

## DETERMINATION OF THE METAL CONCENTRATIONS IN AN ANODE MATERIAL FOR SOLID-OXIDE FUEL CELLS

### DOLOČITEV VSEBNOSTI KOVIN V ANODNEM MATERIALU ZA GORIVNE CELICE S TRDNIM ELEKTROLITOM

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Ni-SDC is a very promising new anode material for SOFC systems. It exhibits a superb ionic and electronic conductivity at intermediate temperatures (400–700 °C) in comparison to Ni-YSZ. Ni-SDC is a composite material requiring careful microstructural and compositional tailoring during the preparation of the material. Ni-SDC was synthesized using a simplified Pechini method with a reaction between metal acetates and ethylene glycol, the latter serving as a chelating agent, and a reaction medium. The molar ratio between cerium and samarium in the ceramic part was 83 : 17 and the overall nickel content in the final product was set to 38 %. During the preparation of the material, several different intermediates were synthesized (i.e., a powdered product after the synthesis, an oxide mixture after the calcination and a mechanically ground powder after the milling), which may differ according to their chemical and morphological properties. In this respect, the material chemical composition expressed as concentrations of nickel, cerium and samarium was followed through the preparation sequence using various analytical techniques, i.e., the volumetric and gravimetric methods, ICP-OES, SEM-EDS and XRD. It appears that the obtained results diverge consistently with the analytical techniques used. Volumetry and gravimetry were used only for the nickel-content determination. Additionally, all the metals were simultaneously determined with ICP-OES and XRD Rietveld refinement in a bulk sample and with SEM-EDS for a point analysis. There is no unique answer as to which analytical method should be used at various preparation steps. Instead, suitable analytical methods or their combinations were chosen with respect to the analyzed material's appearance and its morphological and microstructural characteristics.

Keywords: NiO-SDC powders, gravimetric method, volumetric method, SEM-EDS, XRD, ICP analysis

Kermet Ni-SDC se uporablja kot anodni material v SOFC gorivnih celicah (gorivne celice s trdnim elektrolitom). V primerjavi z navadno uporabljenim anodnim materialom Ni-YSZ ima Ni-SDC višjo ionsko in elektronsko prevodnost pri temperaturah od 400 °C do 700 °C. Kermet Ni-SDC zahteva pazljivo prilagajanje mikrostrukture in sestave med svojo pripravo. Ni-SDC je bil sintetiziran s poenostavljeno Pechinijevo metodo, kjer poteka reakcija med kovinskimi acetati in etilen glikolom. V končnem produktu je bilo molsko razmerje med cerijem in samarijem 83 : 17, volumenski delež niklja pa 38 %. Za ustrezen anodni material je potrebnih več stopenj obdelave, sinteza prekursorja Ni-SDC, kalcinacija in mletje v atritorju. V vsaki stopnji se pri materialu lahko spreminjata ali sestava ali morfologija. Kemijska sestava vseh treh materialov je bila izražena s koncentracijami niklja, cerija in samarija. Za določitev teh koncentracij so bile uporabljene različne analize metode: volumetrija, gravimetrija, ICP-OES, SEM-EDS in XRD. Med dobljenimi rezultati se glede na uporabljeno metodo pokažejo razlike. Volumetrijo in gravimetrijo smo uporabili za določanje koncentracije niklja v vzorcih. Vsebnost vseh treh kovin istočasno pa smo določili z ICP-OES, XRD in SEM-EDS, kjer se s slednjo točkovno določi koncentracije, s prvima dvema metodama pa v večjem volumnu. Unikatnega odgovora, katera analitska metoda je najbolj primerna, ni. Najprimernejšo metodo oziroma njihovo kombinacijo izberemo glede na morfološke in mikrostrukturne lastnosti analiziranega materiala.

Ključne besede: NiO-SDC-prahovi, gravimetrična metoda, volumetrična metoda, SEM-EDS, XRD, ICP-analiza

