THE PREPARATION OF NICKEL/ZIRCONIA DISPERSIONS FROM NICKEL HYDROXIDE/HYDROUS ZIRCONIUM OXIDE GEL-PRECIPITATE PRECURSORS: INFLUENCE OF THE REACTION CONDITIONS ON THE CHARACTERISTICS

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Abstract: Dispersions of nickel in a zirconia ceramic matrix were prepared by the gel-precipitation method from a methanol solution and subsequent thermal treatment (drying, calcination and TPR). Substituting methanol for water and using gaseous ammonia for initiation of gelation provides a reaction medium in which the system of hydrolysis reactions and above all condensation reactions can be controlled to a large degree. A study is made of the influence of the reaction conditions, temperature and final pH of the reaction mixture on the composition and characteristics of the composite materials. Well defined dispersions of nickel in zirconia matrix could be obtained in this way.

Priprava disperzij nikelj/cirkonijev dioksid z gel-precipitacijo nikljevega hidroksida in hidratiziranega cirkonijevega oksida: vpliv reakcijskih pogojev na karakteristike

Povzetek: Disperzije niklja v keramični matrici cirkonijevega dioksida so bile pripravljene z uporabo gel-precipitacijske metode iz metanolnih raztopin in kasnejše termične obdelave (sušenje, kalcinacija in TPR). Zamenjava vode z metanolom kot reakcijskim medijem in uporaba plinastega amoniaka za sprožtev hidroliznih in kondenzacijskih reakcij zagotovi reakcijski medij, v katerem lahko v večji meri kontroliramo potek hidroliznih in predvsem kondenzacijskih reakcij. Namen prispevka je študij vpliva reakcijskih pogojev (temperature in končne pH vrednosti reakcijske mešanice) na karakteristike končnih kompozitnih materialov. Z uporabo gel-precipitacijske metode lahko pripravimo homogene disperzije niklja v matrici cirkonijevega dioksida.

Introduction

The reaction medium has a significant effect on the course of the gel-precipitation and the properties of the end product. Although accepted as a standard reaction medium, water restricts the reaction conditions to its physico-chemical properties. Solvation reactions can be modified substantially if water is replaced by other in particular organic media such as methanol. This alcohol has a lower dielectric constant and dipole moment than water ($\varepsilon_{MeOH}^{25°C} = 32.6$, $\varepsilon_{H2O}^{25°C} = 78.5$, $\mu_{MeOH} = 1.70$, $\mu_{H2O} = 1.84$), so that the influence of the electrostatic potential in methanol is consequently greater /1,2/. The dipole moment of the solvent or reaction medium determines the range of the influence of the individual sol particles on the neighboring particles. In this way the electrostatic double layer of the sol and so the sol coagulation process are affected. One of the major problems concerning the sol-gel processes is the reproduction and the reliability of the results obtained. Thus, the study of hydrolysis and condensation reactions can be very helpful to set-up the appropriate reaction conditions in preparing composite materials with well defined final microstructural and morphological properties.

Zirconium oxide and its solid solutions are materials of current scientific and technological interest. They find application in various fields of materials science such as high technology ceramics and ionic conductors /3/. Recently it became clear that non-equilibrium and metastable phases, prepared by decomposing hydrous zirconium oxide at temperatures below 1000 K, might also be of great interest, for instance, to find new func-

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tional materials in heterogeneous catalysis /4/. A composite such as nickel - zirconia can be prepared in several ways. The most used and reported process for the preparation of nickel dispersion in zirconia matrix is the subsequent deposition of nickel on the already formed zirconia /5-7/. The degree of homogeneity of such composites can be enhanced by the simultaneous gel precipitation of both precursors needed for composite formation /8/. Suitability of such processes for the preparation of nickel dispersions in zirconia matrix was the objective of our work. We also investigated the effect of the Ni^{2+} ions on some solid-state properties of zirconia, such as crystallization and thermal behavior. These materials could be used for further preparation of solid oxide fuel cell (SOFC) anodes.

