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A STUDY OF NICKEL ZIRCONIA COMPOSITE MATERIALS PREPARED BY GEL PRECIPITATION METHOD IN NONAQUEOUS MEDIA

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Dispersions of nickel in a ceramic support was made by gel precipitation method and hydrolysis of a mixture of nickel chloride and zirconium tetrachloride dissolved in methanol. The substitution methanol for water was made to obtain a reaction medium in which a better control over the hydrolysis and condensation reactions, and thus also a better control over the final properties of the composite material, could be obtained. The mixed precipitates were dried and calcined. Homogeneous dispersion, of nickel in the ceramic matrix were obtained by temperature programmed reduction. A study of the influence of reaction conditions and chemical compositions on the properties of the final products was made. Besides chemical analysis, BET method and particle size determination, the final products were characterised by conductivity measurements, XRD and SEM. High homogeneity of the products obtained in this process and their appropriate chemical composition assure good conductivity of the samples. Crystalization of the ceramic support changes with the chemical composition of the thermally treated mixed composite material.

1. *Introduction*

A composite such as nickel–zirconia can be prepared in several ways. The most frequently used process for the preparation of nickel dispersion in zirconia matrix is the subsequent deposition of nickel on the already formed zirconia. The degree of homogeneity of such composites can be improved by the simultaneous gel precipitation of both precursors needed for formation of the composite. Suitability of such processes for the preparation of nickel dispersion in zirconia was the objective of our work. These materials could be used for further preparation of the solid oxide fuel cell (SOFC) anodes.

The choice of the solvent in sol-gel processes has a substantial effect on the properties of the final product. The solvent plays an important role in the preparation of the gel, in addition to its role during thermal treatment. Methanol has a lower dielectric constant and smaller dipole moment than water. According to the theory (DLVO) Derjaguin, Landan, Verveg and Overbeek, the size of gel-precipitates can be greatly affected by the introduction of an organic solvent with a smaller dipole moment and lower dielectric constant and by changing the gelling conditions [1]. The size of the basic particles of gel-precipitate and their subsequent amalgamation greatly influence the stabilization of the crystal structure of the zirconium dioxide ceramic carrier [2]. The critical size of zirconium dioxide crystals, which enables stabilization of the thermodynamically-metastable tetragonal phase at room temperature, is approximately 3×10^{-22} cm^3. If the ZrO_2 particles are captured in a ceramic matrix which resists the volume change accompanying the phase transition from tetragonal to monoclinic (transformation toughening), the critical size of ZrO_2 crystals, enabling stabilization of the tetragonal structure, can be substantially increased [2]. In the NiO-ZrO_2 system the ZrO_2 particles are held in an NiO matrix. The suggested critical size for the transformation $t_{\mathrm{ZrO_2}} \rightarrow m_{\mathrm{ZrO_2}}$ is approximately 0.2 mm [4]. Crystallites exceeding the critical size for stabilization of the tetragonal structure, transform at room temperature into the thermodynamically–stable monoclinic forms. ZrO_2 crystallites, which do not exceed the critical size, retain their metastable tertragonal structure even at room temperature, due to the increased stability caused by higher surface energy [3]. The crystalline structure of zirconium dioxide is strongly affected by the addition of other stabilising oxides (e.g. magnesium, calcium, yttrium). Many oxides can be used to stabilise zirconium dioxide, providing the formation of solid solutions and that their cations have the required ionic radius [2].

Electrical conductivity of Ni-ZrO_2 composite materials is dependent on the content of nickel in the composite. If the nickel content is small, electrical conductivity of the composite is similar to that of the ceramic matrix. With a high nickel content, electrical conductivity of the composite is closer to that of metallic nickel. The change in mechanism occurs at 30 to 40 vol % of Ni in the composite Ni-ZrO_2 material [5].

2. Experimental

Zirconium and nickel were precipitated from the methanol solutions by the gel coprecipitation method. The starting solutions of the metal clorides were prepared by dissolving 38 g of $NiCl_2 \times 6H_2O$ (Kemika Zagreb, p.a.) and the corresponding amount of $ZrCl_4$ (Fluka, assay > 98%) in 400 ml of methanol, to which a twofold stoichiometric excess of water necessary for the reaction was added. A hydrolysis reaction was initiated by the introduction of gaseous ammonia (flow rate 3.88 l h^{-1}). The product was filtered off, washed with distilled water and dried for six hours at 120 °C. The dried samples were milled in a ball mill and then further thermally treated (e.g. calcination and temperature programmed reduction-TPR in a dynamic atmosphere of 4 vol% of hydrogen and 96 vol% of argon).

