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## STRUCTURE FORMATION OF NANOSCALE SCANDIA STABILIZED ZIRCONIA POWDERS OBTAINED BY CO-PRECIPIATION METHOD

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**Abstract:** We analyzed the physicochemical processes of nanostructure formation of stabilized zirconia powders prepared by co-precipitation method. It has been established that scandium (III) precipitates in the same pH range as that of zirconium (IV). When preparing  $ZrO_2$  from co-precipitated zirconium scandium hydroxides, through their thermal dehydration two types of water molecules and two types of OH groups are formed in intermediate compounds. The number of high-temperature OH groups correlates with the number of additive ions which are localized near additive ions and form bridge OH groups. On the basis of a concept on zirconium (IV) tetrameric structure in solutions, a physicochemical model of nanoparticles formation in scandium (III) stabilized zirconia powders prepared by co-precipitation method has been proposed.

**Keywords:** scandium stabilized zirconia, co-precipitation, NMR study, structural and chemical pattern of zirconia particles formation, solid oxide fuel cells.

### *Introduction*

Scandia stabilized zirconia is used in SOFC application as solid electrolyte and anode [1]. To manufacture these SOFC elements powders with different disperse and phase composition are needed. Therefore technology for zirconia powders production must be predictable and controlled.

The commonly used method that allows to actively control the process of oxides solid phase formation is co-precipitation method. One of the disadvantages of the method is extremely high activity of intermediate zirconium compounds (zirconium hydroxide) which leads to aggregation and agglomeration of precipitation products and consequently the finished powders which in turn leads to a wide range in sizes both primary particles and their agglomerates. In other words this method in its classical application does not allow to prepare non-agglomerated nano-sized powders. To solve these problems systematical studies of physicochemical processes and phenomena that accompany the formation of zirconia solid phase throughout the entire formation sequence:

«Solution→Zirconium hydroxide precipitate→  
→Amorphous zirconium hydroxide→  
→Crystalline zirconium dioxide»

are needed.

The paper deals with physicochemical processes

of the nanostructure formation in stabilized zirconia powders while obtaining it from aqueous solutions of zirconium salts containing soluble additives of stabilizing elements by co-precipitation method.

### *Experimental technique*

8-aqueous zirconium oxychloride ( $ZrOCl_2 \cdot 8H_2O$ ), scandium chloride ( $ScCl_3$ ), ammonia (10% aqueous solution), n-butanol, distilled water were used as original substances. All of these reagents were of CP grade.

Process solutions of zirconium oxychloride were prepared by dissolving  $ZrOCl_2 \cdot 8H_2O$  in distilled water up to concentration of 0.5 mol/l Zr(IV). Stabilizing additive ( $ScCl_3$ ) was introduced directly into zirconium oxychloride solution.

Precipitation of zirconium hydroxide was performed by adding an aqueous solution of ammonia to the solution of zirconium oxychloride with stabilizer while stirring intensively and continuously. The obtained precipitate was filtered and washed with distilled water until no  $Cl^-$  ions were detected in wash water.

Zirconium hydroxide was dehydrated by azeotropic distillation. Azeotropic distillation was done as follows: 90 g of n-butanol were added to 100 g of zirconium hydroxide and azeotropic mixture was distilled off while stirring intensively and continuously. The obtained xerogels were roasted at temperature range 150–1200°C for 1 hour.

The composition of intermediate compounds

formed during the process of coprecipitation and products of thermal decomposition of precipitates was determined by methods of chemical, nuclear magnetic resonance (NMR) and radiographic analyses.

The calculations of equilibrium distribution of ions and hydroxocomplexes in system Zr(IV)–Sc(III)–H<sub>2</sub>O and solubility of hydroxides depending on pH of medium were made in accordance with procedures presented in publications [2,3]. Hydrolysis constants for zirconium and scandium were taken according to authors' data [4,5].

