

HIGH CaO CONTENT ZIRCONIA POWDER FROM HYDROTHERMAL PROCESSING

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Abstract - A response of a co-precipitated uniform deposit of hydrous zirconia and calcium hydroxide to hydrothermal and subsequent high temperature treatments is described in the paper. A nominal oxide composition of the deposit was 30 mol% CaO and 70 mol% ZrO₂. The hydrothermal treatment of the deposit was performed for 4 h at 240°C to obtain crystalline product which was subsequently heated at temperatures ranging from 410°C to 1450°C without soaking. Calcium oxide escape was monitored by ICP-OES over the processes of co-precipitation, washing and hydrothermal treatment of the deposit. X-ray diffraction was used to study the development of phase composition and crystallite size of the product, additionally observed by TEM. The behaviour of the hydrothermally crystallized powder during heat treatment was studied by means of thermogravimetric, differential thermal and evolved gas analyses. Evidences were collected on the calcium segregation in the form of calcium carbonate during the hydrothermal preparation of high content CaO nano-zirconia powder.

Résumé – Poudre de zircone à haute teneur en CaO obtenue par traitements hydrothermaux.

La réponse d'un dépôt uniforme co-précipité de zircone hydratée et de l'hydroxyde de calcium à des traitements hydrothermaux suivis par des traitements à haute température a été étudiée dans ce travail. La composition nominale du dépôt a été 30 mol% de CaO et 70% mol ZrO₂. Le traitement hydrothermal du dépôt a été effectué pendant 4 h à 240 ° C pour obtenir un produit cristallin qui a ensuite été chauffé à des températures allant de 410 ° C à 1450 ° C sans trempage. L'oxyde de calcium a été contrôlé par ICP-OES au cours des procédés de co-précipitation, de lavage et de traitement hydrothermal du dépôt. Diffraction des rayons X a été utilisée pour étudier la composition de phase et la taille des cristallites du produit observé aussi par MET. Le comportement de la poudre cristallisée pendant le traitement thermique a été étudié par la thermogravimétrie et par analyse thermique différentielle couplée à l'analyse des gaz émis. Les preuves ont été recueillies de la ségrégation du calcium sous forme de carbonate de calcium au cours de la préparation hydrothermale pour la haute teneur en CaO.

1. INTRODUCTION

Calcium-zirconia nanopowders are produced by several methods, including powder mixing [1-2], co-precipitation [3-4], thermal decomposition of metal alkoxides [5], rapid combustion [6], citrate technique [7-8] and the most commonly used hydrothermal crystallization [9-14].

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Preparation of calcia-zirconia solid solutions via hydrothermal treatment of co-precipitated gel often yields compositional inhomogeneities due to loss or segregation of calcium species [12-14]. Several compositions of CaO-ZrO₂ system containing from 6 mol% to 20 mol% of CaO prepared under hydrothermal conditions have been studied.

Grahl-Madsen *et al.* [13] conducted the hydrothermal crystallization of co-precipitated gel with a Ca:Zr ratio of 1:1 for 48 h at 250°C. As a result, 14.2±4 mol% CaO stabilized zirconia with cubic symmetry and crystallite size of 7 nm was obtained, and residual amount of Ca²⁺ was determined in the liquid.

Cheng Hu-Min *et al.* studied the influence of pH in the range of 0.2-14.3 on the phase composition of 8 mol% CaO-ZrO₂ [14]. The monoclinic, tetragonal and cubic polymorphs were detected in a mixture of composition which depended on the pH. The presence of Ca²⁺ ions in the mother liquor after hydrothermal reaction confirmed that CaO did not incorporate quantitatively into the lattice of ZrO₂.

Pyda [10, 11] studied the phase composition and morphology of 6 mol% CaO stabilized zirconia nanopowders synthesized at pH values coming from the range 8.2-12.4 that were adjusted by NaOH solution. The pH values higher than 10 provided the quantitative keeping calcium in the zirconia nanopowder after hydrothermal treatment at 240°C, as indicated by AAS monitoring of the mother liquor. But this result does not indicate the quantitative incorporation of CaO into the zirconia solid solution in the context of above mentioned settlements.

One can guess that the problem of non-quantitative incorporation of CaO into the zirconia powder intensifies when the calcium oxide concentration increases over the earlier reported 6-20 mol% range. Therefore, the aim of this research was to study effects of hydrothermal crystallization of high CaO content zirconia precursor gel of nominal composition 30 mol% CaO – 70 mol% ZrO₂. Because the nanopowder is assigned for obtaining fully densified calcia stabilized cubic zirconia – calcium zirconate polycrystalline nanoceramics by sintering, its behaviour during thermal treatment was investigated. This two phase polycrystal is a purely oxygen ion conductor at a temperature range of 600-1000°C under oxygen partial pressures of 22-100 000 Pa [15], and is suggested as a promising solid electrolyte for high temperature electrochemical devices.