The amount of nickel in the samples was determined by volumetric method. The particle size distribution of the precipitates was determined by laser beam diffraction on a Fritsch Analysette 22 apparatus. Scanning electron microscopy (Jeol T-300 microscope) and specific surface area determination by BETT method and Ströhlein area meter were used for further characterisation of the samples. Samples for SEM were heat pre-treated, i.e. calcined at 500 °C and TPR at 500 °C, compressed into a tablet, and sintered at 1200 °C in a dynamic reductive atmosphere (4 vol% H_2 and 96 vol% Ar by vol.). The thermally treated samples were also characterised by X–ray powder diffraction using Philips PW-1710 instrument (30 mA, 40 kV and Cu-K_α radiation) and a Guinier de Wolf camera. CD-rom database PDF, sets 1-42, was used for the identification of samples. AC impedance measurements were made using an impedance analyser (Hewlett Packard 4284A) over the frequency range from 20Hz to 1MHz at 1000 °C in a dynamic reductive atmosphere (4 vol% H2 and 96 vol% Ar).

3. Results and discussion

Gel coprecipitation from solution is one of the possible techniques for the preparation of mixed oxides. Several parameters, such as pH, mixing rates, temperature and concentration have to be controlled to produce satisfactory products. However, it is very hard to prepare completely homogeneous products because of different rates of precipitation of components [6,7].

In our coprecipitation experiments in methanol solutions, the gel precipitation of zirconia overtakes the precipitation of nickel hydroxide. The pH of the suspension rises very rapidly within the range of pH values at which the precipitation of both gels is most intensive. Formation of the hydrated zirconia gel is not finished yet at the point when precipitation of nickel hydroxide begins. The gel of hydrated zirconia is a very voluminous 3D network with ample space inside the structure. Nickel hydroxide precipitates inside this 3D framework give spatially very uniform dispersions. Upon syneresis, drying and further thermal treatment of the mixed product, the fine dispersion of nickel is preserved.