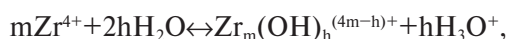
NMR spectra were recorded on a Bruker Avance 400 spectrometer. The study was made using NMR MAS <sup>1</sup>H and stationary NMR <sup>45</sup>Sc.

Mass loss was determined using the technique of thermogravimetric analysis.

The phase composition was determined by X-ray phase analysis.

*The Chemistry of Aqueous Solutions of Zirconium and Scandium Salts*

In aqueous medium Zr(IV) hydrolyzes forming hydroxo complexes with the general formula Zr<sub>m</sub>(OH)<sub>n</sub><sup>(4m-h)+</sup> according to the following equation:



where m is the number of zirconium atoms in the complex, h is the number of hydroxo groups.

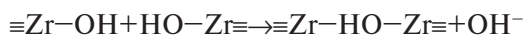
The authors [2] have shown the possibility of existence (Zr(OH)<sub>3</sub>)<sub>n</sub><sup>+</sup>, (Zr<sub>2</sub>(OH)<sub>7</sub>)<sub>n</sub><sup>+</sup> and (Zr(OH)<sub>4</sub>)<sub>n</sub>, hydroxo complexes in Zr(IV) solutions where n is the degree of polymerization. As the solution gets less acidic Zr<sub>4</sub>(OH)<sub>15</sub><sup>+</sup> is likely to be formed. Hydroxo complex Zr<sub>4</sub>(OH)<sub>15</sub><sup>+</sup> undergoes hydrolysis producing neutral tetrameric complex. (Zr(OH)<sub>4</sub>)<sub>4</sub> gets polymerized to form a solid phase:



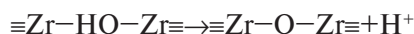
(Zr(OH)<sub>4</sub>)<sub>4</sub> particles are primary base units of hydroxide zirconia solid phase.

Further transformations of tetrameric complex are connected with olation and oxolation reactions.

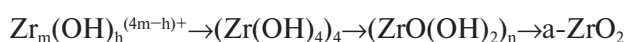
Olation:



Oxolation:



The formed oxolation bonds are very strong and it is practically impossible to break them. Thus, in general the formation of zirconium oxide solid phase can be described by the following equation:



Co-precipitation process can occur by chemical interaction, absorption or occlusion.

*Thermodynamic Analysis of Coprecipitation Process Zr(IV)–Sc(III)*

Coprecipitation process is a heterogeneous process so the composition of the solid phase in the Zr(IV)–Sc(III)–OH<sup>-</sup> system is significantly dependent upon medium pH and upon chemical properties of co-precipitating cations.

Formation of complex hydroxides such as Zr<sub>1-x</sub>Sc<sub>x</sub>(OH)<sub>y</sub> and their precipitation as a solid phase is the most important stage in the process of coprecipitation.

It is commonly thought [6] that adding alkali solution to salts mixture is bound to cause a stepwise hydroxide precipitation i.e. first metal with lower precipitation pH is precipitated and then that with higher one.

To analyze the processes occurring in the process of scandium and zirconium hydroxide coprecipitation, Fig. 1 shows relation between logarithmic solubility of zirconium and scandium hydroxides and pH value.

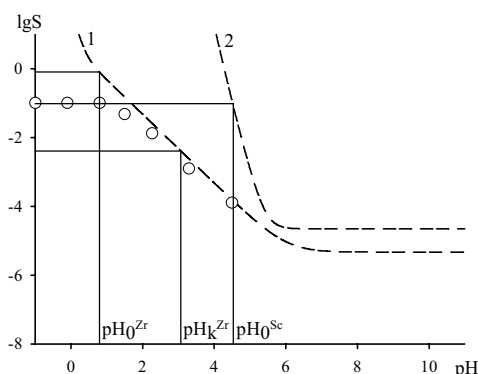


Figure 1. Relation between zirconium (1) and scandium (2) hydroxides and pH value. Dots show experimental data of scandium content in the solution above the precipitate

It was established (Fig. 1) that zirconium precipitates at pH levels ranging from 0.4 to 4.4 and scandium precipitation occurs at pH levels ranging from 4.5 to 6.0.