## 1 INTRODUCTION

The solid-oxide fuel cell (SOFC) is one source of alternative energy. These cells have a more efficient and pollution-free transformation of fuel into electrical power than the traditional combustion engines, which is the reason for the growing research in this field. A SOFC is typically composed of an anode, a cathode and electrolytes, which should each have their specific properties. The anode should have a high ionic and electronic conductivity for the transportation of oxide ions to the reaction site and electrons from it. Its microstructure should provide a good contact between the reactive gas, electronic and ionic conductors (the triple-phase boundary; hereafter: TPB). Finally, the desired molar ratio of the metals in the cermet<sup>1,2</sup> is also very important. The

volume content of nickel in the cermet influences the open porosity of the material, which enables a contact between the gasses and the anode.<sup>3</sup> The electronic conductivity increases with the increasing nickel content; meanwhile, the ionic conductivities of the cermet decrease due to the weak connections among the SDC grains.<sup>4</sup> Furthermore, the ceramic phase of the cermet (samaria-doped ceria; hereafter: SDC) should have a proper composition of samarium and cerium. It is experimentally determined that the best ionic conductivity is achieved when the molar ratio of Ce : Sm is 80 : 20, and the samarium is distributed homogeneously in the cerium.<sup>5</sup> It is necessary to fulfill all these conditions to provide a high-efficiency material for SOFCs. Previous contributions<sup>6–8</sup> mostly stress the importance of the metal content in such materials, but this was rarely determined,

even partially. The value of the metal content has the highest importance when developing the materials for SOFCs.

This report describes the material's composition expressed as concentrations of nickel, cerium and samarium, which are followed through the preparation steps, using several analytical techniques, such as the volumetric and gravimetric methods, ICP-OES, SEM-EDS and XRD.

## 2 EXPERIMENTAL WORK

### 2.1 Sample preparation

A mixture of 17.68 g of  $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot x\text{H}_2\text{O}$  (Sigma Aldrich, 99.9 % pure, metals basis) and 3.65 g of  $\text{Sm}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot x\text{H}_2\text{O}$  (Sigma Aldrich 99.9 % pure, metals basis) was dissolved in 150 mL of deionized water. After the acetates dissolved 100 mL of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ , Sigma Aldrich, puriss. p. a. 99.5 %) was added. The mixture was heated to 50 °C for 30 min, then the temperature was raised to 80 °C and 32.93 g of nickel acetate  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (Riedel-de Haën, min 98 % purity) was added. The metal molar ratio in the reaction mixture was 5.0 : 4.6 : 1. This mixture was heated and vacuum dried for two and half hours in a vacuum dryer (Büchi Heating bath B-490 Rotavapor R-200), equipped with a vacuum pump (PC 2003 VARIO). Afterwards, the product was dried at 80 °C for three days until the final crystals were formed, which were then used as an intermediate (Sample 1) to produce the anode material. This intermediate was calcined at 900 °C in air for 1 h to form a mixture of metal oxides (Sample 2). Sample 2 was homogenized in an attritor mill by wet milling in isopropanol for one hour which resulted in Sample 3.

Nickel concentrations in the NiO-SDC material were determined with the gravimetric method, using dimethylglyoxime, and the volumetric method with the EDTA titration. To determine cerium and samarium, and the nickel weight content, SEM-EDS, XRD method and ICP-OES analysis were used.

The samples that were used for gravimetry, volumetry and the ICP analysis were dissolved in different solvents. The intermediate after the synthesis (Sample 1), which was a water-soluble product, was dissolved with distilled water. Sample 2 was a cermet composed of nickel oxide, samarium oxide and cerium oxide. It was dissolved in concentrated (96–98 %) sulfuric (VI) acid and evaporated to form the sulfates of the metals present. The residue of metallic sulfates was then dissolved in 37 % hydrochloric acid and diluted in distilled water. Sample 3 was dissolved using the same acid procedure as for the Sample 2.

### 2.2 Analytical procedures

#### 2.2.1 Thermal decomposition of Sample 1

Thermal decomposition of Sample 1 was analyzed in the range from room temperature to 1000 °C in air with a

heat rate of 10 K min<sup>-1</sup> with the TG/DTA analysis using a Netzsch STA 449 F3 Jupiter apparatus.

#### 2.2.2 Gravimetric determination with dimethylglyoxime

The nickel content was determined in 10 mL aliquots of dissolved samples diluted with distilled water in an Erlenmeyer flask. The pH level was adjusted to between 4 to 5 with an ammonia or hydrochloric solution, depending on the pH value of the previous solution. Then, 0.5 mL of  $\text{NaCOOCH}_3$  and 20 mL of  $\text{CH}_3\text{COOH}$  were added to form an acetate buffer. The solution was then boiled with an electric heater. After the mixture cooled down slightly, 10 mL of dimethylglyoxime (1 % ethanol solution) was added and the red nickel precipitate was filtered through the ceramic filter and washed with hot water. The precipitate containing nickel was dried at 120 °C for 1 h, cooled down in a desiccator and weighed. This was repeated at least three times. The weight percentage was calculated from the weight of the complex.<sup>9</sup> It is recommended that the analysis of the standard sample be carried out in the same method of analysis that was used for our samples. Therefore, the gravimetric method was also used for the nickel (II) oxide (NiO), the Aldrich nanopowder that was taken as the standard material.