Experimental

By the gel-coprecipitation method zirconium and nickel were precipitated from the water or methanol solutions. The starting solutions of the metal chlorides were prepared by dissolving 38 g of $NiCl_2 \cdot 6H_2O$ tetrachloride (Kemika Zagreb, p.a.) and the corresponding amount of $ZrCl_4$ (Fluka, assay >98%) in 400 ml of water or 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 lh^{-1}) through a glass frite into the solution of metal chlorides. This solution was vigorously agitated by a pitched-blade turbine ($\approx$ 2000 revsmin^{-1}).

The introduction of ammonia initiates hydrolysis of the reaction mixture and precipitation of the hydrated zirconia and nickel hydroxide. The product was filtered and washed with distilled water until no reaction on chloride ions was observed ($AgNO_3$ test). In cases of a final pH of 7, the chloride ions cannot be washed out completely. The precipitate was dried for six hours at 120°C. The dried sample was milled in a ball mill and calcined for two hours at 500°C in air flow (18 lh^{-1}). After calcination, temperature programmed reduction (TPR) in a dynamic atmosphere of 4 vol% hydrogen and 96 vol% argon with a flow rate of 18 lh-1 was used for the reduction of nickel. A tube furnace, a heating rate of 5 Kmin-1, a final temperature of 500°C and thermostating for two hours at this temperature were used. The samples were cooled down in the same atmosphere.

The amount of nickel in the samples was determined by the volumetric method and by atomic absorption spectroscopy using a Perkin Elmer Zeeman 5100 apparatus. The particle size distribution of the precipitates was determined by laser beam diffraction on a Fritsch Analysette 22 apparatus. Auger Electron Spectroscopy (AES) depth profiling was performed on a PHI SAM 545 A analyser using electron static beam of primary electrons (3 keV, 0.5 mA and 40 μm in diameter). The sample was etched with Ar+ ions at an incident angle of 47° and etching rate of 2 nmmin-1. The thermal properties of the samples and the temperature of the crystal structure transformations were determined using a Netsch 409 STA thermoanalyser. Scanning electron microscopy (Jeol T-300 microscope) and specific sur-

face area determination by the BET method and Ströhlein area meter were used for further characterization of the samples.

The thermally treated samples were also characterized by X-ray powder diffraction using a Philips PW-1710 instrument (30 mA, 40 kV in Cu-Kα radiation) and a Guinier de Wolff camera. The PDF CD-ROM database, sets 1-42, was used for the identification of samples.

Results and Discussion

Nickel dispersions in a ceramic matrix can be prepared either by separate formation of nickel and ceramic powders and their subsequent homogenization, by impregnation of zirconia powder by nickel, or by coprecipita- tion of nickel and ceramic precursors followed by appropriate thermal treatment and reduction. Our research was focused on the formation of nickel dispersions in a zirconia matrix by gel-coprecipitation. This method is attractive inasmuch as it reduces the number of operations required and yields a product with a high degree of homogeneity. A nonaqueous solvent, namely methanol, was used for the experiments besides water, in order to control the precipitation and gel formation reactions better.

A major difficulty in coprecipitation reactions of binary cation systems is the difference in precipitation rates of precipitation of both cations especially when they differ appreciably, as is the case of nickel and zirconium cations. In addition to the discrepancy in hydrolysis rates, the polymerization reactions of the two species also differ.

The course of coprecipitation of nickel hydroxide and hydrated zirconium oxide was followed by atomic absorption spectroscopy (AAS). The results of progress of hydrolysis reaction followed by AAS are summarised in Table 1. Precipitation of nickel hydroxide slightly lags behind that of hydrated zirconium oxide. The pH of the suspension rises very rapidly within the range of pH values at which precipitation of both gels is most intense, so that the two gel-precipitates overlap in their formation. Although, by terminating the flow of ammonia into the reaction mixture the reactions did not stop completely but nevertheless the results of AAS measurements show that precipitation of zirconia overtakes the precipitation of nickel hydroxide. The concentrations of the two cations change very little up to pH value 3. Between pH 3 and 4, condensation reactions take place and formation of the gel-precipitate of hydrated zirconium oxide occurs, /9,11,13,14,17/ while polymerization should be complete at pH 9 /16/. Nickel precipitates at pH>7 as $Ni(OH)_2$. With an excess of the precipitating reagent a soluble hexaamino complex of nickel is formed($[Ni(NH_3)_6]Cl_2$), which lowers the nickel content in the product /12/. In all cases the highest nickel content in the ceramic matrix was obtained at pH 8.