To determine the pH value of the beginning and ending of scandium hydroxide precipitation in the presence of zirconium we performed a series of precipitation experiments at various pH values.

Compositional analysis of obtained precipitates and measurement of the metals residual concentration in the solution showed that precipitation of scandium begins at pH value as low as ~1 i.e. as soon as zirconium hydroxide solid phase appears in the solution.

It can thereby be concluded that precipitation pH range for scandium is the same as that for zirconium. This fact is well accounted for possibility

of scandium and zirconium hydroxide co-precipitation e.g. as a result of formation of a separate chemical compound of scandium and zirconium such as  $Zr_{1-x}Sc_xO(OH)_y \cdot nH_2O$ . It can also be assumed that scandium cations can be absorbed on zirconium hydroxide surface, but this hypothesis also grounds on possibility of formation surface hydroxo complexes of zirconium and scandium.

*NMR Study of the Processes of Zirconium Compounds of  $Zr_{(1-x)}Sc_xO_y$  Type Formation*

In thermal decomposition of zirconium compounds hydroxo complex  $ZrO(OH)_2 \cdot nH_2O$  [7] is the main intermediate form, its decomposition leads to formation of zirconium dioxide solid phase. When added to initial solutions, stabilizing additives in the process of co-precipitation interact with the main matrix, forming appropriate complexes such as  $Zr_{1-x}Sc_xO(OH)_y \cdot nH_2O$ , or surface compounds due to absorption forces. In the process of thermal treatment precipitates are dehydrated to form solid replacement solutions such as  $Zr_{(1-x)}Me_xO_y$ .

Effects of scandium (III) as well as ligands ( $H_2O$ ,  $OH^-$ ) on structural and chemical characteristics of forming the products of hydroxo zirconium complexes thermal decomposition were studied in samples of  $Zr_{0.92}Sc_{0.08}O(OH)_{0.5} \cdot nH_2O$ .

As seen in Fig. 2 NMR MAS  $^1H$  spectra for zirconium oxides with Sc additive are significantly changing during thermal treatment of the sample. The initial sample spectrum consists of a single line shifted towards the high frequencies side at  $\delta=83.6$  ppm relative to Larmor frequency and width at half height ( $\Delta\nu_{1/2}=2.4$  ppm). Heating the sample to  $100^\circ C$  causes shifting of the line at  $\delta=84.4$  ppm and the sample expansion  $\Delta\nu_{1/2}=6.8$  ppm). Heating the sample to  $150^\circ C$  results in further shifting of this line towards the higher frequencies at  $\delta=85.4$  ppm, its width remaining unchanged.

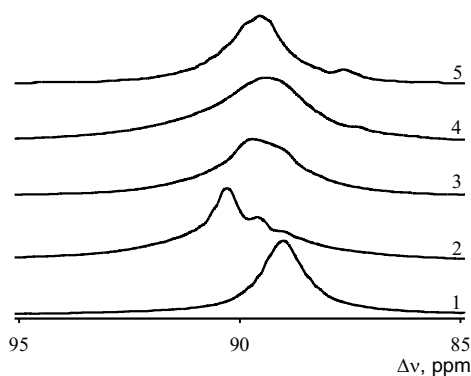


Figure 2. NMR MAS  $^1H$  spectra of  $Zr_{0.92}Sc_{0.08}O(OH)_{0.5} \cdot nH_2O$  sample calcined at temperatures,  $^\circ C$ : 1 – 20; 2 – 150; 3 – 400; 4 – 600; 5 – 800

Besides, against a wide line background there

stand out distinctly at least three relatively narrow components of equal width ( $\Delta\nu_{1/2}=1$  ppm) with chemical shifts  $\delta_1=85.66$ ;  $\delta_2=84.43$  and  $\delta_3=83.26$  ppm and intensity relations 6:3:1 accordingly. Calcination of the sample to  $150^\circ C$  leads to a shift of the whole spectrum towards the low frequencies side, lessening of the spectrum intensity, retention of multiplicity and relationship between the intensities of the narrow components. Calcination of the sample to  $400^\circ C$  causes a further shift towards the low frequencies side.