1.1. Experimental

Zirconia nanopowder doped by 30 mol% (16.32 wt%) calcium oxide was manufactured and studied. A gel precursor was prepared via co-precipitation using ZrOCl₂ (>99%) and CaCl₂ (a.p.) aqueous solutions. The 5.5M solution of sodium hydroxide (a.p.) was used as a precipitating agent at pH = 10. The as-received co-precipitated calcia-zirconia gel was hydrothermally treated for 4 h at 240°C under the autogenous water vapour pressure in a autoclave stainless steel. The crystallized powder was washed with a 0.2% solution of aqueous ammonia to remove sodium chloride, then dried at 120°C and sieved through the 100 µm mesh sieve. The presence of sodium chloride in the powder was monitored by the flame test, the reaction with silver nitrite and the ICP method. For investigation of phase composition after thermal treatment, the powder was consolidated by using cold uniaxial pressing under a pressure of 200 MPa. The compacts were then heated at a heating rate of 10 °C/min to temperatures ranging from 410°C to 1450°C with no soaking.

The inductively coupled plasma optical emission spectroscopy ICP-OES method (OPTIMA 7300DV spectrometer) was applied to control calcium concentration in mother liquors coming from the co-precipitation and hydrothermal crystallisation processes, and in the filtrate which has been produced during the ammonia water washing stage. The values were used to calculate the concentration of calcium oxide in the calcia-zirconia gel, the as-received crystalline powder and the powder washed for removing sodium chloride.

X-ray diffraction was used to study phase compositions of the as-received product of the hydrothermal crystallization, and the product subsequently subjected to the heat treatment. The $\text{CuK}\alpha_1$ radiation, measuring range of $10\text{-}90^\circ 2\theta$ and an X'Pert Pro PANalytical diffractometer were used. The size of zirconia solid solution crystallites has been determined, taking into account X-ray line broadening of the (111) peak.

The behaviour of the hydrothermally crystallized powder during the thermal treatment was studied by means of thermogravimetric, differential thermal and evolved gas analyses (TG, DTA, EGA, respectively), using a thermogravimetric analyser TG 449 F3 Jupiter® (Netzsch).

The morphology of the powder was investigated by transmission electron microscopy (JEOL JEM-CX-100). A test sample was dispersed in absolute ethyl alcohol before placing it on a copper grid covered with a carbon film.

3. RESULTS AND DISCUSSION

The studies were focused on determination of the following features of the hydrothermally manufactured and high CaO content zirconia powder: composition of the gel precursor on each stage of its preparation, comprising co-precipitation, hydrothermal treatment and washing, the morphology and phase composition of hydrothermally produced powder, and the behaviour and phase composition of the powder during the subsequent heat treatment up to 1450°C .

3.1. Chemical and phase composition

Data of *table 1* demonstrate the CaO concentration in the calcia-zirconia precursor after the subsequent stages of processing, measured by ICP-OES. The data indicate that any stage of calcia-zirconia powder preparation procedure applied in the study is fully quantitative. The lowest CaO loss occurs during the hydrothermal crystallization process (1.23%). Washing is the most crucial stage due to the largest loss of CaO, which indicates that highly soluble calcium species have formed in the powder during the hydrothermal crystallization.

Table I. Calcium oxide concentration in calcia-zirconia gel, as-received crystalline powder and the powder washed for removing sodium chloride. Analysis of CaO losses is included.

Sample		Co-precipitated gel	As-received powder	Finally washed powder
CaO concentration	mol%	29.35±0.02	28.99±0.02	27.7±0.6
	wt%	16.02±0.01	15.86±0.01	15.3±0.3
Loss as a percent of initial CaO concentration, %	by mole	2.17±0.04	3.37±0.08	7.67±0.12
	by mass	3.09±0.06	4.76±0.11	9.48±0.15
Preparation stage		Co-precipitation	Hydrothermal crystallization	Final washing
CaO loss during the stage, %		2.17	1.23	4.45

The XRD patterns of the as-received and finally washed hydrothermal zirconia powder are presented in *figure 1*. In case of the as-received powder, the zirconia polymorph of cubic symmetry and sodium chloride are detected in amounts of 89% and 11%, respectively. After washing the powder with 0.2% ammonia water, the zirconia polymorph of cubic symmetry was the main phase detected. The very weak peak at 53.8° suggests the presence of some small amount of the tetragonal zirconia polymorph. The absence of sodium chloride is proved on the measuring error of the XRD

method. If calcium species like $\text{Ca}(\text{OH})_2$ and/or CaCO_2 exist in the powder, evidencing *e.g.* the segregation of alloying calcium oxide during the hydrothermal crystallization, the amount of them is also out of the sensitivity range of the XRD method. A crystallite size of 5.9 nm and lattice parameter a of 5.1356 Å were measured.