#### 2.2.3 Volumetric method using EDTA as a titration reagent

For a determination of nickel, 10 mL aliquots of dissolved samples were diluted with distilled water in an Erlenmeyer flask to 100 mL. The pH value was adjusted to 10 with an ammonia solution. Then a solid murexide indicator was added that formed a bright yellow color. The sample was titrated with the standard 0.01 M EDTA until the yellow color of the nickel-murexide complex started to change to the purple color of a free indicator. The volumetric-determination procedure was repeated ten times for each sample. The weight percentage was calculated from the EDTA volume used for the titration of the nickel ions.<sup>9–11</sup> Using this method, the nickel content was also determined for the nickel (II) oxide (NiO), the Aldrich nanopowder that was taken as the standard material.

#### 2.2.4 SEM-EDS

All the samples were characterized on an FE-SEM Zeiss Ultra Plus microscope equipped with EDS (an Oxford X-Max SDD 50 mm<sup>2</sup> detector and INCA 4.14 X-ray microanalysis software). The sample preparation included a fixation onto a conductive C tape and a subsequent sputtering with platinum, without any polishing. The detector was calibrated just before the analysis with the Co-standard under operating conditions. The EDS spectra were recorded on the flat regions of the samples using a process time of 5, a lifetime of 120 s and an accelerating voltage of 14 kV, which is an acceptable compromise between the analyzing volume and the overvoltage needed to excite the Ce, Sm and Ni X-rays,

whose emission lines are found in the interval between 4.84 ( $L\alpha_1$ ) keV, 5.64 ( $L\alpha_1$ ) keV and 7.48 ( $K\alpha_1$ ) keV, respectively. Using the Anderson-Halser estimation,<sup>12</sup> the X-ray production depth was approximately 0.6  $\mu\text{m}$ . The quantification of the X-ray spectra was performed with respect to the standard procedure provided by the software manufacturer (ZAF-based method<sup>13</sup>). For the statistically reliable data in each case, five to seven different fields of view in various regions of interest were analyzed.

### 2.2.5 XRD analysis

The X-ray powder-diffraction data for Samples 1, 2 and 3 were collected using a PANalytical X'Pert PRO MPD diffractometer with the  $\theta$ - $2\theta$  reflection geometry, a primary-side Johansson-type monochromator and the  $\text{CuK}\alpha_1$  ( $\lambda = 0.154\ 059\ \text{nm}$ ) radiation. The room-temperature-reflection data were acquired from the  $2\theta$  angles of  $5^\circ$  to  $90^\circ$  in the steps of  $0.034^\circ$ . A quantitative XRD analysis with the Rietveld method using the *TOPAS2.1* program suite<sup>14</sup> was performed for Samples 2 and 3. The background was modeled with a third-order polynomial. We also refined zero error, scale factor, lattice parameter  $a$  and one profile parameter (the crystallite size) for NiO and SDC. The atom parameters were fixed, taken from the published structures of SDC and NiO.<sup>15,16</sup> The final match between the observed and calculated profiles is shown in **Figures 1** and **2**. The agreement factor  $R_{\text{wp}}$  was 0.094 5 and 0.078 5 for Samples 2 and 3, respectively.

### 2.2.6 ICP-OES

An analysis of nickel, samarium and cerium was carried out with an inductively coupled plasma-optical emission spectrometer (Varian 715-ES ICP-OES Spectrometer). The ICP-OES spectrometer is used to define concentrations of several elements in the solution. The ICP-OES method was already used to detect the metals (Ni, Ce, Gd, Ag) in the materials used for SOFCs.<sup>1,17-20</sup> Details about the instruments' operating conditions are depicted in **Table 1**.

## 3 RESULTS AND DISCUSSION

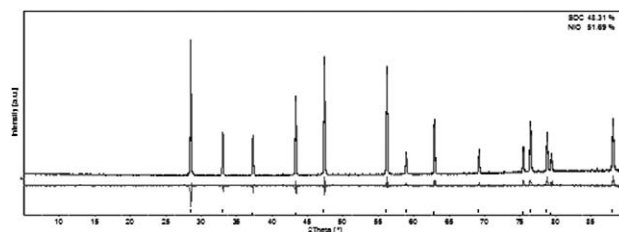
The results for the metal contents in Samples 1, 2 and 3 are shown in **Tables 2**, **3** and **4**, respectively. The calculated concentrations of cations for Samples 2 and 3 were determined according to the initial amounts of added cations. It was assumed that during the process there were no losses of the metals and that the entire chemical reaction took place in line with the expectations, meaning that Samples 2 and 3 consist of oxides only. The calculated metal mass fractions for Sample 1 were calculated by considering its thermal decomposition into oxides (**Figure 3**). The concentration range of the elements that are in the samples is in the detection range of the classical analytical methods (gravimetry, volumetry). The systematic error in the gravimetric determination of nickel had to do with the specific characteristics of the