In proton resonance spectrum of the sample heated in the temperature interval  $600-800^\circ C$  three weakly resolvable components at  $\delta=83.5$  ppm are observed. A shift of the whole spectrum towards the high frequencies side, next towards the low frequencies side and again towards the high frequencies side is connected with changes in volume magnetic susceptibility of the sample while it is dehydrated and dehydroxylated. Appearance of peak ( $\delta=95-85$  ppm) at temperatures around  $150^\circ C$  and its disappearance at  $400^\circ C$  are connected with changes in proton group structure of zirconia when calcined.

To evaluate the number of various proton groups, mass loss control had been carried out in the whole temperature interval. Comparing NMR data and loss on ignition it is possible to single out various groups and their thermal stability. So, most of mass loss (29.56%) occurs at temperatures under  $150^\circ C$  which is connected with desorption of water molecules from  $ZrO_2$  nanocrystals surface.

On the other hand, in NMR  $^1H$  spectra shift of the line towards the high frequencies side and their broadening were observed. This indicates the presence of OH groups on the surface of the crystals and between these groups and water molecules an intensive proton exchange is occurring which slows down when a significant amount of water molecules is lost. Other proton groups are singled out at higher temperatures in three stages:  $150-400^\circ C$ ,  $400-600^\circ C$  and  $600-800^\circ C$  and amount to 9.22, 2.42 and 0.82 mass % accordingly (Fig. 3). These three stages fully correlate with three stages of change in proton spectra.

In our opinion multiplet structure in NMR spectra results from separate lines that represent water molecules localized in open mezopores of various diameter. Intensity of high frequency component at  $\delta=85$  ppm shows the number of smaller pores and component intensity at  $\delta=83$  and 82 ppm reflects the number of water molecules in micropores. It follows that in micropores water molecules are more strongly connected to the surface which means that protons are more strongly shielded by zirconium oxide electrons. The openness of pores results from an intensive proton exchange between various proton groups and from mixing of water molecules at open

surface and in the mezopores.

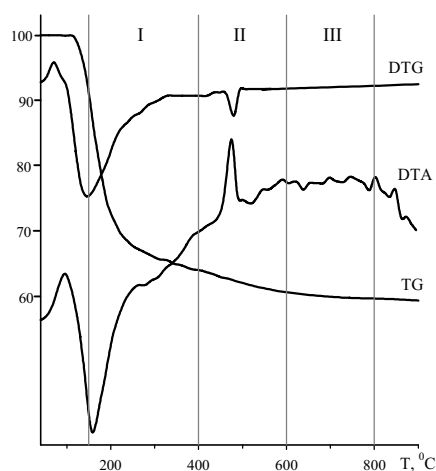


Figure 3. TG/DTG-DTA curves of the  $Zr_{0.92}Sc_{0.08}O(OH)_{0.5} \cdot nH_2O$  sample. TG – thermogravimetric curve; DTG – differential thermogravimetric curve; DTA – differential thermal analysis curve

The first stage of water loss in temperature interval between 150 and 400°C is connected with water release from mezopores and amounts to 9.22 weight %.

The second stage of water release corresponds to temperature interval 400–600°C and manifest itself in two weakly resolvable components at  $\delta=84.2$  and 83.0 ppm in NMR spectra. Component with less chemical shift was put into OH groups localized at  $ZrO_2$  particles surface, and that with big shift into OH groups that are located inside crystal structure (particle).