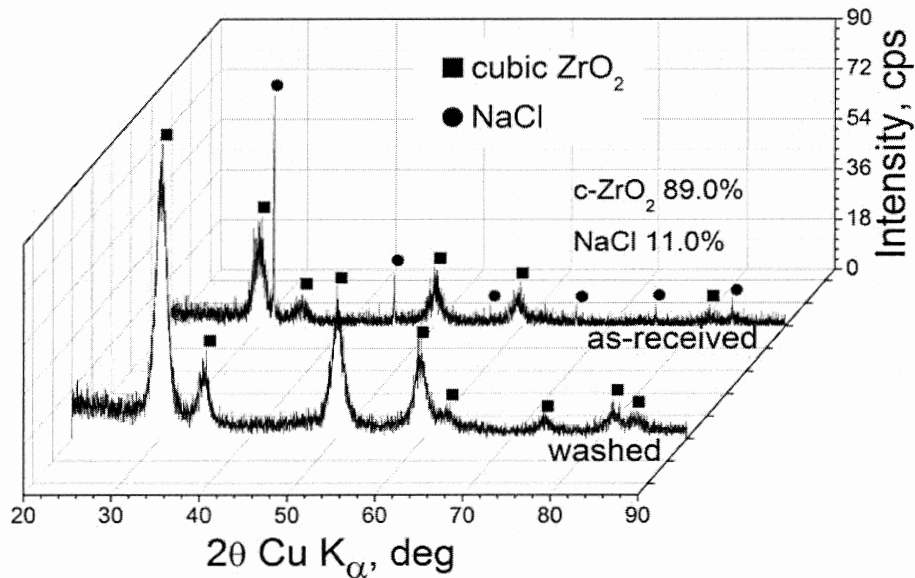


Figure 1. X-ray diffraction patterns of CaO-ZrO_2 nanopowder crystallized hydrothermally for 4 h at 240°C: as-received and washed with ammonia water of pH = 10.

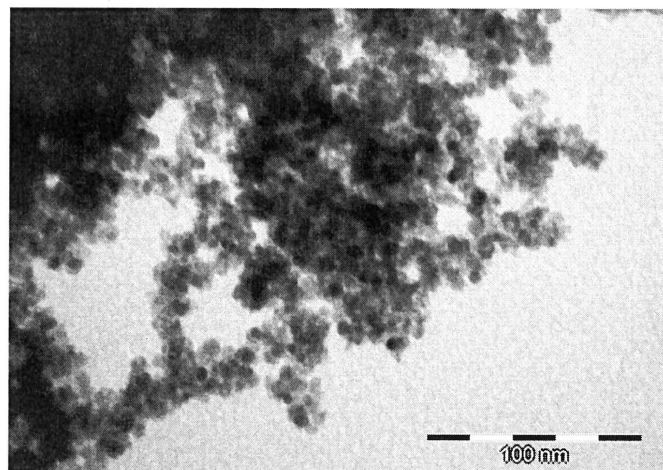


Figure 2. TEM image of an agglomerate of cubic CaO-ZrO_2 solid solution nanocrystallites in the fully washed powder.

TEM observations of the fully washed powder revealed an agglomerate morphology of the powder. The particles are isometric in shape and nanometric in size. Other morphologically different particles are not visible, indicating that the powder is composed of cubic and tetragonal zirconia crystallites, as indicated by XRD measurements (*figure 1*). However, the presence of amorphous zirconia particles cannot be excluded because they show a size close to 5 nm and are isometric in shape.

3.2. Thermal behaviour

The results of TG/DTA and EGA measurements shown in *figure 2* contribute some important information towards understanding evolution of the phase composition of the high CaO content zirconia powder with effect from the hydrothermal crystallization and subsequent heat treatment.