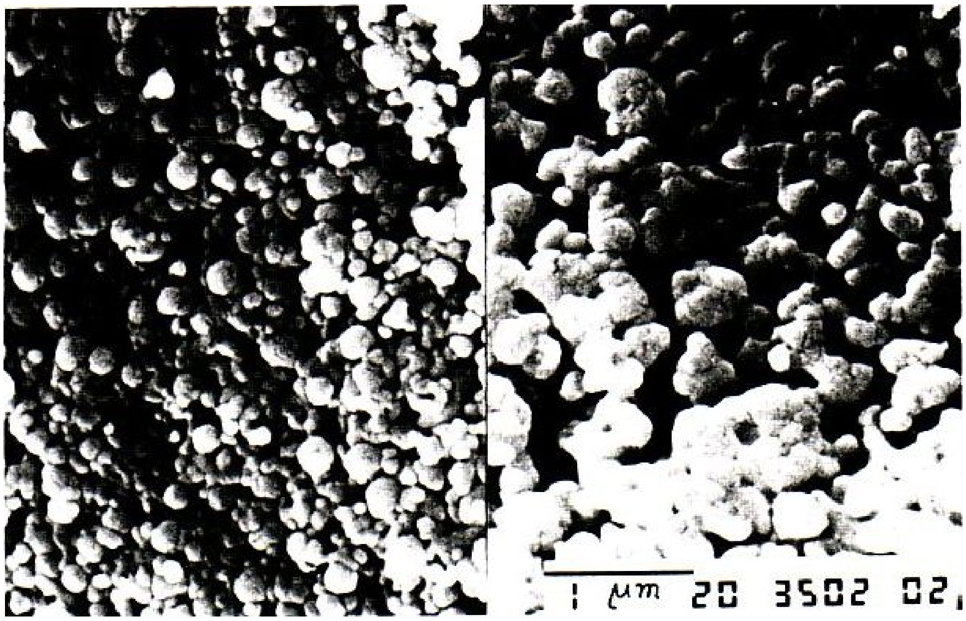


Fig. 1a. SEM of surface of NiZ5 sample (40.39vol % of Ni*)*

Fig. 1b. SEM of surface of NiZ5 sample after etching with HCl *(right).*

SEM micrographs of the NiZ5 sample with 40 vol% of Ni by vol. in ZrO_2 matrix, after heat treatment, reduction and sintering (Figs. 1 and 2), show the homogeneity or heterogeneity of nickel dispersion in Ni-ZrO_2 composite materials at the microscopic level. Figure 1 shows the surface of the compressed and sintered sample tablet (Fig. 1a), and the surface of an identical sample previously etched with HCl (Fig.1b). Figure 2 shows a fracture in the NiZ5 sample tablet (Fig. 2a) and a fracture in the etched sample (Fig. 2b). Both images show the nickel dispersion in the ceramic matrix to be relatively homogeneous, although there are microscopic areas where one or the other phase is dominant. The distribution of the zirconium oxide phase in the composite material can be seen in Figs. 1b and 2b. The zirconium oxide forms a three-dimensional voluminous skeletal structure inside which nickel hydroxide precipitates. The nickel hydroxide then reacts to form nickel particles after thermal treatment. During sintering, the zirconium oxide skeletal structure restricts the formation of excessively large nickel grains, preserving the nickel dispersion within the ceramic structure. Microstructural properties, such as distribution of nickel in the composite material, porosity, size of the grains, and, even more importantly, the assurance of contact between nickel particles, all contribute to the suitability of Ni-ZrO_2 composites for the application in the manufacture of SOFC anodes.

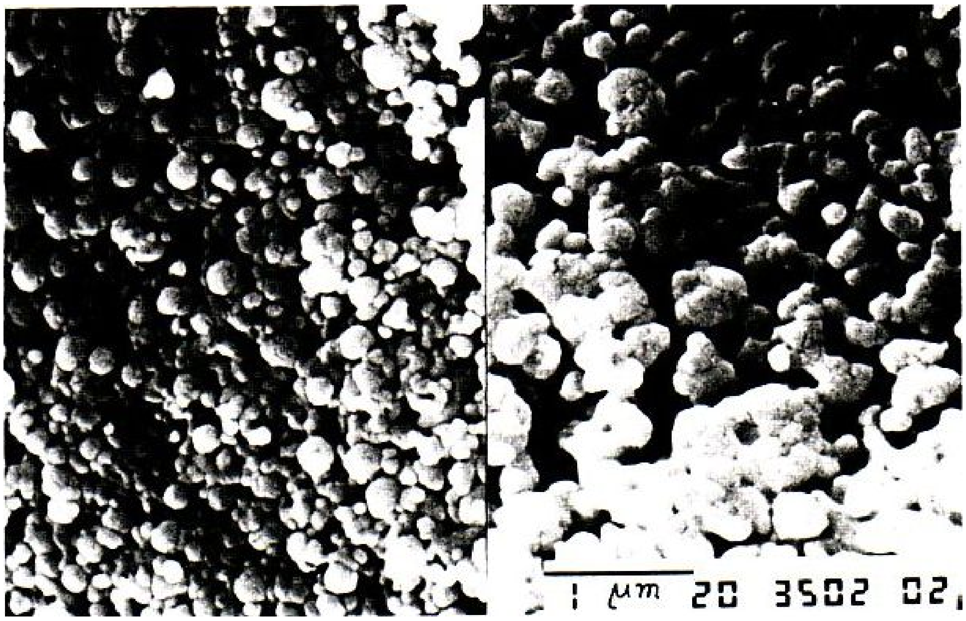


Fig. 2a. SEM of cross section of NiZ5 sample (40.39vol % of Ni*).*

Fig. 2b. SEM of cross section of NiZ5 sample after etching with HCl *(right).*

The crystalline structure of the phases of the composite material was determined by X–ray powder diffraction. The compositions of the composite materials and the effects of thermal treatment on the stability of the crystalline structure of zirconium oxide are shown in Table 1. The X-ray diffraction pattern of sample NiZ0 (Fig. 3) after thermal treatment (calcination and TPR at 500 °C), shows the formation of metastable tetragonal and thermodynamically-stable monoclinic crystalline ZrO_2. As nickel and zirconium oxide do not form stable mixtures essential for ZrO_2 stabilization, and monoclinic ZrO_2 is stable at higher temperatures (samples NiZ1 and NiZ2), the presence of the tetragonal phase at lower temperatures is probably a result of the crystalline arrangement of hydrated zirconium gels. Crystallization of amorphous zirconium gels occurs due to the low surface energy in the first step, via the metastable tetragonal structure [8]. At higher temperatures, or after prolonged thermal treatment, the tetragonal form of ZrO_2 transforms into a thermodynamically-stable monoclinic form.