The third stage of water release corresponds with temperature interval 600–800°C and manifests itself in a single component at  $\delta=84.2$  ppm and width  $\Delta\nu_{1/2}=3.2$  ppm in NMR spectra of sample. This component ranks among structural OH groups. This indicates that in heterovalent isomorphism according to a scheme  $Zr^{4+}-Me^{3+}$  the charge is insufficient to achieve electric neutrality, this is compensated by substitution of  $OH^-$  for  $O^{2-}$  in the anionic part of zirconium dioxide structure.

To check the assumption for presence of bridge-type OH groups in  $ZrO_2$  with Sc additive static NMR of  $^{45}Sc$  nuclei spectra were studied (Fig. 4).

Spectrum of the original sample is made up of a single component with width at half height  $\Delta\nu_{1/2}$  226 ppm shifted towards high frequencies area at  $\delta=126$  ppm relative to Larmor frequency (97.199 MHz). Calcination of the sample at temperatures 150, 400 and 600°C i.e. at temperatures when surface water, pore water and OH groups are practically completely separated proved the following: when heated up to 1200°C the parameters of the

narrow component remained practically unchanged and in the spectrum of the sample calcined at 150°C, first, broader (~1000 ppm) component is identified which intensity relative to the narrow component increased along with temperature increasing and was 1:2 at 800°C and remained unchanged up to 1200°C. Its breadth increased to 3000 ppm while heating to 800°C and remained unchanged during further heating. Further increase in calcination temperature has not revealed marked changes in  $^{45}Sc$  NMR spectrum. Annealing at 800°C led to shifting of the broad component into high frequencies area at  $\delta=500$  ppm. Further calcination showed practically no changes in chemical shift.

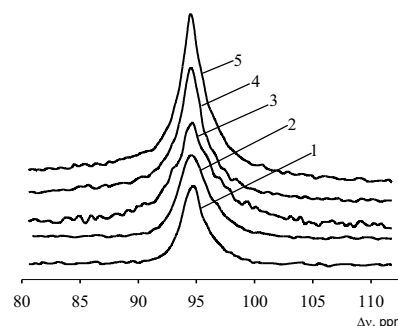


Figure 4. NMR  $^{45}Sc$  spectra of  $Zr_{0.92}Sc_{0.08}O(OH)_{0.5} \cdot nH_2O$  samples calcined at temperatures, °C: 1 – 20; 2 – 150; 3 – 400; 4 – 600; 5 – 800

The obtained NMR  $^{45}Sc$  spectra in  $ZrO_2$  connected with central lines, are specified by two nonequivalent positions of scandium ions.

$OH^-$  groups removal is followed by generation of anion vacancies and decreasing of local symmetry close to additive ions and thus leading to broadening of NMR line. It is significant that the intensity of the narrow component when heated remains practically unchanged while the broad component appears and grows in intensity. And this component is distinctly identified in the sample heated to 400°C i.e. at the temperature when water molecules connected by strong hydrogen bond with mezopores surface are being removed. This means that in the sites of location most of scandium ions, molecules of water generate strong and inhomogeneous electric-field gradients which due to quadrupole expansion lead to disappearance of the component in NMR  $^{45}Sc$  spectrum. Removal of water molecules causes partial decrease in quadrupole expansion, appearance of the broad component and chemical shift of the narrow component. In this case no significant change in electronic environment in both groups of scandium ions occurs.

Removal of surface and structural OH groups does not lead to significant quadrupole expansion (breadth and intensity of the second component has been increasing up to 800°C) but it significantly



increases electronic shielding near most of Sc ions, and causes removal of this component into high frequencies area. The breadth of a NMR Sc spectrum component localized close to the surface and at the surface of ZrO<sub>2</sub> nanocrystals, results from significant scattering of their chemical shifts. This follows from the fact that when thermal (800–1200°C) changes near the surface and at the surface are terminated, no changes are observed in NMR scandium spectrum as well.