At higher pH values the results obtained in methanol differ greatly from those obtained in water. The solubility of the nickel hexaamino complex is appreciably lower

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in this reaction medium than in water, so that at higher pH values the nickel concentration in the reaction medium decreases further and the nickel content of the product correspondingly increases. Washing the product in water can redissolve part of the nickel thus precipitated.

It was expected from the start of experimentation that completely homogenous products could not be obtained by coprecipitation processes. The precipitation of hydrated zirconia begins at lower pH values and furthermore takes place at different rates as the precipitation of nickel hydroxide. In these precipitation experiments hydrated zirconium oxide and nickel hydroxide are obtained. Because the zirconium precipitation begins earlier, the nuclei and also the centers of the precipitated particles should be composed to a larger extend of hydrated zirconium oxide and the outer layers of nickel hydroxide. Between these two extremes a zone of intermediate composition should exist. However, the inhomogeneity of dominance of zirconium or nickel phase are limited to the microscopic level as it was confirmed by the Auger and SEM analysis (Figures 1 and 2).

Table 1: Results of precipitation reactions as followed by AAS

Sample	pH	Zr^{4+} [gl^{-1}]	Ni^{2+} [gl^{-1}]
A1	1.0	12.50	17.41
A2	4.0	10.50	17.21
A3	5.0	<100 ppm	17.20
A4	6.0	<100 ppm	16.09
A5	8.0	<100 ppm	11.55
A6	10.0	<100 ppm	13.94
B1	1.0	12.50	17.63
B2	3.0	12.25	17.61
B3	4.0	<100 ppm	17.58
B4	6.0	<100 ppm	15.26
B5	7.0	<100 ppm	8.07
B6	8.0	<100 ppm	0.45
B7	10.0	<100 ppm	<100 ppm

* A samples were prepared from aqueous solution

* B samples were prepared from methanol solution with an addition of twofold stoichiometric amount of water needed for the hydrolysis reaction

The etching of the pressed tablets of the coprecipitated product during the Auger analysis reveals rather uniform composition in both cations although the etching depth was 120 nm that is deeper than the average particle diameter. The deviation from the average con-
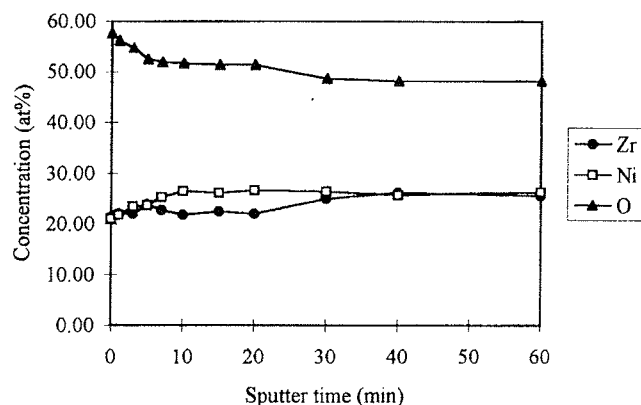

Fig. 1: AES composition - depth profile of C10ZrN83.16 sample (36.68 wt% of Ni and 63.32 wt% of zirconia)

centration is for zirconium and nickel at most 2,36 at. %. The reason for mentioned results could be, that in gel precipitation reactions we should not adhere to the standard theories of precipitate formation. The gel of hydrated zirconia is a very voluminous 3D network with ample space inside the structure for the remaining reaction mixture. Nickel hydroxide precipitates inside this 3D framework as well as on the already formed surface area of the hydrated zirconia giving spatially very uniform dispersions. Upon syneresis and drying of the gel this fine dispersion of nickel is preserved.