precipitated nickel dimethylglyoxime (the voluminosity of the formed complex).<sup>21</sup> The values obtained with the complexometric titration of nickel deviate more from the expected calculated values than in the case of gravimetry. It was difficult to determine the color leap of the organic indicator that provided the endpoint of titration. The pH value of the prepared solution had a significant influence on the results, as did the absence of oxidants in the analyte.<sup>21</sup> The rare elements showed a great similarity in the chemical properties; therefore, the concentration of these elements (cerium and samarium) was determined only with instrumental methods.

Determination of the chemical compositions of the samples was quite a challenge with regard to the quantification of the collected EDS spectra. The main difficulty was found in the fact that the Ce and Sm characteristic X-ray peaks in the EDS spectra mostly overlap. This problem was particularly pronounced in the case of Sm, since the superimposed Ce peaks on all the main Sm peaks made a consistent quantitative compositional calculation rather difficult. From this point of view, the related WDS analysis seems to be more suitable for a compositional investigation of such samples. However, when compared to WDS, EDS has its advantages: it is more available, quicker, simpler and easier to perform. In fact, in material science, the EDS analysis is one of the basic tools for compositional investigations and, as such, it is very popular.

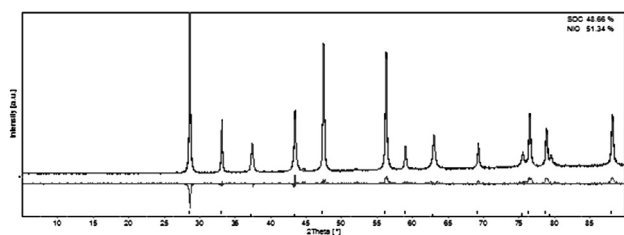
EDS and XRD are nondestructive approaches to a material investigation, but both are less accurate than the other three used analytical methods. Additionally, EDS and XRD are both based on a similar physical phenomenon; however, there is one distinguishable difference between them. The XRD quantitative analysis always refers to the bulk-sample composition, while EDS denotes the chemical composition in a much smaller sample region. For this reason, EDS results always depend upon the specimen surface preparation and are also influenced by the sample topography.

From this point of view, the three investigated samples were somewhat dissimilar. After the synthesis, the sample was composed of tiny crystals (**Figure 4**). To determine the homogeneity of this sample, an X-ray sur-



**Figure 1:** Rietveld refinement for Sample 2: experimental and calculated (upper curves) and difference (lower curve) profiles. Vertical bars denote the position of reflections for SDC (upper) and NiO (lower).

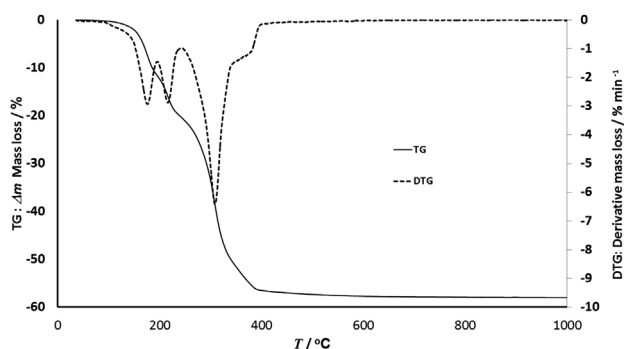
**Slika 1:** Rietveldovo prilaganje za vzorec 2: izmerjena in izračunana krivulja (zgoraj) ter diferenčna (spodaj). Pokončne črtice označujejo lego uklonov za SDC (zgoranje) in NiO (spodnje).