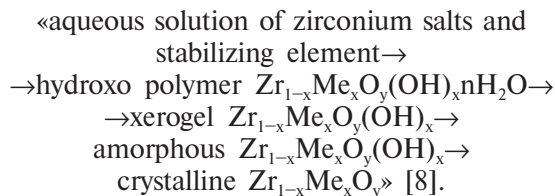
It is rather well established that when preparing ZrO<sub>2</sub> from co-precipitated zirconium hydroxides – Sc, through their thermal dehydration two types of water molecules and two types of OH groups are formed in intermediate compounds. Low-temperature water (up to 150°C) is at the crystal surface and high-temperature water is (up to 400°C) in pores. Low-temperature (up to 600°C) OH groups are at the surface and high-temperature (up to 800°C) OH groups are in the crystal structure.

It is also established that the number of high-temperature OH groups in ZrO<sub>2</sub> with Sc(III) additive correlates with the number of additive ions which are localized near additive ions and form bridge OH groups Sc–OH–Zr. <sup>45</sup>Sc NMR showed that in zirconium hydroxides structure with addition of 8% of Sc<sub>2</sub>O<sub>3</sub> the removal of pore water and structural OH groups is followed by formation of two structurally nonequivalent positions of Sc ions with a quantitative ratio of 1:2 – purely oxygen polyhedra and polyhedra with OH groups and anionic vacancies and strongly defective nanocrystal surface is a major obstacle for formation of large crystals and phase transformations.

*Structural and Chemical Pattern of Zirconia Particles Formation on a Micro-Level When Preparing Them from Solutions*

On the basis of the present-day ideas about chemistry of zirconium, domestic and foreign authors researches it can be stated that tetrameric hydroxo

zirconium complex, which is the basis for formation of all intermediate heterophase nanostructures, is the main structural unit in formation of stabilized zirconia powder solid phase throughout the entire formation sequence:



The pattern of the main physicochemical processes which lie at the basis of nanosized zirconia powders formation at different stages of their preparation from solutions on the basis of carried out research and analysis of works by K. Matsui [9–12] is shown in Fig. 5.

Let us now take a closer look at the process of stabilized zirconia powder micro structure formation while preparing it from aqueous zirconium oxychloride solution by co-precipitation method. In this case polymerization processes which occur in aqueous medium could be interpreted as «tetramer-tetrameric interaction» and as interactions between complexes which are going on as polymerization process is progressing.

It is known that tetrameric structure of aqueous zirconium oxychloride is stable in solution at high HCl concentrations (<5 M). Under these conditions crystallization of zirconium dioxychloride salt occurs with formation of the same tetrameric structure which can be observed in aqueous solution of zirconium oxychloride. At mid-level HCl concentrations (1–5 M) tetramers do not structurally interact. At low HCl concentrations (<1 M) an effect of automatic polymerization has been observed.

Whatever the reasons may be behind tetramer structural interaction whether it is («outer») alkaline

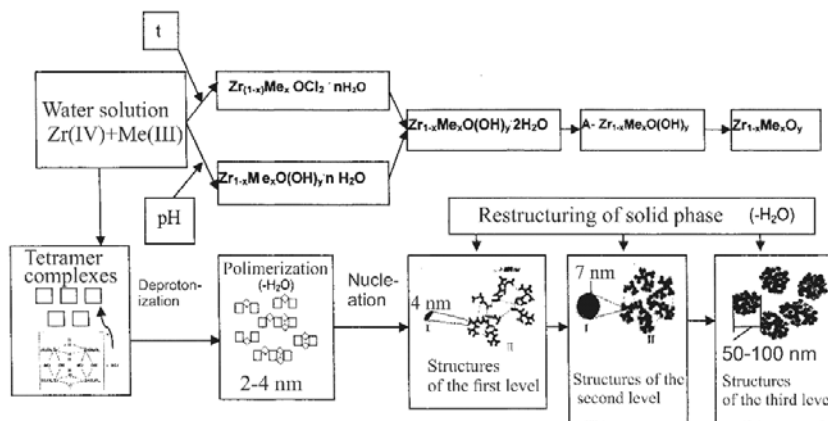


Figure 5. A generalized scheme of structural and chemical transformations of initial zirconium(IV)+Me(III) solutions while preparing nano-sized stabilized zirconia powders

protolysis by adding OH groups to a salt solution or «kinetic» protolysis with chipping off the boundary ion pair and two tetramers of  $K_2$  complex from the tetramer. As they approach each other a new polymer complex is formed from two tetramers.