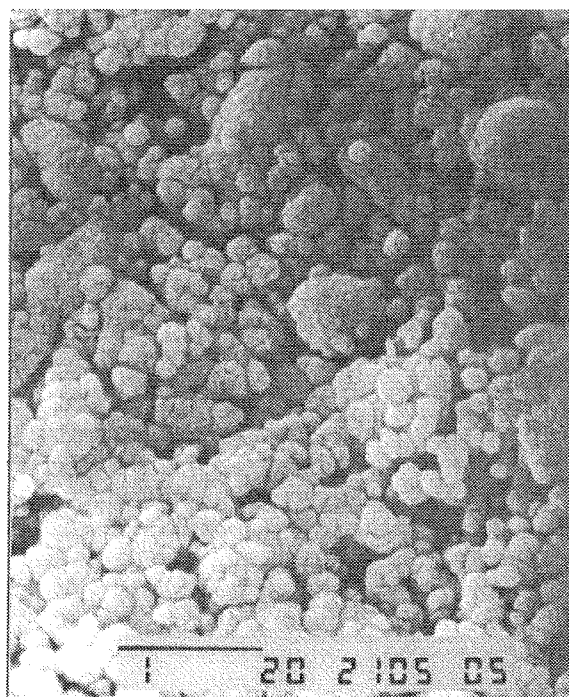SEM micrographs of the C10ZrN88.44 sample with 40.18 vol% nickel in ZrO2 matrix after heat treatment,

Fig. 2a: SEM surface of C10ZrN88.44 sample (40.18% of Ni)

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reduction and sintering show the homogeneity or heterogeneity of nickel dispersion in Ni-ZrO$_2$ composite materials at the microscopic level. Figure 2 shows a fracture in the C10ZrN8$_{8.44}$ 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.
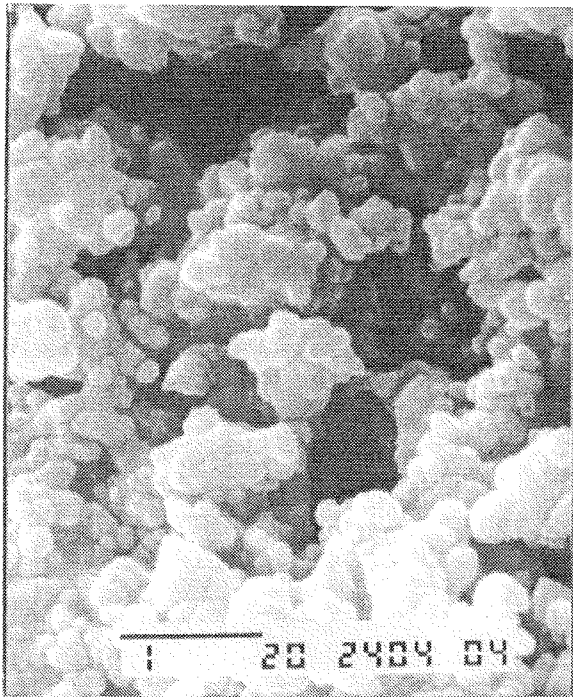

Fig. 2b: Surface of C10ZrN8$_{8.44}$ sample after etching with HCl

The particle size and distribution affect the possible application of these cermets since they influence also the specific surface, porosity, density, etc. of the fired products. The characteristics of the intermediate gel-precipitate can be changed to a degree by the reaction conditions and therefore the influence of reaction conditions, i.e. pH and temperature and the mixing rate, on the size of the precipitates was studied (Table 2). The mixing rate was throughout all experiments kept constant in order to minimise its influence on the particle size by breaking the gel into smaller particles. Higher pH values of the reaction mixture and higher temperatures lead to precipitates of lower mean particle size.