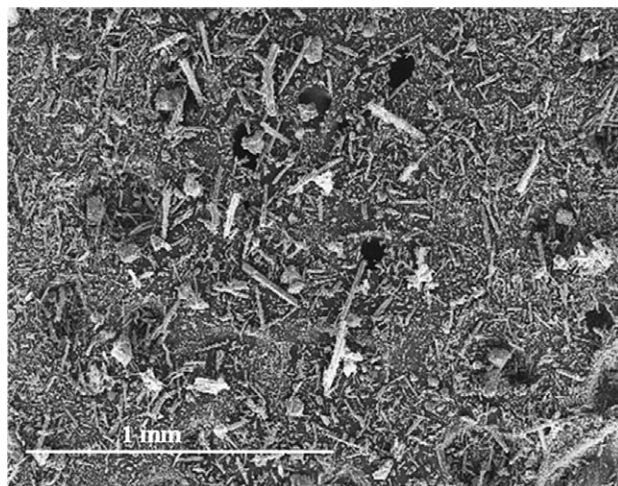
**Figure 2:** Rietveld refinement for Sample 3: experimental and calculated (upper curves) and difference (lower curve) profiles. Vertical bars denote the position of reflections for SDC (upper) and NiO (lower).

**Slika 2:** Rietveldovo prilaganje za vzorec 3: izmerjena in izračunana krivulja (zgoraj) ter diferenčna (spodaj). Pokončne črtice označujejo lego uklonov za SDC (zgoranje) in NiO (spodnje).

face mapping was performed (**Figure 5**). As expected, Ce, Sm, Ni, O and C were the only elements detected in the sample. From the element maps it could be seen that the specimen was rather inhomogeneous. Some variations in the grayscale maps may be associated with the specimen topography; however, it was evident that the sample contains two separate phases. The elongated crystals, typically 20–40  $\mu\text{m}$  long and  $\approx 5 \mu\text{m}$  wide, were Ce- and Sm-rich, while smaller particles (3–10  $\mu\text{m}$  in diameter) of an undefined shape were Ni-rich. This was also supported by the XRD diffraction pattern of Sample 1, presented in **Figure 6**. The qualitative XRD analysis revealed that the sample consisted of an SDC metal-organic precursor with a known structure and formula<sup>22</sup> and of at least one additional crystalline phase with an unknown composition and structure. The positions of the first reflections of the unknown phase were at the angles lower than  $10^\circ 2\theta$ . They also had significantly lower intensities in comparison with the SDC precursor phase. Both facts indicated that the unknown phase could be a metal-organic nickel complex, i.e., a precursor of NiO. The XRD quantitative analysis using Rietveld refinement was not possible for this sample, since it requires the knowledge of the composition and the structure of all the crystalline phases. Due to the observed inhomogeneity, the only practical way of performing a quantitative EDS analysis was by collecting the X-ray signals from the regions of interest (ROI) of approximately 0.25  $\text{mm}^2$  in



**Figure 3:** Thermal decomposition of Sample 1 to Sample 2 in air  
**Slika 3:** Termični razpad vzorca 1 do vzorca 2 na zraku



**Figure 4:** Tiny crystals in Sample 1 after the synthesis  
**Slika 4:** Kristalčki vzorca 1 po sintezi

**Table 1:** Operating conditions for the ICP-OES analysis

**Tabela 1:** Pogoji merjenja za ICP-OES analize

Parameter	Value
RF generator power / kW	1.2
Frequency of RF generator / MHz	40
Plasma-gas flow rate / $\text{L min}^{-1}$	15.0
Auxiliary-gas flow rate / $\text{L min}^{-1}$	1.50
Nebulization-gas flow pressure / kPa	200
Gas	Argon
Sample-uptake rate / $\text{mL min}^{-1}$	1.9
Type of detector	CCD
Type of spray chamber	Sturman-Masters double pass
Type of nebulizer	V-groove
Element $\lambda/\text{nm}^{-1}$	Ce: 418.659 446.021
	Sm: 359.259 360.949
	Ni: 216.555 231.604

**Table 2:** Results of metal mass fractions for Sample 1 obtained with different analytical methods

**Tabela 2:** Masni deleži treh kovin v vzorcu 1, določeni z različnimi analitskimi metodami

Used method	w(Ni)/%	w(Ce)/%	w(Sm)/%	w(Ni) : w(Ce) : w(Sm)
Calculated value	16.1	14.6	3.2	5.0 : 4.6 : 1.0
Gravimetric method	16.5 $\pm$ 0.3	/	/	/
Volumetric method	15.47 $\pm$ 0.02	/	/	/
SEM-EDS	12.3 $\pm$ 0.5	12.6 $\pm$ 1.5	2.5 $\pm$ 0.5	5.0 : 5.1 : 1.0
ICP-OES	14.9	13.5	2.8	5.4 : 4.9 : 1.0

w/% – mass fraction, w/% – masni delež

size (6–7 ROIs on each field of view). According to the results summarized in **Table 2**, the determined element-content ratio (ECR) among Ni, Ce and Sm (w(Ni):w(Ce):w(Sm) = 5.0 : 5.1 : 1.0) was not in good accordance with

the calculated ratio  $w(\text{Ni}) : w(\text{Ce}) : w(\text{Sm}) = 5.0 : 4.6 : 1.0$ . The highest deviations were observed for the Ce-content determination, which was estimated to be too high and the Sm-content determination, which was estimated to be too low. The reason for the inaccurate Ce- and Sm-content determinations was probably a poor deconvolution of the overlapping peaks in the EDS spectra.