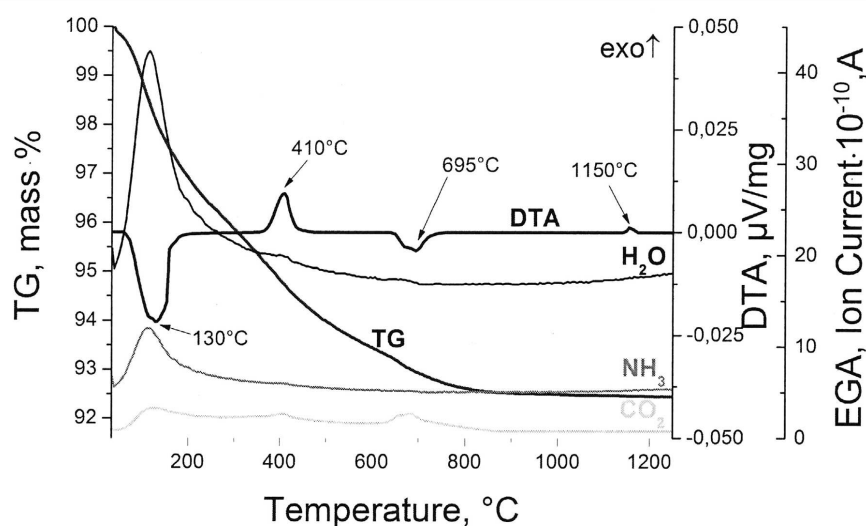


Figure 3. TG, DTA, EGA curves of 28 mol% CaO-ZrO₂ nanopowder hydrothermally treated for 4 h at 240°C

The DTA curve shows two endothermic peaks at 110°C and 675°C, and two exothermic peaks at 410°C and 1150°C, first three accompanied by a total mass loss of 7.5% (TG curve). The first endothermic peak can be attributed to releasing water and ammonia vapours from the studied powder, as indicated by the EGA measurement.

The exothermic peak at 410°C is accompanied additionally by realising of CO₂. Lach *et al.* suggests desorption of water layers, covering nano-zirconia particles and forming nano-capillary meniscuses, responsible for that effect [16]. The 8 mol% Y₂O₃-ZrO₂ powder crystallized under hydrothermal conditions is reported in that study. However, crystallization of pure zirconia crystallites from amorphous zirconia nanoparticles cannot be excluded in the case of high CaO content zirconia powder due to good consistency of the measured temperature of the peak maximum and the pure zirconia crystallization temperature which is well reported in the literature [e.g. 17]. If the process exists it can indicate kinetic effects attributed to temperature, pressure and time of the crystallization process applied.

The EGA curve, which correlates with the endothermic effect at 675°C, shows mainly a release of CO₂, suggesting the presence of calcium carbonate in a small amount in the studied powder. Such interpretation is supported by data of differential thermal analysis of calcium carbonate reported in

Ref. [18]. This proves calcium segregation during the hydrothermal treatment of the co-precipitated precursor of calcia-zirconia solid solution, but the process is rather limited.

Interpretation of a phenomenon which is responsible for appearing the exothermic very weak effect at 1150°C comes from analysis of phase composition of the heat treated powder at elevated temperatures. The results are shown in *figure 4*. The cubic zirconia polymorph is detected as the only phase in the powders heated up to 800°C. Further heating resulted in the appearance of calcium carbonate CaZrO_3 . There are two plateaus of CaZrO_3 concentration: one of about 1 wt% in the

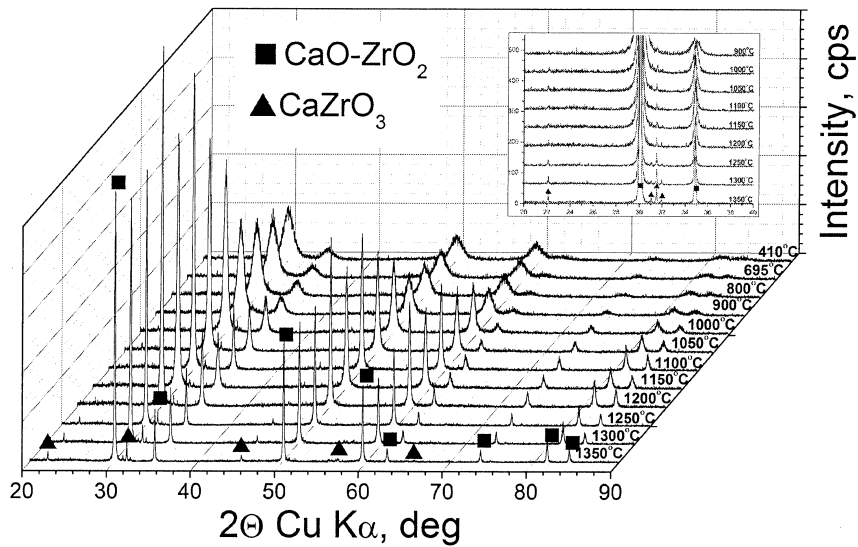


Figure 4. X-ray diffraction patterns of 28 mol% CaO-ZrO_2 nanopowder heat treated at temperatures ranging from 410°C to 1350°C.