The pH of the reaction medium can influence the reaction and the product through changes in reaction kinetics and by changing the charge of the particles in the solution. Up to pH 7 the reactions proceed in a similar way in all cases. Hydrolysis that is highly sensitive to the pH of the reaction medium is assumed to be completed before this pH value is attained. The stages subsequent to the hydrolysis reaction, i.e. gelation, aging and possibly agglomeration of the precipitate, influence particle size even more strongly. Being faster

in alkaline media, the aging process in particular favors smaller agglomerate sizes that agrees with the results. Like the mean particle size, the standard deviation falls as temperature and pH increase, leading to a narrower distribution of particle sizes.

Table 2: Nickel content, mean agglomerate size and standard deviation, as a function of temperature and pH of the reaction mixture

Sample	Gel-precipitation		Composite		
	Temperature (°C)	Final pH	Ni content (wt%)	d (μm)	σ (μm)
A10ZrN7	10	7	9.71	27.99	14.68
A10ZrN8	10	8	27.57	23.71	12.80
A10ZrN9	10	9	24.94	20.44	12.45
A10ZrN10	10	10	18.58	17.10	9.43
A20ZrN7	20	7	9.51	22.98	12.03
A20ZrN8	20	8	26.84	18.10	9.59
A20ZrN9	20	9	24.22	16.25	8.42
A20ZrN10	20	10	18.30	13.16	7.64
A30ZrN7	30	7	9.09	20.66	10.30
A30ZrN8	30	8	23.38	16.48	8.92
A30ZrN9	30	9	20.67	11.99	7.47
A30ZrN10	30	10	16.93	9.21	6.58
B10ZrN7	10	7	24.34	23.38	10.56
B10ZrN7.7	10	7.5	25.29	19.52	9.71
B10ZrN8	10	8	31.52	17.74	8.54
B10ZrN8.5	10	8.5	30.63	16.71	9.32
B10ZrN9	10	9	29.55	16.11	9.13
B10ZrN10	10	10	28.00	12.16	6.87

* A series samples were prepared from aqueous solution

* B series samples were prepared from methanol solution with an addition of twofold stoichiometric amount of water needed for the hydrolysis reaction

The mean agglomerate size of the gel-precipitation obtained in methanol is greater than in an aqueous medium under the same conditions. This accords with the mentioned interaction of the charged sol species in the solvent with a lower dielectric constant and smaller dipole moment. Since the gelation-precipitation system is bimodal, not only the major constituent, i.e. the zirconia precursors, but also the presence of nickel hydroxide in the product has a large influence on the

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course of the reaction (table 3). A higher initial Ni^{2+}/Zr^{4+} ratio influences the amount of nickel in the precipitate as well as the mean particle size, which diminishes with higher initial ratio of metals.

Table 3: *Nickel content in the ceramic matrix, mean particle size of the precipitate, standard deviation and specific surface area as a function of the initial Ni^{2+}/Zr^{4+} molar ratio*

| Sample | Initial | | | Composite | |
	Ni^2/Zr^{4+} ratio	Ni (wt%)	d (μm)	σ (μm)	Spec. surf. area (m^2g^{-1})
C10ZrN8$_0$	0	0	19.69	8.79	71
B10ZrN8	2.04	31.52	17.74	8.54	55
C10ZrN8$_{3.16}$	3.16	36.68	17.20	8.40	51
C10ZrN8$_{4.94}$	4.94	41.82	15.71	9.32	48
C10ZrN8$_{8.44}$	8.44	50.76	12.23	5.07	47
C10ZrN8$_{27.22}$	27.22	75.98	10.26	7.11	33
C10ZrN8$_\infty$	∞	99.13	3.48	1.46	19

* all samples were prepared from methanol solutions at 10°C with an addition of twofold stehiometric amount of water, final pH value of 8 and calcination in air at 500°C for two hours followed by TPR to 500°C