The EDS spectra of Sample 1 also exhibited a characteristic carbon peak, which made the absolute quantitative analysis unrealistic. The C peak was attributed to two origins; i) carbon was contained in the structure of the metal-organic intermediate in Sample 1, and ii) the characteristic C peak was partially a consequence of a sample contamination due to its exposure to air ( $\text{CO}_2$ ) before the analysis, as well as some cracking of the hydrocarbons in the vacuum system of the electron microscope under the electron beam.<sup>23</sup>

Sample 2 was obtained with the subsequent thermal treatment of Sample 1 without performing any other mechanical operation. Such a preparation path for Sample 2 also meant that the ECR for the metals should be the same as for Sample 1. However, the absolute

values of the Ni, Ce, Sm and O element contents should increase during the thermal treatment due to a mass loss when the metal-organic compound in Sample 1 was transformed into an oxide mixture of NiO and SDC.

After the thermal decomposition, the sample retained its degree of homogeneity (Figure 7). For that reason, the X-ray signals for the quantitative EDS analysis of Sample 2 were repeatedly collected from ROIs of approximately  $0.25 \text{ mm}^2$  in size (6–7 regions of interest on each field of view), similarly to the EDS analysis of Sample 1. Since the treatment at  $900 \text{ }^\circ\text{C}$  transformed the sample into a mixture of oxides, the summation of the Ni, Ce, Sm and O contents was normalized to 100%. The EDS spectra of Sample 2 also exhibited a characteristic C peak, which was attributed only to the sample contamination and subsequently entirely omitted in the quantitative calculations. The average absolute values for the Ni, Ce and Sm contents as obtained by the EDS measurements are given in Table 3. The errors were estimated on the basis of the variations of the data. The results of the quantitative EDS analysis of the Ni, Ce and Sm contents (38.7%, 39.7% and 7.0%, respectively) were in a relatively good agreement with the expected calculated values for Sample 2. However, due to the local inhomogeneity, the measured absolute values of the element contents may differ substantially between ROIs, resulting in a relatively high standard deviation ( $\pm 4.8\%$  for Ni). The calculated ECR for Sample 2 implied that the Sm content was again estimated too low.

The quantitative XRD phase analysis with the Rietveld method resulted in  $(48.3 \pm 3.0)\%$  of SDC and

**Table 3:** Results of metal mass fractions for Sample 2 obtained with different analytical methods

**Tabela 3:** Masni deleži treh kovin v vzorcu 2, določeni z različnimi analitskimi metodami

Used method	$w(\text{Ni})/\%$	$w(\text{Ce})/\%$	$w(\text{Sm})/\%$	$w(\text{Ni}) : w(\text{Ce}) : w(\text{Sm})$
Calculated value	38.2	34.7	7.6	5.0 : 4.6 : 1.0
Gravimetric method	$38.58 \pm 0.09$	/	/	/
Volumetric method	$36.8 \pm 0.2$	/	/	/
SEM-EDS	$38.7 \pm 4.8$	$39.7 \pm 4.1$	$7.0 \pm 1.5$	5.5 : 5.7 : 1.0
XRD	$40.6 \pm 3.0$	$32.9 \pm 3.0$	$7.2 \pm 2.0$	5.6 : 4.6 : 1.0
ICP-OES	37.4	36.5	7.6	4.9 : 4.8 : 1.0

