MICROSTRUCTURE DEVELOPMENT OF THE Ni-GDC ANODE MATERIAL FOR IT-SOFC

RAZVOJ MIKROSTRUKTURE Ni-GDC ANODNEGA MATERIALA ZA SREDNJETEMPERATURNE SOFC

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The NiO-GDC-based material is a potential candidate for an anode material for the low-temperature SOFCs. In this work a modified combustion synthesis was used for the preparation of NiO-GDC. The main advantage of the preparation method employed was that after the synthesis both phases, NiO and GDC, in the ash product were randomly distributed on a nanometre scale. The citrate-nitrate (*c/n*) ratios in the combustion-reaction mixtures varied from 0.15 to 0.18. The prepared powders were isostatically pressed into pellets, sintered at 1200 °C, 1250 °C, 1300 °C, 1350 °C or 1400 °C, reduced and subsequently submitted to a microstructure analysis. The crystallite sizes of both phases in the as-prepared powders, as well as the grain sizes of nickel in the final reduced samples greatly depended on the slight variation of the *c/n* ratio in the starting reaction gel mixture. In the as-synthesized samples, crystallite sizes were calculated to be 4.3 nm or 40.0 nm for the GDC phase and 7.6 nm or 48.0 nm for the NiO phase for the samples with the *c/n* ratios of 0.15 or 0.18, respectively. After sintering under different conditions and reductions, the final average particle size of Ni varied from 71 nm to 146 nm or from 143 nm to 254 nm, while the average size of GDC grains ranged from 84 nm to 193 nm or from 96 nm to 247 nm for the samples with the *c/n* ratios of 0.15 or 0.18, respectively. The temperatures from 1200 °C to 1250 °C were recognized as the most appropriate temperature interval that provided good connectivity between the grains and the smallest one-phase regions in the final Ni-GDC cermets with an average Ni-particle diameter of around 70 nm.

Keywords: combustion synthesis, nanocomposites, microstructure, fuel cells, Ni-GDC

Materiali na osnovi NiO-GDC spadajo med potencialne kandidate za izdelavo anod v srednjetemperaturnih SOFC. NiO-GDC smo pripravili z modificirano zgorevalno sintezo. Največja prednost metode je ta, da sta po sintezi obe fazi NiO in GDC naključno porazdeljeni na nanometrskem nivoju. Citratno-nitratno razmerje *c/n* v reakcijskih zmeseh je bilo 0,15 in 0,18. Pripravljeni prah smo po sintezi izostatsko stisnili v tablete, jih sintrali pri temperaturah 1200 °C, 1250 °C, 1300 °C, 1350 °C in 1400 °C, reducirali ter izvedli kvantitativno analizo mikrostruktur. Razmerje *c/n* v začetni raztopini močno vpliva na velikost kristalitov faz (NiO in GDC) v vzorcu po sintezi, kot tudi na velikost zrn faz v sintranih in reduciranih vzorcih. Najmanjša nikljeva zrna (povprečna velikost okoli 70 nm) v končnem Ni-GDC-kompozitu keramika-kovina so nastala po sintranju in kasnejši redukciji v temperaturnem intervalu med 1200 °C in 1250 °C.

Ključne besede: zgorevalna sinteza, nanokompoziti, mikrostruktura, gorivne celice, Ni-GDC

1 INTRODUCTION

Fuel cells are environmentally friendly energy converters that can transform chemical energy directly to electricity, resulting in high-energy conversion efficiencies. Solid-oxide fuel cells (SOFCs) have several advantages over the other types of fuel cells, including flexibility of the fuels used, high-reaction kinetics due to high-temperature operation and relatively inexpensive materials formed in thin layers. However, the high-temperature operation results in a number of inherent challenges, such as mechanical stress, electrode sintering and low start-up time. First, it is difficult to obtain gas-tight seal between the chambers. Moreover, an addition of a large amount of steam to hydrocarbon fuels is required to avoid carbon deposition on the anode, resulting in a complicated water management in the SOFC systems.[1,2]