The relation between various parameters of the system under observation is given in Figures 3 and 4 according to mathematical correlation of the results. Correlation equations were derived for the samples obtained from methanol solutions at a constant pH value of 8 or at a constant initial Ni^{2+}/Zr^{4+} molar ratio of 2.04.
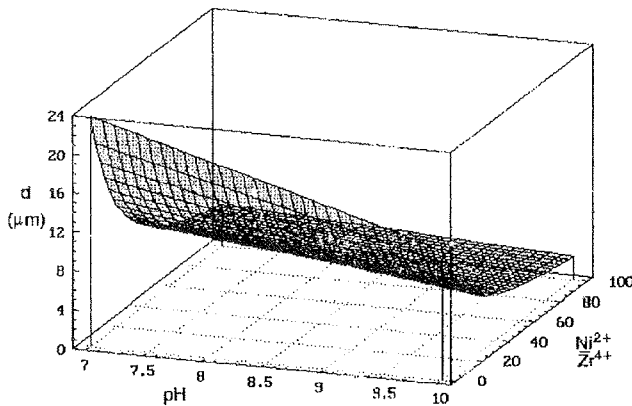

Fig. 3: *Average particle size profile of precipitated composites as a function of final pH in the reaction mixture and initial molar ratio Ni^{2+}/Zr^{4+}*
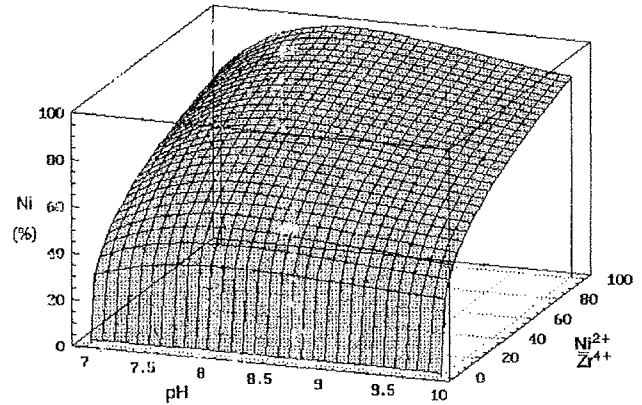

Fig. 4: *Chemical composition of finally prepared composites as a function of final pH in the reaction mixture and initial molar ratio Ni^{2+}/Zr^{4+}*
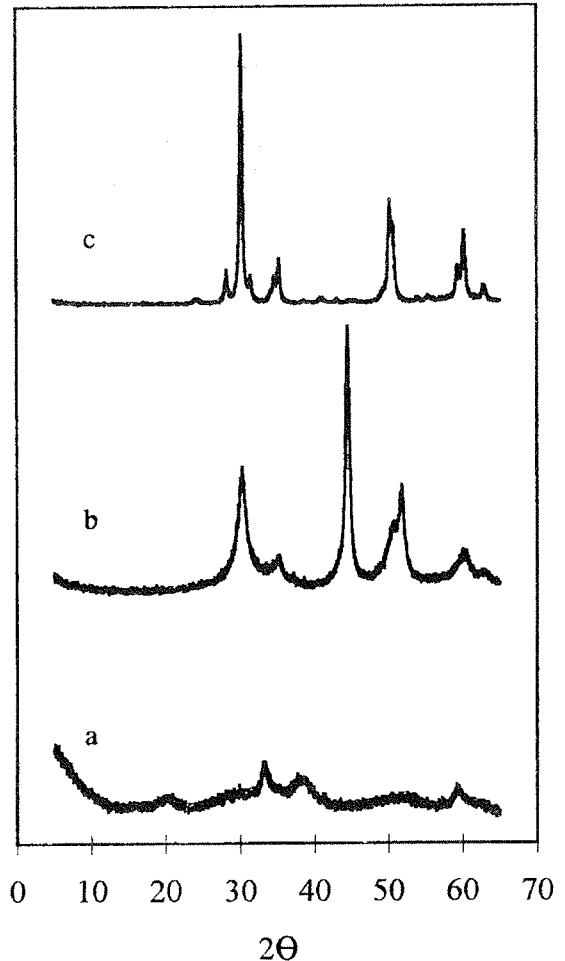