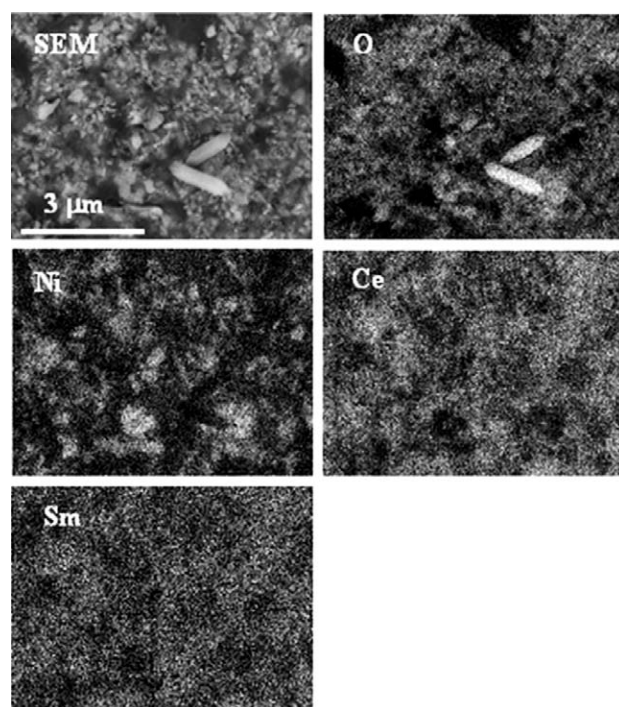
$w/\%$  – mass fraction,  $w/\%$  – masni delež

**Table 4:** Results of metal mass fractions for Sample 3 obtained with different analytical methods

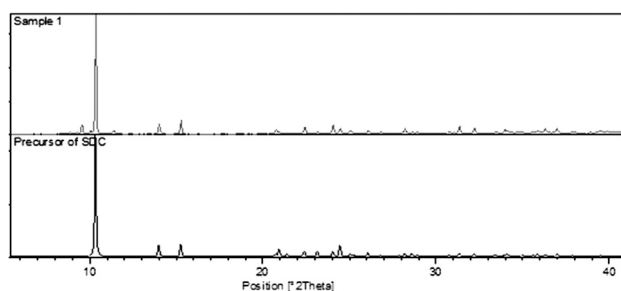
**Tabela 4:** Masni deleži treh kovin v vzorcu 3, določeni z različnimi analitskimi metodami

Used method	$w(\text{Ni})/\%$	$w(\text{Ce})/\%$	$w(\text{Sm})/\%$	$w(\text{Ni}) : w(\text{Ce}) : w(\text{Sm})$
Calculated value	38.2	34.7	7.6	5.0 : 4.6 : 1.0
Gravimetric method	$38.5 \pm 0.2$	/	/	/
Volumetric method	$36.45 \pm 0.09$	/	/	/
SEM-EDS	$37.6 \pm 2.3$	$38.9 \pm 2.1$	$7.0 \pm 0.7$	5.4 : 5.6 : 1.0
XRD	$40.3 \pm 2.0$	$33.1 \pm 2.0$	$7.3 \pm 2.0$	5.5 : 4.5 : 1.0
ICP-OES	38.0	36.7	7.5	5.1 : 4.9 : 1.0

$w/\%$  – mass fraction,  $w/\%$  – masni delež



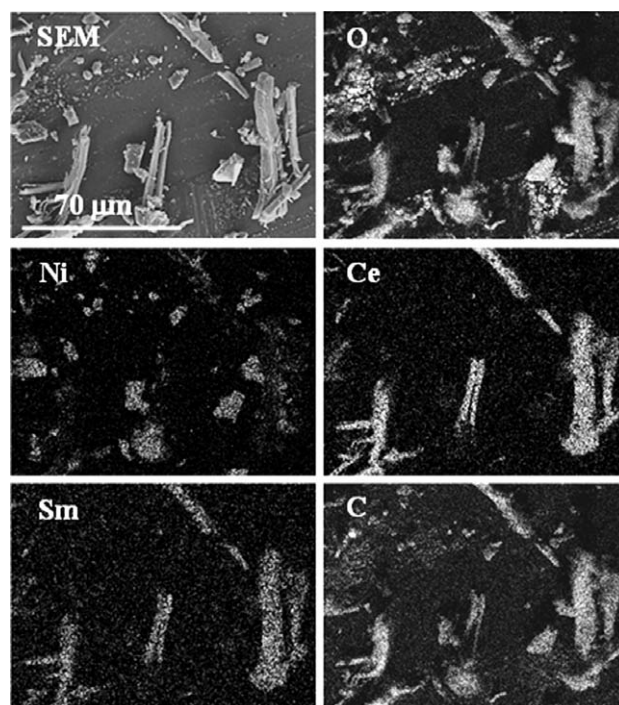
**Figure 5:** X-ray surface mapping of Sample 1  
**Slika 5:** Elementna porazdelitev vzorca 1