One approach to overcoming the above challenges is to reduce the operating temperatures of SOFCs to 800 °C or less to enable the metal materials (stainless steels) to be used as interconnect materials.[3,4] Another approach towards addressing the above challenges is to design an SOFC with only one gas chamber. This type of SOFC is called a "single chamber SOFC" (SC-SOFC), wherein both anode and cathode are exposed to the same fuel-oxidant gas mixture. As a result, the gas-sealing problem can be inherently avoided since no separation between fuel and air is required, while carbon deposition is less of a problem due to the presence of a large amount of oxygen in the mixture. Materials used as the components in two-chamber SOFCs (LSM strontium-doped lanthanum manganite as a cathode, yttrium stabilized zirconia-YSZ as an electrolyte and Ni-YSZ cermet as an anode) are not appropriate for the use in an SC-SOFC due to their insufficient selectivity toward electrode reactions under operating conditions. However, there are only a few materials selective enough that can operate at the temperatures below 700 °C. Currently the most widely adopted SC-SOFC materials are gadolinium stabilized ceria (GDC) as electrolyte, Ni-GDC as anode and strontium-doped samarium cobaltite (SSC) as cathode. GDC is a better oxygen ionic conductor than

YSZ, as it has a higher ionic conductivity than YSZ in the temperature range from 300 °C to 700 °C.

Anode materials are usually prepared by mechanically mixing the separately synthesized powders of NiO and GDC that were formed, sintered and reduced to obtain Ni-GDC cermets.[5–7] In this way, an accurate chemical composition can be attained, but it is rather difficult to achieve a uniform distribution of separate phases in the anode composite that will result in a non-homogeneous structure and a poor anode performance. However, homogeneous composite powders of NiO-GDC were synthesized using a hydroxide co-precipitation.[8,9] The co-precipitation method is still a solution-based technique with several consecutive steps and, as such, it is rather time consuming. Consequently, the preparation of complex metal oxides by using combustion synthesis has recently become an interesting area of research based on the promising results of this technique surpassing the conventional method.[10,11] The main advantage of the combustion synthesis is the ability to produce complex oxide powders directly from the precursor solution. Therefore, the combustion synthesis could be, in principle, a good method for preparing the composite powder of Ni-GDC with a uniform distribution of fine Ni particles within the GDC framework.

The aim of this work was a synthesis and a subsequent thermal treatment of nano-scaled highly sinterable NiO-GDC dispersions prepared with the citrate-nitrate combustion synthesis technique. High sinterability of the prepared powders is of the prime importance for the preparation of dense bodies at the relatively low temperatures (close to 1200 °C). With an examination of the densification process of such ceramic powders, we also demonstrated a microstructure evolution from the synthesized NiO-GDC nano-powder to the Ni-GDC anode cermet.

2 EXPERIMENTAL PROCEDURES

The NiO-GDC powders were prepared with a modified citrate-nitrate combustion synthesis. The combustion system was based on the citrate-nitrate redox reaction. In this combustion method, the starting substances were $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 6H_2O$, nitric acid (65 %) and citric acid (analytical reagent grade). All solid compounds were dissolved with minimum additions of water in the amounts that allowed the Ni volume content in the final composite to be 50 %. The $Ce(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 6H_2O$ additions were found to allow the GDC composition to be $Ce_{0.8}Gd_{0.2}O_{1.9}$. The reactive mixture was prepared by mixing the five reactant solutions and then kept over a water bath at 60 °C under vacuum ($p =$ 5–7 mbar) until it transformed into a light green gel (at least 5 hours). The initial citrate/nitrate molar ratios in the starting solution were 0.15 and 0.18. The corresponding citrate-nitrate gel was then gently milled in an agate