Complexes  $K_{8-8}$  are primary particles when precipitating zirconium hydroxides with regular structure. These complexes are supramolecular structures with characteristic linear dimensions which are equivalent to dimensions of a polymer formed from four – ten tetramers.

Fig. 5 shows a generalized scheme of structural and chemical stages of zirconia particles formation while preparing it from solutions.

Size of such primary particles is 20–30 Å. These primary nano-particles of zirconium hydroxopolymer complex are formed by spontaneous composition of solution initial tetramers involving ololation and oxolation processes. It is practically impossible to extract these particles from the solution as they represent intermediate cluster (supramolecular) heterostructures between true solutions and colloids. At this level and with adequate delay the formed nanostructures can come to an equilibrium state and to form defectless hydroxo polymer nanostructures amounting to 3 nm. Formation patterns of such zirconium hydroxo polymer structures are discussed in works [9–13]

#### *A Generalized Scheme of Stabilized Zirconia Nanostructures Formation While Preparing It From Hydroxides*

If no preventive measures are taken up aggregation of secondary and tertiary particles can proceed when ageing, keeping hydroxide in mother solution before further usage, or when further thermal dehydration of xerogels is occurring. In the long run this leads to formation of low-reactive aggregated zirconia powders with low specific surface. That specific surface area of the final powders (after being calcined at 750–800°C) amounts to 10–20 m<sup>2</sup>/g when prepared by traditional co-precipitation method is one of the evidences of this effect. In this case microparticles size is 35–60 nm according to X-ray data. Powders with such properties rank among super disperse powders and this ensures decrease of ceramic products sintering temperature up to 1450–1500°C while the ceramics density is 5.95–6.01 g/cm<sup>3</sup>.

It is impossible to achieve such parameters of zirconia ceramics with commercially and laboratory-prepared powders by co-precipitation method even if the temperature increases to 1600°C.

This is accounted for by aggregated powders due to aggregate strength do not break down when ceramics is mechanically formed and preserve or change their structure only at high temperatures while being further sintered. On the basis of the above study a fractographic scheme of transformations (Fig. 6) of solid phase thermal decomposition of

respective zirconium compounds was suggested. This is know-how of technology and is not always covered by producers or researchers in scientific and technical literature.

As shown in Fig. 6 in order to control the structure of zirconia powders it is necessary to actively affect intermediary products structure with various physical and chemical factors. Some techniques for controlling the processes of final stabilized zirconia powders preparation are connected with variations in process-dependent parameters, and some with the use of specific physical (ultrasound, electromagnetic oscillation) and chemical (aggregation process blocking compounds) factors to affect the intermediate products in preparation of nano-sized stabilized zirconia powders.

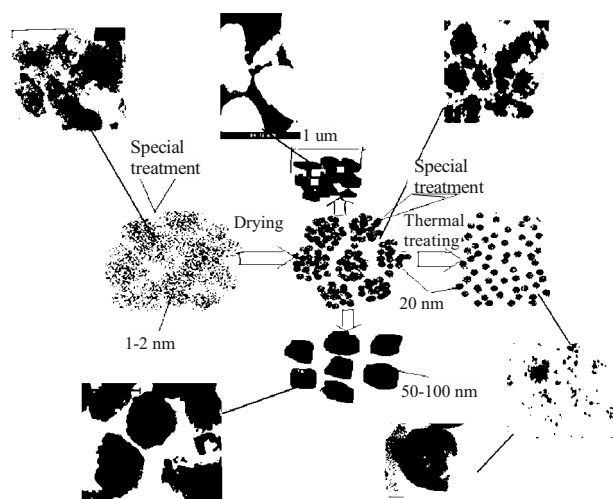


Figure 6. A generalized scheme of stabilized zirconia nanostructures formation while preparing it from hydroxides

#### **Conclusions**

It has been established that scandium (III) precipitates in the same pH range as that of zirconium (IV), forming with the latter –Zr–OH–Sc– bridging bonds. This is borne out by formation of polynuclear zirconium and scandium hydroxo complexes of  $Zr_{1-x}Sc_xO(OH)_y \cdot nH_2O$  type during their co-precipitation.