In contrast, the X–ray diffraction patterns of calcined, non-reduced NiOZ samples (Fig. 3) show the presence of tetragonal ZrO_2 throughout the entire temperature range between 500 °C and 1200 °C. Although the solubility of nickel oxide in zirconium oxide is too low for the preparation of partially stabilized zirconia (PSZ), some of the ZrO_2 particles crystallize in a tetragonal structure. The reason for the existence of this partially-stabilized tetragonal ZrO_2 is the formation of zirconia dispersed ceramic (ZDC) [4], i.e. zirconium oxide grains smaller than the critical size for stabilization of the tetragonal structure that forced by the nickel oxide matrix to retain the tetragonal structure. Such grains, usually formed inside the nickel oxide grains, are not in contact with neighbouring zirconium oxide grains. This restricts their capacity for growth and prevents them exceeding the critical size for stabilization of the tetragonal structure. In contrast, ZrO_2 particles forming a continuous zirconium phase or located on the boundaries between NiO particles, which are able to grow during sintering, crystallize in a monoclinic form after prolonged thermal treatment. In the example from this study, only some of the zirconium oxide had a tetragonal structure, indicating that only some of the zirconium oxide crystallized inside the nickel oxide grains. The ZrO_2 grains which grow during the sintering process (which is indicated by the relative shrinkage of the NiOZ samples) lose their tetragonal structure.

TABLE 1.
Shrinkage and phases of ZrO_2 *obtained after thermal treatment.*

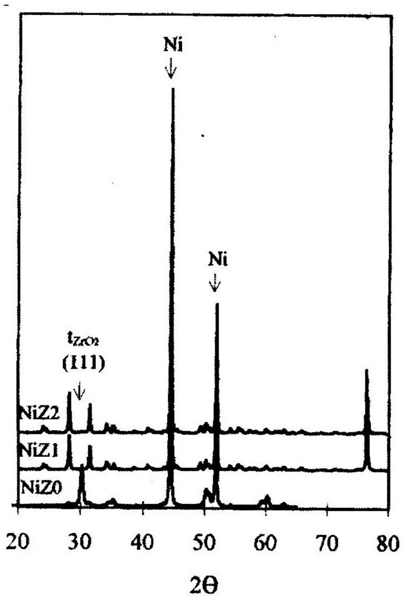
Sample	Molar ratio	Firing conditions	Shrinkage ($\Delta L/L$) [%]	Phases ZrO_2 obtained
NiZ0	Ni/ZrO_2=3.92	500 °C, 1h		m+t
NiZ1	Ni/ZrO_2=3.92	1200 °C, 2h	21.31	m
NiZ2	Ni/ZrO_2=3.92	1200 °C, 4h	24.53	m
NiOZ0	NiO/ZrO_2=3.92	500 °C, 1h		m+t
NiOZ1	NiO/ZrO_2=3.92	1200 °C, 2h	11.29	m+t
NiOZ2	NiO/ZrO_2=3.92	1200 °C, 4h	13.57	m+t

m = monoclinic ZrO_2, t = tetragonal ZrO_2.

A comparison of the relative shrinkage, which increases with the sintering temperatures of the tablets, indicates that contraction is more pronounced in the case of NiZ composite materials (Table 1). In this case the sintering of the nickel phase (after prior reduction) produces greater contraction of the tablet samples at 1200 °C. Contraction of non-reduced samples at the same temperature is less smaller because the sintering of nickel oxide occurs at much higher temperatures than the sintering of nickel. However, nickel oxide is sufficiently volatile at temperatures above 1100 °C, to enable mass transport within NiOZ samples [4]. Contraction of NiOZ samples at 1200 °C is, therefore, the result of the sintering of the zirconium phase and the transport of nickel oxide in the gaseous phase. The volatility and subsequent mass transport of nickel oxide at the temperatures of the thermal treatment make a crucial contribution to the formation of ZDC the formation of the nickel oxide matrix in which zirconium oxide particles are trapped, and by this the partial retainment of the tetragonal zirconium phase.