mortar and uni-axially pressed into pellets ($\Phi = 12$ mm, $h = 30$ mm, $p = 17$ MPa). These samples were placed on a corundum plate and ignited at the top of the pellet with a hot tip to start an auto-ignition reaction. The samples were characterized by the X-ray powder diffraction technique using a PANalytical X'Pert PRO MPD apparatus. Data were collected in the 2θ range from 20° to 70° in steps of 0.033° for 1 s/°. After the synthesis, powders were milled in an agate mortar, uni-axially pressed into pellets (100 MPa) and subsequently also iso-statically pressed (750 MPa). Formed pellets were sintered at different temperatures (1200 °C, 1250 °C, 1300 °C, 1350 °C and 1400 °C) for 2 hours. Material shrinkage during the sintering was measured separately using a BÄHR DIL 802 dilatometer. For the microstructure determination, the sintered tablets were polished (3 μm and 0.25 μm diamond pastes), thermally etched, reduced at 900 °C (2 h) in an H_2/Ar atmosphere and subsequently analyzed with SEM FE Zeiss ULTRA plus. The quantitative analyses of the microstructures were performed on digital images (images were digitized into pixels with 255 different grey values) using the Zeiss KS300 3.0 image-analysis software.

3 RESULTS AND DISCUSSION

The main benefit of the combustion synthesis is the exothermic effect during the fuel (citrate) and nitrate redox reaction that is accompanied by a considerable gas release preventing the formation of hard agglomerates. The combustion reaction takes just a few seconds to turn a reaction mixture into the final product, while a much longer time is required for the same process to be conducted during the calcination process. In the case of an NiO-GDC citrate-nitrate self-sustaining reaction, the maximum temperature gradient (i.e., the heating rate)
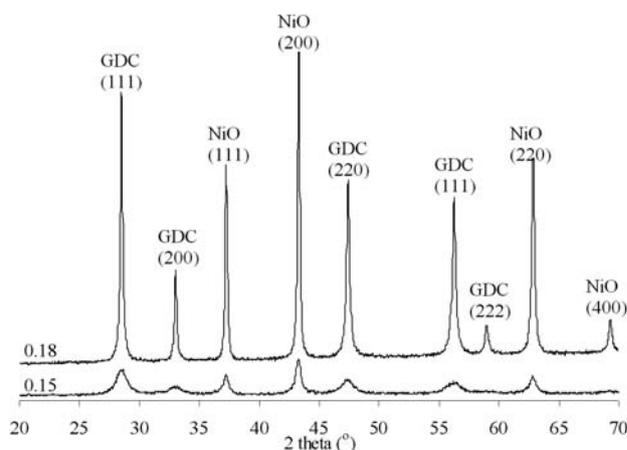

Figure 1: XRD diffraction spectra of the as-prepared powder mixtures of NiO-GDC (obtained from the reactive gels with $c/n = 0.15$ or $c/n = 0.18$)
Slika 1: Rentgenska praškovna posnetka vzorcev NiO-GDC, pripravljenih iz raztopin s citratno-nitratnim razmerjem $c/n = 0,15$ in $c/n = 0,18$

inside the reaction zone (calculated on the basis of the temperature-profile measurements) was 1164 K s^{-1}. Such a high temperature gradient and short reaction times resulted in a unique powder mixture composed of nano-sized particles. The one-phase particle size and the degree of crystallization were found to be the functions of the citrate-nitrate initial ratio. In both samples (c/n = 0.18 or 0.15) the two main phases corresponded to GDC and NiO (**Figure 1**). According to the Sherer X-ray broadening of the peaks, the average crystallite sizes were calculated to be 4.3 nm and 40 nm for GDC and 7.6 nm and 48 nm for NiO for the samples with the c/n ratios of 0.15 and 0.18, respectively.