Fig. 5: *X-ray diffractions of samples;*
a) dry C10ZrN8$_{8.44}$,
b) thermally treated C10ZrN8$_{8.44}$ and
c) thermally treated C10ZrN8$_0$

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The structure of the components was determined from the X-ray powder diffraction data (Figure 5). The dried samples appeared to be amorphous to X-ray. Their diffraction patterns exhibited only a broad band, around $2\Theta = 30.5°$ characteristic for amorphous ZrO_2 and the reflections characteristic for NiO. After thermal treatment (calcination and TPR at 500°C) the undoped ZrO_2 (C10ZrN8$_0$ sample) reveals both, the formation of monoclinic and tetragonal modifications. The formation of a thermodynamically metastable tetragonal structure has been reported in the calcination of amorphous hydrated zirconium gels /10,18-20/. Dollimore /21/ has suggested a scheme for the transformation from the amorphous to the crystalline phase over an intermediate metastable tetragonal phase which at increasing temperatures slowly changes into a stable monoclinic modification. The formation of the intermediate structure is a consequence of the stabilization of the metastable structure in the first phase of crystallization by lower surface energy /15,16,23,24/. X-ray difractograms of the C10ZrN8$_{8.44}$ sample indicate the course of crystallization of the gel-precipitate of hydrated zirconium oxide and nickel hydroxide. Gel dried at 120°C does not display the orderly structure of ZrO_2. The position of the diffraction lines corresponds to nickel hydroxide, but the high background and broad peaks indicate that this hydroxide is not well crystallized. After calcination and TPR the structure of the sample is rearranged. The addition of nickel strongly affected the relative amount of monoclinic and tetragonal zirconia, causing a sharp increase in the tetragonal fraction and a decrease in the monoclinic fraction. The most intense monoclinic line (d=3.16 Å, 2Θ=28.24°) is no longer visible. According to M. Valigi et.all /5/ the increasement of methastable tetragonal fraction is the consequence of an interaction of a limited fraction of nickel with the hydrous zirconia surface during the experimental set-up. The diffraction lines at 2.034 and 1.762 respectively correspond to the face centered metal nickel (FCC) formed by TPR. However, more detailed descriptions of the crystalline phase formation during thermal treatment of mixed nickel-zirconium gels prepared by the gel-precipitation method can be found elsewhere /22/.

The processes occurring during thermal treatment of the samples were monitored by TG/DTA analysis. The TG/DTA curves of the pure Ni(OH)$_2$ (C10ZrN8$_\infty$), C10ZrN8$_{8.44}$ sample (50 wt% Ni and 50 wt% ZrO$_2$ in the end product) and the pure zirconium gel (C10ZrN8$_0$ sample) are shown in Figure 6.

The DTA curve of the C10ZrN8$_\infty$ sample (pure nickel hydroxide precipitate) displays two endothermic peaks at temperatures of 120.1°C and 279°C respectively. The first endothermic peak, which is accompanied by a considerable mass loss, is the result of the removal of physically bonded water, while the endothermic peak at 279°C results from the dehydration of the nickel (II) hydroxide into amorphous nickel (II) oxide. Similar results have been reported by Godall and Livingston /25/. According to the literature the NiO structure develops gradually in the temperature region between 250°C and 815°C /25,26/, which could be assigned to the unpronounced broad exothermic peak that follows dehydration of the nickel hydroxide.

In the DTA experiments for nickel free hydrous zirconium oxide (C10ZrN80 sample) two thermal effects were detected: i) a broad endothermic effect in the range approximately 50-300°C (peak temperature 147°C), due to to the evaporation of methanol and water from the surface of gels, and the elimination of physically bonded water trapped in pores of partially dried gel, and ii) a very sharp exothermic peak at approximately 444°C due to the transition from an amorphous to the crystalline structure (the so-called "glow phenomenon" /19/). More detailed dehydration studies of zirconia gels prepared by the gel-precipitation method and the influence of water partial pressure in the drying atmosphere can be found elsewhere /27/.