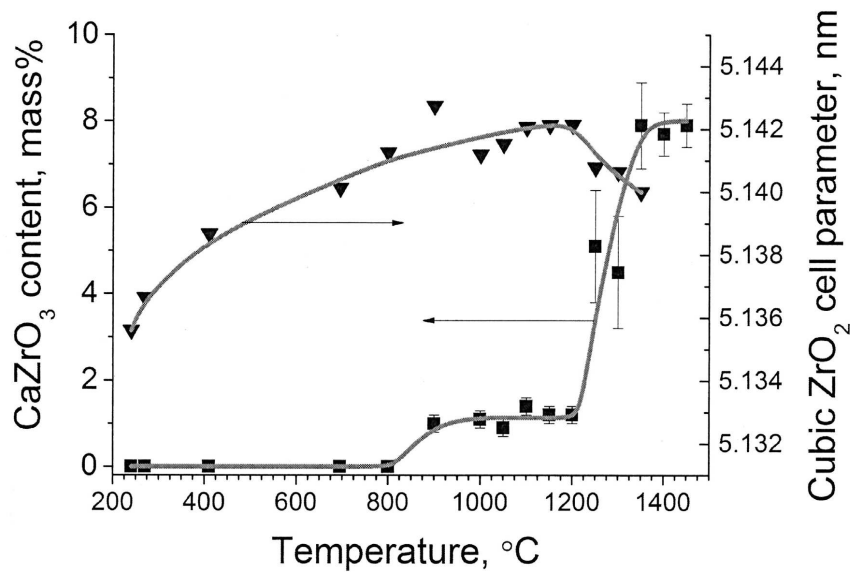


Figure 4. CaZrO_3 content as a function of temperature.

range 900-1200°C, and second one of about 8 wt% above 1300°C, as shown in *figure 5*. This suggests two processes responsible for the formation of calcium zirconate. The first one may be attributed to the reaction between pure zirconia originated from the crystallization of amorphous ZrO₂ at 410°C and calcium oxide, coming from the decomposition of calcium carbonate, and the second one being the result of partitioning, predicted by the CaO-ZrO₂ phase diagram [19]. The latter process is confirmed by a decrease in the cell parameter of cubic zirconia solid solution as shown in *figure 4*. Nucleation and growth of calcium zirconate nuclei can be the process responsible for appearing the exothermic peak at 1150°C.

The appearance of CaZr₄O₉ for the studied composition of 30 mol% CaO-ZrO₂ is predicted by the equilibrium phase diagrams of the CaO-ZrO₂ system [19], but this phase has not been detected, indicating that the heated zirconia nanopowder under the applied conditions was far from the equilibrium.

4. CONCLUSIONS

The stoichiometric manufacturing the 30 mol% CaO – 70 mol% ZrO₂ zirconia nanopowder from zirconyl and calcium chlorides by the co-precipitation/hydrothermal crystallization method is limited. A calcium loss appears during each stage of the nanopowder preparation process. This includes the co-precipitation, the hydrothermal crystallization and the washing stages. The pH of 10 has been applied for the co-precipitation of precursor calcia-zirconia gel with the NaOH solution, and kept during the hydrothermal crystallization of the precursor. However, this pH value has not saved the co-precipitation and hydrothermal crystallization processes to be quantitative during the production of zirconia nanopowder containing as high as 30 mol% of CaO. The removing NaCl from the product of hydrothermal treatment by washing it with the 0.2% aqueous ammonia was the goal of the washing stage, and this stage was crucial due to the largest calcium loss, being 4.45% of the calculated value. The finally washed zirconia nanopowder contained 27.7±0.6 mol% CaO.

The co-precipitation/hydrothermal crystallization method allows us to obtain the nanopowder composed of cubic zirconia solid solution crystallites with small amount of tetragonal polymorph that show isometric shapes and a size close to 6 nm.

Rather small amounts of other secondary phases can appear after hydrothermal processing of the precursor calcia-zirconia gel like calcium carbonate and remnants of amorphous zirconia. They are difficult for quantitative determining.

Heat treatment of the high CaO content zirconia nanopowder with secondary phases being the products of calcium segregation leads to the formation of CaZrO₃ at a temperature as low as 900°C. Further increase in the CaZrO₃ content appears above 1300°C due to the partitioning process.

The equilibrium state has not been achieved during the experiment as indicated by a lack of CaZr₄O₉.

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6. REFERENCES

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