The ideal microstructure of the final Ni-GDC cermet is composed of very small grains of both phases (preferably sub-micrometre or nano-sized), where GDC mainly acts as a matrix to support the Ni electro-catalyst and hinder its fusion under the cell operating conditions. At the same time, GDC is also used to extend the Ni-GDC-gas triple-phase boundary (TPB) into the anode. The length of the TPB is related to the reaction rate for the electrochemical oxidation of hydrogen[12,13] in an operating fuel cell. For this reason, Ni-GDC also has to exhibit continuity of both phases throughout the cermet, since it must serve both as an electronically and ionically conductive material. In principle, high conductivity is achieved when a good contact between particles is ensured; this is normally accomplished through sintering. However, sintering also means grain growth, which is in contradiction to the desire to preserve the NiO-GDC nano-distribution. However, if the sintering temperatures required for the NiO-GDC densification can be lowered, then fine oxide mixtures can also be preserved in the sintered structures.

The determined sintering temperature of the prepared NiO-GDC mixture was influenced by a slight variation of the citrate-nitrate ratio (0.15 or 0.18) in the starting solutions. Being sintered at a significantly lower temperature ($T_{sintr.}$ = 1120 °C for the sample with the c/n ratio of 0.15 and $T_{sintr.}$ = 1280 °C for the sample with the c/n ratio of 0.18), the sample 0.15 sinters through two consecutive stages as a result of the inter- and/or intra-agglomerate sintering, while the shrinkage in sample 0.18 can be described with only one broad densification process (**Figure 2**).

The relatively low sintering temperature determined for the sample with the c/n ratio of 0.15 may be very important from the applicability point of view, since a single cell is normally prepared in several sintering processes. First, the anode and electrolyte layers are co-sintered at higher temperatures (up to 1400 °C) and then the cathode layer is applied and co-sintered at the temperatures of up to 1200 °C. Successful sintering of the NiO-GDC anode material at the temperatures below 1200 °C may result in diverse SOFC-preparation procedures, in which all the layers are co-sintered in a single step.

In order to obtain more detailed information about the microstructure development, the NiO-GDC green bodies prepared from the as-synthesized powders were sintered under various sintering conditions. Sintering temperatures were defined according to the obtained shrinkage curves. The presented microstructures (**Figure 3**) revealed that the nano-sized cermet mixture was no longer present in the sintered and, subsequently, reduced cermets. Instead, the one-phase dominance grew, but remained well within the sub-micrometre range if the cermets had been sintered at the relatively low temperatures. Additionally, it is evident that a fine distribution of phases (metal, ceramic and porosity) can be obtained when using the sintering temperatures no higher than 1200–1250 °C for the samples with a c/n ratio of 0.15, in which GDC serves as a continuous framework, within which the sub-micrometre Ni grains and pores are dispersed. However, in the case of the samples with a c/n ratio of 0.18 (sintered at 1200 °C and 1250 °C) an excessive grain growth of the newly formed metallic Ni particles (during the reduction) may be found. This phenomenon is a consequence of a fairly different surface energy of Ni and GDC, causing the hetero-grains at the interface to lose their chemical affinity.

Consequently, the coarsening of the Ni phase proceeds appreciably due to a poor adhesion of the metal to the ceramic material at the elevated temperatures. From a practical point of view, an excessive growth of the Ni grains results in the TPB length reduction. In the samples with a c/n ratio of 0.18, the grain growth of Ni was noticeable, while in the samples with a c/n ratio of 0.15, the grain growth of both phases (in the reduced state) was controlled predominantly with the sintering temperature and no excessive enlargement of Ni-grains, after the reduction, was observed.

Dense structures after sintering ensure good contact between the particles and a continuity of both phases
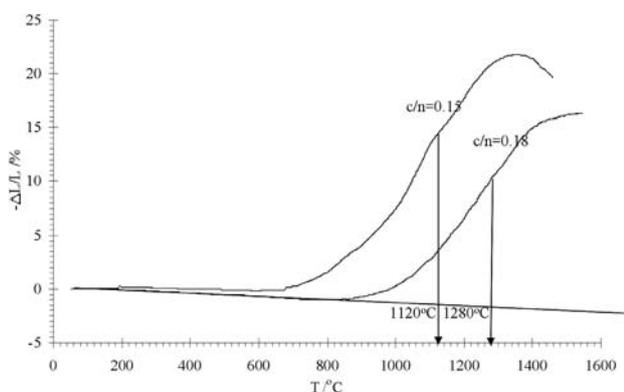