**Figure 6:** XRD patterns at low angles of Sample 1 (upper) and of pure precursor of SDC (bottom)

**Slika 6:** Rentgenski praškovni posnetek pri nizkih kotih: vzorec 1 (zgoraj), čisti prekurzor SDC-ja (spodaj)

( $51.7 \pm 3.0$ ) % of NiO. From these results, the mass fractions of the metals, given in **Table 3**, are calculated; they are close to the expected calculated values (within the experimental error). Sample 3 was prepared by attritor milling of Sample 2. Such milling results in an increased homogeneity of the sample. The region of the one-phase dominance (either a NiO or SDC phase) was estimated on the basis of the morphological characteristics of Sample 3 and expected to be in the sub-micrometer range. Collecting the X-ray spectra of Sample 3 and the subsequent calculations were performed identically to the previous analyses by investigating several ROIs (C was omitted in the quantitative calculations). According to **Table 4**, the consequence of the increased homogeneity in Sample 3 was reflected through a relatively accurate determination of the Ni and Ce contents with a much smaller deviation, practically halved in comparison to Sample 2. The key problem of processing the EDS spectra of the selected system still remains in the fact that the main Sm peaks overlap with the Ce peaks, resulting again in a too low Sm-content and a too high Ce-content estimation and thus making the EDS quantification heavily dependent on the method used to deconvolute the spectrum. The quantitative XRD phase analysis using the Rietveld method of Sample 3 resulted in ( $48.7 \pm 2.0$ ) % of SDC and ( $51.3 \pm 2.0$ ) % of NiO. From these results, the mass fractions of the metals, given in **Table 4**, were calculated, which were close to the expected calculated values (within the experimental error). It has to be emphasized that the Rietveld method gave us the mass fractions for NiO and SDC in the crystalline part of the sample. Consequently, in the case of the presence of a significant amount of an amorphous phase the resulted mass fractions may not be representative for the whole sample (especially if the metal content in the amorphous phase differs significantly in comparison to the crystalline part). Rietveld-refinement results also confirmed that Samples 2 and 3 contained only NiO and SDC with the desired compositions where the lattice parameter  $a$  for SDC is 0.543 2(1) and 0.543 3(1) nm,<sup>22</sup> respectively. The width of the reflections of Sample 3 was larger in comparison with those of Sample 2. Consequently, the crystallite-size parameters resulting



**Figure 7:** X-ray surface mapping of Sample 2

**Slika 7:** Elementna porazdelitev vzorca 2

from Rietveld refinement for both NiO and SDC were larger in Sample 2 than in Sample 3. This was evidently caused by the milling in the attritor. On the other hand, the milling of Sample 3 improved the fit between the calculated and measured curves (**Figures 1 and 2**) due to the grinding of larger grains.

The results of the ICP analysis depend on the treatment of the material before the analysis. This includes homogenization, weighing, dissolving and diluting.

Consequently, if the element contents in the samples submitted to the ICP analysis were higher than the recommended concentrations, multiple diluting was necessary, which eventually caused a deviation from the calculated values. Furthermore, the standard deviation of the ICP results for the analyzed samples could not be defined due to an insufficient number of the analysis repeats. Such repeats of the ICP analyses would have increased the costs.

#### 4 CONCLUSION

Based on various analytical approaches to the analyzed samples used in the process of the final-material development, the following conclusions can be drawn:

The gravimetry and volumetry methods are rather time-consuming showing fairly accurate values in the chosen concentration range; however, both methods can be used only for determining the Ni content. The gravimetry shows better results.

Although the topographies of the prepared samples were not ideal for an X-ray microanalysis, one of the

aims of this work was to demonstrate the feasibility of the quantitative EDS analysis of the selected system. While the Ni content could be determined accurately, the Sm content was generally estimated too low and the Ce content too high due to the overlapping of the Ce and Sm peaks, making the EDS quantification heavily dependent on the method used for deconvoluting the spectrum.

The XRD quantitative analysis using the Rietveld method gave us, in a fast, easy and relatively inexpensive way, the mass contents for all three metals that are in agreement with the expected calculated values within the experimental error. The standard deviations are comparable to those of SEM-EDS and higher in comparison with the volumetry or gravimetry. The advantage of this method was also that the effect of milling on the crystallite-size parameter could be observed and the qualitative-phase analysis checked. The disadvantages of this method are that it requires the knowledge of the structures of all the present crystalline phases and that the obtained mass contents may not be representative for the whole sample, when a significant amount of an amorphous phase is present in the sample.

The instrumental ICP-OES method may be considered to be accurate for all three samples. However, the possibility of an analytical error becomes greater if the concentration of the components is higher than 1 % due to the necessary sample dilution. In addition, ICP-OES is a rather costly method.

In general, to reliably determine the contents of all three metals, we recommend a combination of gravimetry with the alternative instrumental methods (ICP, SEM-EDS and XRD) that also determine cerium and samarium.

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