TABLE 2.
Nickel content, preparation conditions of samples destined for impedance measurements and characteristic values of spec. electric. conductivity at 1000 °C.

Sample	Firing conditions	Nickel content in Ni-ZrO_2 (vol%)	Spec. electric. conductivity $\log \sigma$ (Scm^{-1}) at 1000 °C
NiZ3	1200 °C, 1h	23.23	-4.01
NiZ4	1200 °C, 1h	27.58	-3.89
NiZ5	1200 °C, 1h	40.39	-1.17
NiZ6	1200 °C, 1h	54.93	-0.99
NiZ7	1200 °C, 4h	40.39	-0.11



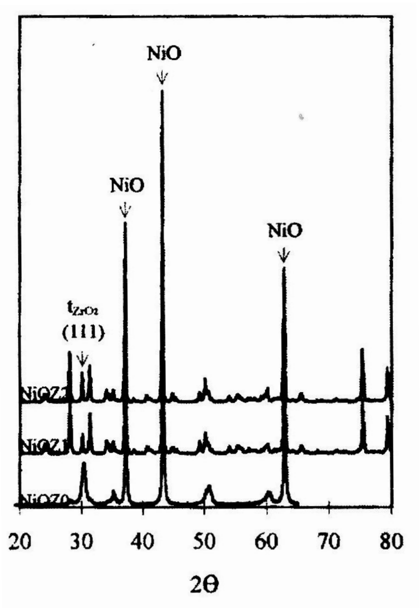
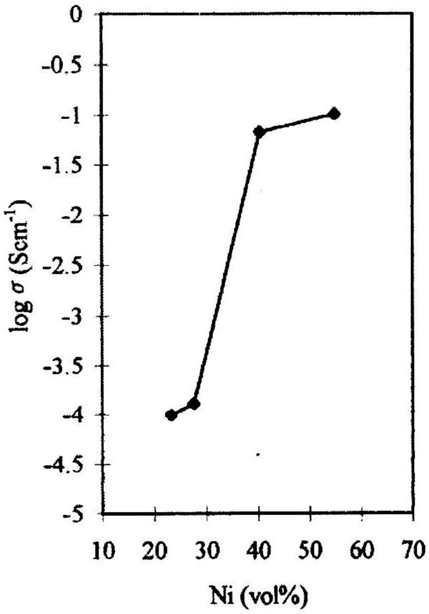


Fig. 3. X-ray diffraction patterns of NiZ samples.

Fig. 4. X-ray diffraction patterns of NiOZ samples (right).

Electrical properties of Ni-ZrO_2 in the composite materials were measured by the AC impedance method. The compositions of samples and conditions of their preparation of samples destined for impedance measurements are shown in Table 2. The electrical properties of composite materials depend mainly on microstructural properties, such as porosity, distribution of the nickel phase, size of the grains and degree of contact between nickel grains [5]. Microstructural properties can be influenced during the preparation of the composite materials (e.g., by changing the gel precipitation conditions [7] or at a later stage by thermal treatment of the composite material). The effect of nickel content on electrical conductivity of Ni-

ZrO_2 composites is shown in Fig 5. Drastic changes of values were obtained with 30% to 35 vol% of nickel by vol. in the composite material. Electrical conductivity of samples at 1000 °C of samples with a nickel content lower than 27% by vol. was a factor of 10^4 greater than that of Ni-ZrO_2 cermets in which the nickel content exceeded 40 % by vol. Electrical conductivity of Ni-ZrO_2 cermets with a low nickel content is similar to the electrical conductivity of the pure ZrO_2 carrier. Only at above 40% Ni by vol. does the electrical conductivity of the composite approach the values of pure Ni. The differences in the values of electrical conductivity depend on the manner of current flow through the composite material. In the case where nickel particles are not in contact, i.e. where the nickel phase is discontinuous throughout the sample, ionic conduction of electric current through the sample is dominant, hence the high resistivity. Metallic conduction of electric current through Ni-ZrO_2 composite materials dominates in cases when the nickel content is large enough to assure contact between nickel particles and thus a continuous nickel phase (Figs. 1 and 2).