Figure 2: Relative shrinkage versus temperature of the NiO-GDC tablets (iso-statically pressed) prepared from the reaction mixtures with the c/n ratios of 0.18 or 0.15
Slika 2: Relativni skrček NiO-GDC izostatsko stisnjenih vzorcev, pripravljenih iz reakcijskih zmesi s citratno-nitratnim razmerjem c/n 0,18 in 0,15
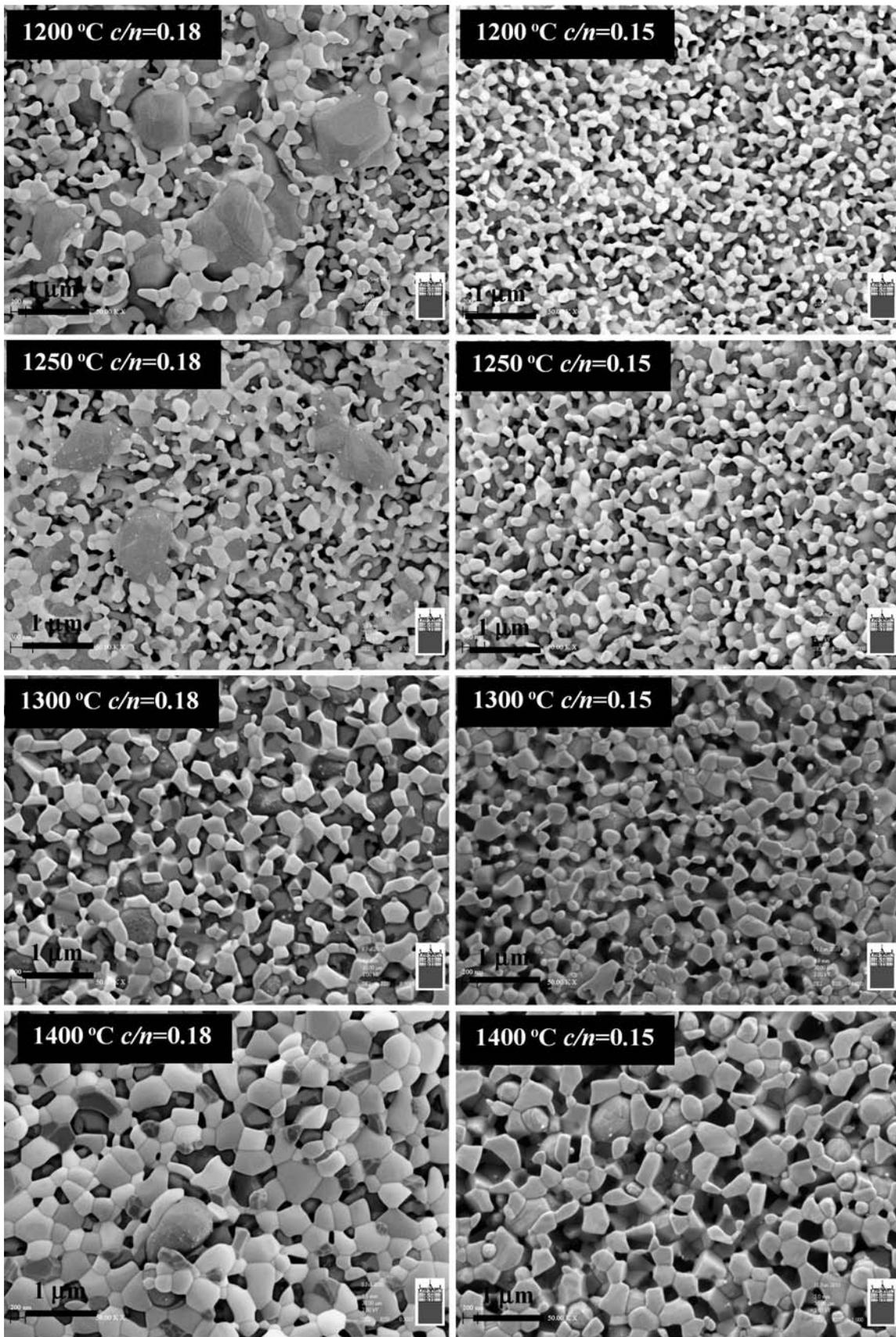
Figure 3: Microstructures of the sintered Ni-GDC samples after the reduction
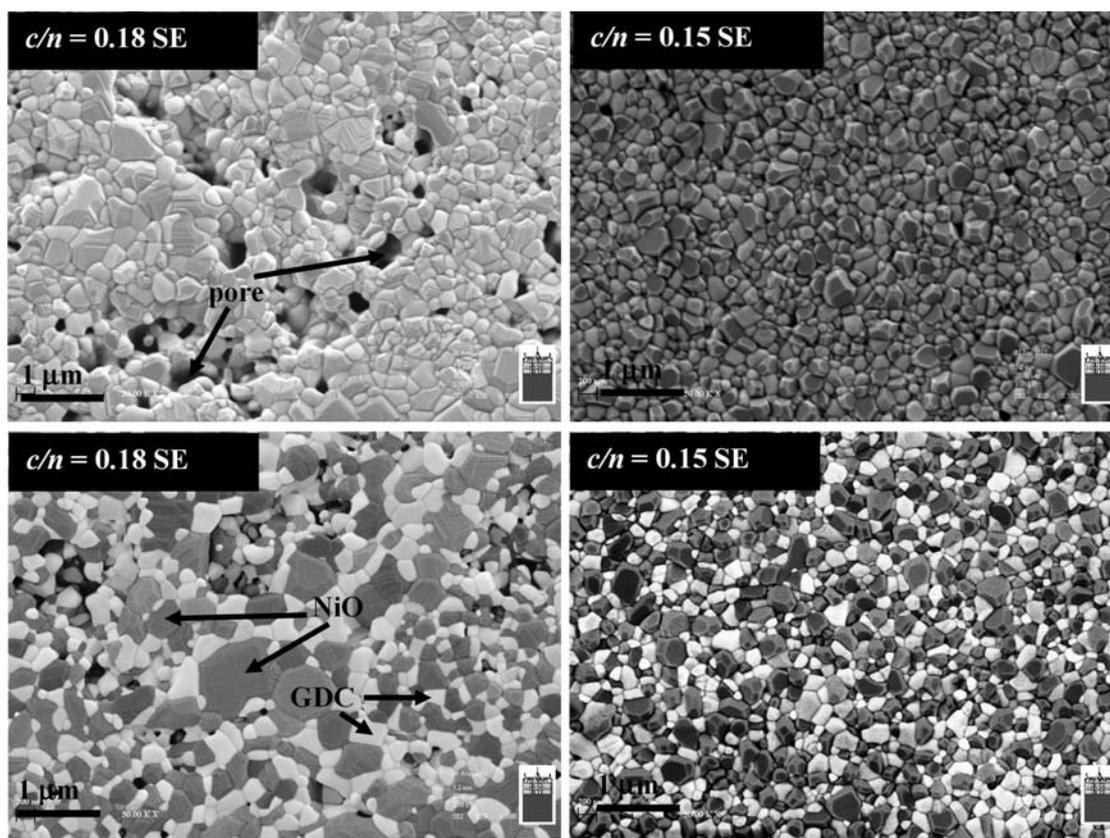**Slika 3:** Mikrostrukture sintranih vzorcev Ni-GDC po redukciji