The TG/DTA analysis of the zirconium and nickel gel-precipitate mixture (the C10ZrN8$_{8.44}$ sample) shows that the TG and DTA curves are not simple combinations of the hydrated zirconium oxide and nickel hydroxide curves. The drying process proceeds over a broad temperature interval, as in the case of the C10ZrN8$_\infty$ sample. Two endothermic effects, attributed to the elimination of physically bonded water and the dehydration of Ni(OH)$_2$, and a broad unpronounced exothermic effect of zirconia crystallization and NiO structure formation were detected. Likewise, the endothermic peak of the dehydration of the nickel
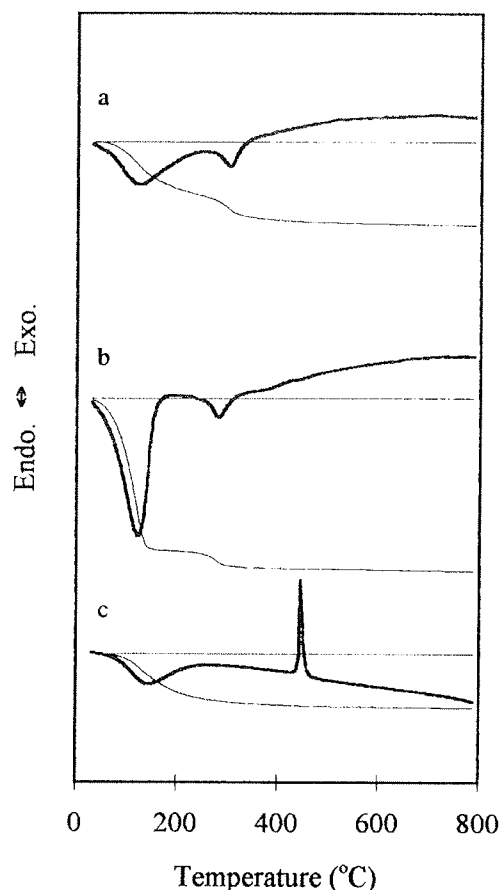

Fig. 6: TG (---), DTA (—) analysis of samples:
a) C10ZrN8$_{8.44}$,
b) C10ZrN8$_\infty$ and
c) C10ZrN8$_0$

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hydroxide occurs at 300°C rather than at 279°C there is no clear exothermic peak of the zirconium oxide crystalline arrangement at 444°C, which may be attributable to the masking of this process by that of the formation of nickel oxide in the same temperature region (Figure 6). The exothermic peak was affected by the presence of nickel and was shifted to higher temperature and broadened as the nickel content increased. Similar results were reported by M. Valigi et. all /5/ who attributed such a behavior of the drying gel to the nickel interaction with hydrous zirconia matrix. He suggested, that because of the nickel interaction a fraction of the zirconia may not be able to crystallize or its crystallization rate is too slow that the process escapes detection.

Conclusions

Processes for preparation of nickel dispersions in zirconia matrix by the gel coprecipitation method were studied in nonaqueous media. The use of methanol as a solvent facilitated a controlled and stepwise hydrolysis of zirconium tetrachloride precursor that cannot be otherwise obtained in aqueous medium. The improvement to the so far described processes is the substitution of aqueous ammonia solution, used for the pH correction, for the gaseous ammonia. Thus the water needed for the hydrolysis and ammonia are introduced separately that enables a wider choice of experimental conditions and due to the lower volume concentration of gaseous ammonia and its better dispersion in the reaction mixture also less pronounced local supersaturations. Although the stability of zirconium and nickel cations in the methanol solution toward pH of the medium and the rates of depletion of the reaction mixture on these cations differ the products show rather high degree of homogeneity. In order to solve the problems concerning the reliability of the results obtained the relation between various parameters of the system was proposed. The addition of nickel to the composite strongly affect the course of crystallization of the composite. Higher imputes of nickel cause a sharp increase in the tetragonal fraction and a decrease in the monoclinic fraction. The crystallization of the composites is attributed by the exothermic effect detectable by DTA analysis. The exothermic peak of crystallization was shifted to higher temperature and broadened as the nickel content increased.

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