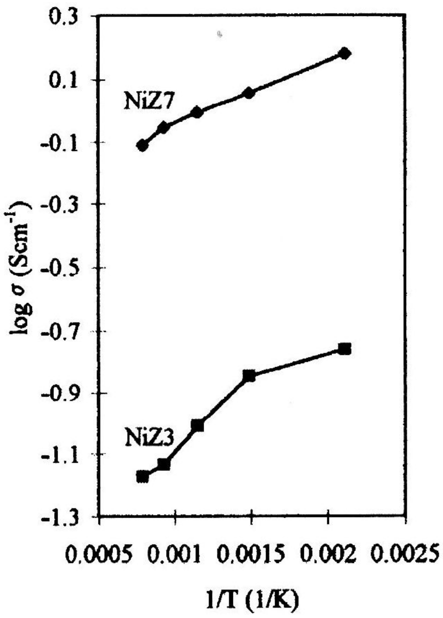


Fig. 5. Effect of Ni *content on specific electrical conductivity of* Ni-ZrO_2 *cermets at 1000* °C.

Fig. 6. Arrhenius plots of Ni-ZrO_2 *cermets prepared at different firing conditions (right).*

Electrical properties of Ni-ZrO_2 composite materials change considerably with the temperature of the thermal treatment. The dependence of the specific conductivity σ on the temperature of thermal treatment of the samples is shown in Fig. 6. A longer period of thermal treatment at 1200 °C reduces resistivity and increases the specific electrical conductivity of the samples. The change in conductivity caused by thermal treatment is the result of changes in the microstructural properties of the cermet. With prolonged thermal treatment, the contraction of composite materials is greater, and sintering is more pronounced (Table 1). Sintering of the nickel phase increases the contact between nickel particles, forming a continuous nickel phase and opening the possibility for metallic conduction of electric current. Grain growth and increased contact between nickel particles lowers the grain boundary resistivity, a phenomenon occurring at the boundary between neighbouring grains. The creation of excessively-large nickel grains during the sintering process and corresponding loss of porosity, and the reduction of the number of active nickel sites is prevented by the ZrO_2 ceramic matrix.

4. Conclusion

The Ni-ZrO_2 composite materials were prepared by the gel precipitate method. Despite differences in pH values and the speed of precipitation of nickel hydroxide and hydrated zirconium oxide, the samples show a high level of homogeneity after thermal treatment. Areas of dominance of zirconium or nickel phases are limited to the microscopic level. Crystallization of the zirconium phase in Ni-ZrO_2 composite materials is achieved via a thermodynamically-metastable tetragonal structure which after time or with increased temperature with increased heat transforms into a thermodynamically-stable monoclinic form. In contrast, ZDC formation in Ni-ZrO_2 composite materials causes some of the ZrO_2 to crystallize in the tetragonal form throughout the temperature range between 500 and 1200 °C. A condition of ZDC formation is the crystallization of zirconium oxide particles inside the nickel oxide matrix, which prevents their growth during the contraction process. Electrical properties of the cermets prepared largely depend on the method of preparation used and on the nickel content of the composite. Metallic conduction of electric current was found in samples in which the nickel content exceeded 40% by vol. Similarly, the resistivity of composite materials is reduced by prolonged thermal treatment. The increase of conductivity after prolonged thermal treatment of cermets is mainly a result of sintering of the nickel phase, which increases contact between nickel particles. The microstructural and electrical properties of the Ni-ZrO_2 cermets prepared also indicate that these composite materials are suitable for the application in the manufacture of SOFC anodes.

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PROUČAVANJE KOMPOZITNIH MATERIJALA Ni-ZrO_2 PRIPREMLJENIH GEL PRECIPITACIJOM U NEVODENIM OTOPINAMA

Disperzija nikla u keramičkoj strukturi načinjena je gel precipitacijom i hidrolizom otopine nikal klorida i cirkonij tetraklorida u metanolu. Metanol je odabran umjesto vode radi bolje kontrole hidrolize i kondenzacijskih reakcija. Precipitati su sušeni i kalcinirani. Homogena disperzija nikla u keramičkoj matrici postignuta je redukcijom uz programiranu temperaturu. Načinjene su kemijske analize i određivanje veličine zrna, a za keramički materijal načinjena su mjerenja vodljivosti, rendgenska difrakcija i skaniranje u elektronskom mikroskopu.