Figure 4: Microstructures of the samples with the *c/n* ratios of 0.18 and 0.15 sintered at 1250 °C
Slika 4: Mikrostrukture vzorcev (razmerje *c/n*: 0,18 in 0,15) sintranih pri 1250 °C

(NiO and GDC). The continuity of the phases is essential not only with regard to conductivity, but also for the microstructure stability. The reason for the inhomogeneous microstructure in the reduced samples may be due to the inhomogeneous and partly porous microstructure after sintering. One good example of an insufficiently stable NiO-GDC microstructure is shown in the case of a sample with a *c/n* ratio of 0.18 (sintered at 1250 °C), in which more porous regions, accompanied with the grains of both phases that are significantly larger than in an average sample, can be found (**Figure 4**).

One possible reason for the differences in the microstructure development in the samples with a *c/n* ratio of 0.18 or 0.15 is in the nature of the combustion reaction itself. A slight increase in the citrate-nitrate molar ratio from 0.15 to 0.18 may lead to a carbon residue after the synthesis (0.18 sample), followed by a porosity enlargement due to carbon burning during the sintering process. Additionally, the peak combustion temperature in the reaction mixture with a *c/n* ratio of 0.18 is close to 1180 °C, while the peak temperature in the reaction mixture with a *c/n* ratio of 0.15 does not exceed 600 °C. Higher combustion temperatures and higher temperature gradients within the combusting reaction mixture may cause the formation of hard agglomerates.

The microstructure parameters important for an exact cermet analysis and obtained with a detailed quantitative microstructure analysis of the sintered and reduced samples are summarized in **Tables 1** and **2**. For statistically reliable data, several different regions were analyzed in each case. Parameters $\bar{d}$, d_x and d_y, d_{por} and ψ are represented as the diameter of the area-analogue circle – DCIRCLE, the intercept lengths in the *x* and *y* directions – FERETX, Y, and the maximal intercept length – FERETMAX and FCIRCLE, respectively. Porosity ε was determined as the microstructural porosity (on the basis of a microstructure analysis).

According to the results of the quantitative microstructure analysis, the porosity of the sintered samples decreased with the sintering temperature as expected. The higher sintering temperature also resulted in a pronounced grain growth. The average particle size of NiO exceeds the GDC average particle size in all the samples; however, the difference between average particle sizes is less pronounced at higher sintering temperatures. From this fact we can deduce that NiO in a NiO-GDC composite sinters first and more intensely. The average particle sizes of NiO and GDC in the samples with a *c/n* ratio of 0.15 range from 92 nm to 230 nm and from 84 nm to 193 nm, respectively, while in the samples with a *c/n* ratio of 0.18 they range from 127 nm to 249 nm and from 96 nm to 247 nm, respectively.

Table 1: Quantitative microstructure analysis of the sintered NiO-GDC samples
Tabela 1: Rezultati kvantitativne analize mikrostruktur sintranih vzorcev NiO-GDC

$T/°C$	c/n	$\varepsilon/\%$ Mikr.	(nm)		ψ		d_x/nm		d_y/nm		d_{por}/nm
			NiO	GDC	NiO	GDC	NiO	GDC	NiO	GDC	
1200	0.15	12	92	84	0.70	0.70	107	98	106	97	187
1250	0.15	11	121	95	0.77	0.78	138	108	137	108	158
1300	0.15	8	143	128	0.75	0.74	161	147	162	146	167
1350	0.15	6	189	163	0.80	0.76	210	186	209	186	177
1400	0.15	3	230	193	0.78	0.71	257	223	255	227	236
1200	0.18	13	127	96	0.71	0.72	142	107	143	108	358
1250	0.18	10	155	122	0.72	0.73	174	137	176	138	274
1300	0.18	7	182	152	0.72	0.73	203	173	204	172	335
1350	0.18	6	214	197	0.74	0.73	235	218	235	216	382
1400	0.18	4	249	247	0.77	0.72	269	267	268	267	370

Table 2: Quantitative microstructure analysis of the reduced Ni-GDC samples
Tabela 2: Rezultati kvantitativne analize mikrostruktur reduciranih vzorcev Ni-GDC

