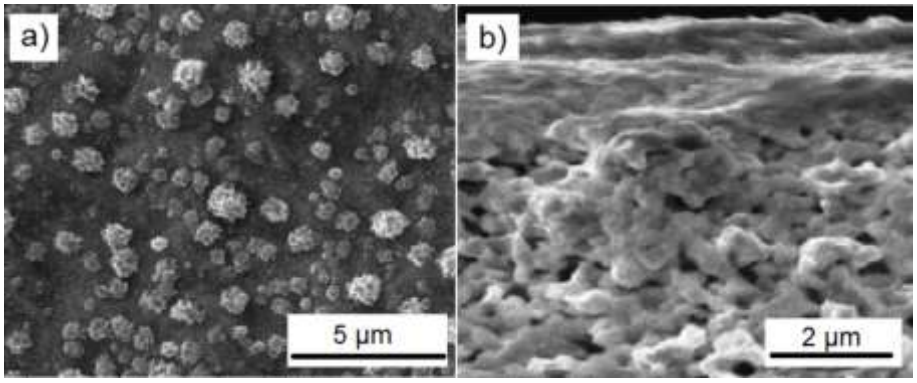

Fig. 14. Surface (a) and cross-sectional (b) SEM images of thin-film CuO/GDC AFLs annealed at a temperature of 800 °C in air and reduced in hydrogen (power of Cu magnetron - 500 W).

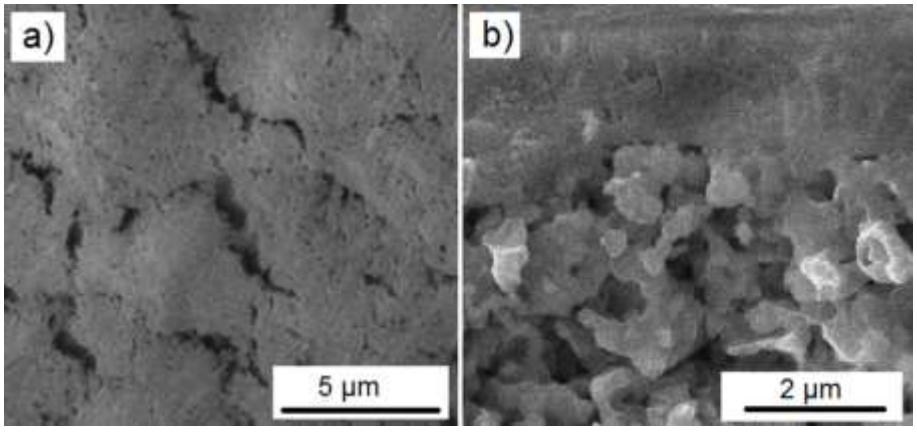

Fig. 15. Surface (a) and cross-sectional (b) SEM images of thin-film CuO/GDC AFLs annealed at a temperature of 1000 °C in air and reduced in hydrogen (power of Cu magnetron - 500 W).

These results show that magnetron sputtering is also a good technique for preparation of the thin-film copper-cermet anode material for SOFC. However, electrochemical properties of magnetron sputtered CuO/GDC thin films are under investigation.

CONCLUSIONS

Uniform and porouscompositethin films consisting of oxygen ionic conductivephase (YSZ or GDC) and electronic conductive phase (Ni or Cu) may be prepared by reactive magnetron sputtering. Annealing the as-deposited films in hydrogen resulted in NiOor CuOreduction to metallic Ni or Cu, which then segregated to the film surface with particles formation. However in the case of nickel based films, pre-calcination of the as-deposited films in air at 1200 °C followed by reduction produces films consisting of uniformly distributed nano-grains having extensive three-phase boundaries. The exceptionally high degree of dispersion andintermixing of the anode components promotes generation of veryextensive three phase boundaries.Moreover, under thermalcycling in both oxidizing and reducing atmospheres, nickel based anode functional layersare robust against morphologicalchanges and delamination from an YSZ substrate. Accordingly, because their thinnessrenders them robust against strain-induced separation from the substrate, they are also promisingcandidates for use as highly conducting, stabilizing buffer layers for accommodating strain between conventional anodes and the YSZ electrolyte, and for fabrication of graded-compositionNi-YSZ anodes for use in SOFC applications. The SOFC performance is significantlyincreased using a nanostructured Ni/YSZ or Ni/GDC AFL as compared to the performance of cells without it. The increasing the TPB density near the electrolyte and anode interface increases the number of sites available for the charge transfer bythe AFL, leading to an enhancement in the cell performance.

Magnetron sputtered AFLs can be used to improve the efficiency of various types of cells, such as electrolyte-supported, anode-supported, and micro-SOFC. The only exceptions are metal-supported SOFC, because as-deposited AFLs require annealing in air after deposition.

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МАГНЕТРОННОЕ ОСАЖДЕНИЕ АНОДНЫХ ФУНКЦИОНАЛЬНЫХ СЛОЕВ ДЛЯ ТВЕРДООКСИДНЫХ ТОПЛИВНЫХ ЭЛЕМЕНТОВ

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Предлагаемый обзор посвящен последним достижениям в области магнетронного осаждения тонкопленочных анодных функциональных слоев(АФС) для твердооксидных топливных элементов (ТОТЭ) различных конструкций (на несущем электролите, на несущем аноде и микро-ТОТЭ). Производство компонентов ТОТЭ остается в настоящее время важнымфактором для промышленного развития этого электрохимического устройства. Формирование тонких наноструктурированных анодных слоев методами физического газофазногоосаждения позволяет повысить эффективность ТОТЭ за счет уменьшения поляризационных потерь на аноде. В обзоре обсуждается использование тонкопленочных анодов для различных конструкций ТОТЭ, работающих в диапазонах низких, средних и высоких температур. Проанализировано влияние параметров осаждения, микроструктуры и химического состава АФС на характеристики ТОТЭ.
Ключевые слова: *ТОТЭ, анодный функциональный слой, тонкая пленка, магнетронное распыление, поляризационные потери.*

BƏRK OKSİD YANACAQ ELEMENTLƏRİ ÜÇÜN ANOD FUNKSİONAL ÖRTÜKLƏRİN MAQNETRON ÇÖKDÜRÜLMƏSİ

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Təqdim olunan icmal müxtəlif konstruksiyalı bərk oksid yanacaq elementləri üçün anod funksional təbəqələrinin maqnetron çökdürmə yolu ilə alınmasına həsr olunub. Nazik nanostrukturlu anod təbəqələrinin qaz fazadan çökdürmə usulu ilə formalaşması bərk oksid yanacaq elementlərinin effektivliyini anodda polyarizasiya itkisinin azalması hesabına artırır.
İcmalda aşağı, orta və yüksək temperatur intervalında işləyən müxtəlif konstruksiyalı bərk oksid yanacaq elementləri üçün nazik təbəqəli anodların istifadəsi müzakirə olunur. Anod funksional təbəqələrinin mikrostrukturu və kimyəvi tərkibinin, eləcə də çökdürmə parametrlərinin bərk oksid yanacaq elementlərinin xarakteristikalarına təsiri analiz edilib.
Açar sözlər: *anod funksional örtükləri, bərk oksid yanacaq elementləri, maqnetron səpilmə metodu*