$T/°C$	c/n	$\varepsilon/\%$ Mikr.	(nm)		ψ		d_x/nm		d_y/nm		d_{por}/nm
			Ni	GDC	Ni	GDC	Ni	GDC	Ni	GDC	
1200	0.15	34	73	86	0.75	0.70	84	102	80	100	352
1250	0.15	29	71	97	0.75	0.78	82	108	77	108	304
1300	0.15	26	85	125	0.71	0.79	100	140	100	137	351
1350	0.15	25	109	154	0.72	0.79	133	176	125	165	407
1400	0.15	23	146	192	0.72	0.78	173	217	168	214	646
1200	0.18	40	169	95	0.70	0.71	191	106	203	107	378
1250	0.18	36	143	121	0.71	0.76	160	135	165	135	438
1300	0.18	34	168	150	0.74	0.78	194	168	183	167	385
1350	0.18	35	193	195	0.75	0.77	224	217	193	216	413
1400	0.18	21	254	244	0.76	0.78	301	264	275	260	361

Additionally, with higher sintering temperatures, the grains of both phases became rounder (ψ parameter).

Comparing the sintered and reduced samples, the size of the Ni-grains is reduced relative to the NiO particle size and, consequently, the porosity is increased. When analysing the microstructure of the metal-ceramic anode layer, we find that its appropriate volume porosity is between 30 % and 40 % [14–17]. Considering that about 41.1 % of the initial NiO volume is transformed into pores during the reduction of NiO to Ni, we find that the porosity of the sintered materials should be close to 10 %.

For a high TPB value, an average particle size of both phases should remain as small as possible; for suitable electrical properties, the contact between the particles should be good. For these reasons, the sintering temperature for a sample with a c/n ratio of 0.15 is in the range from 1200 °C to 1250 °C, while for a sample with a c/n ratio of 0.18 the sintering temperature below 1300 °C may be considered to be too low due to the clear microstructural instability of the final Ni-GDC composite, which was characterized for its exaggerated Ni growth. The final average particle sizes of Ni and GDC in a sample with a c/n ratio of 0.15 were 73 nm and 86 nm after the sintering at 1200 °C , and 71 nm and 97 nm after the sintering at 1250 °C, respectively. Nevertheless, the nano-sized initial oxide mixture and careful powder treatment enabled the preparation of well-sintered materials with the relative densities above 90 %, as well as subsequently reduced composites, in which the average particle sizes of both phases are still well within the sub-micrometer range.

4 CONCLUSIONS

The nano-sized NiO-GDC composites were prepared using a citrate-nitrate self-sustaining reaction from the initial reactive gel. After the synthesis, the average crystallite sizes were calculated to be 4.3 nm and 40 nm for GDC and 7.6 and 48 nm for NiO for the samples with the c/n ratios of 0.15 and 0.18, respectively. Such crystallites, partially agglomerated, were the starting material for a pellet preparation and the subsequent microstructure-development investigations. Relatively dense bodies (not more than ≈ 10 % of the residual porosity) were prepared at the sintering temperatures as low as 1200 °C for the samples with a c/n ratio of 0.15. Higher sintering temperatures did not significantly decrease the porosity. For the samples with a c/n ratio of 0.18, the sintering temperatures lower than 1300 °C were recognised as insufficient due to a clear microstructure instability, where more porous regions accompanied with the grains of both phases, larger than in an average sample, can be found. The average grain size of the GDC

phase increased with the increasing sintering temperature. The NiO grains also grew with the increasing sintering temperature; however, the dimensions of the final Ni grains formed during the reduction were very much influenced by the microstructure stability of the GDC framework formed during the sintering. The smallest Ni grains, still well in the sub-micrometer range, with the average particle sizes of 73 nm and 71 nm were obtained in the sample with a *c/n* ratio of 0.15 sintered at 1200 °C and 1250 °C, respectively.

Acknowledgements

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