It is rather well established that when preparing  $ZrO_2$  from co-precipitated zirconium scandium hydroxides, through their thermal dehydration two types of water molecules and two types of OH groups are formed in intermediate compounds. Low-temperature water (up to 150°C) is at the crystal surface and high-temperature water is (up to 400°C) in pores. Low-temperature (up to 600°C) OH groups are at the surface and high-temperature (up to 800°C) OH groups are in the crystal structure.

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On the basis of concept on zirconium (IV) tetrameric structure in solutions, a physicochemical model of nanoparticles formation in scandium (III) stabilized zirconia powders prepared by co-precipitation method has been proposed.

## REFERENCES

1. Vereschak V., Brychevskiy M., Vasylyev O. Mechanical and electrophysical properties of electrolyte ceramics based on zirconia stabilized with Scandia // *Voprosy khimii i khimicheskoi technologii*. – 2008. – № 2. – P.135-138.
2. Pasenko O.O., Vereshchak V.G., Nikolenko N.V. Thermodynamic analysis of zirconium hydroxide precipitation process // *Voprosy khimii i khimicheskoi technologii*. – 2009. – № 3. – C.155-157.
3. *The thermodynamic analysis of the process of joint deposition of zirconium and rare earth elements* / O.O. Pasenko, V.G. Vereshchak, N.V. Nikolenko, K.V. Nosov // *Voprosy khimii i khimicheskoi technologii* – 2009 – № 5. – C.107-109.
4. *Thermodynamic stability of zirconium(IV) complexes with hydroxy ions* / Veyland A., Dupont L., Pierrard J.-C. at al. // *Eur. J. Inorg. Chem.* – 1998. – Vol.11. – P.1765-1770.
5. Aveston J. Hydrolysis of scandium(III): ultracentrifugation and acidity measurements // *J. Chem. Soc. A.* – 1966. – P.1599-1601.
6. Wasserman I.M. *Chemical precipitation from solutions* – Leningrad: Chemistry. – 1980. – 208 p.
7. *Synthesis of nanodispersed powders of zirconium dioxide stabilized by scandium* / Vereshchak V.G., Nosov K.V., Baskevich O.S., Brychevsky N.N., Vasylyev O.D. // *Voprosy khimii i khimicheskoi technologii*. – 2007. – № 5. – C.80-84.
8. *Investigation of fractal structure nanosized powders partially stabilized zirconia* / V.G. Vereshchak, U.P. Gomza, O.O. Pasenko, K.M. Suhoj // *Voprosy khimii i khimicheskoi technologii*. – 2007. – № 6. – C.80-84.
9. Matsui K., Ohgai M. Formation Mechanism of Hydrous-Zirconia Particles Produced by Hydrolysis of ZrOCl<sub>2</sub> Solutions // *J. Am. Ceram. Soc.* – 1997 – Vol.80. – I.8. – P.1949-1956.
10. Matsui K., Ohgai M. Formation Mechanism of Hydrous-Zirconia Particles Produced by Hydrolysis of ZrOCl<sub>2</sub> Solutions: II // *J. Am. Ceram. Soc.* – 2000 – Vol.83. – I.6. – P.1386-1392.
11. Matsui K., Ohgai M. Hydrolysis of ZrOCl<sub>2</sub> Solutions: III, Kinetics Study for the Nucleation and Crystal-Growth Processes of Primary Particles // *J. Am. Ceram. Soc.* – 2001. –

Vol.84. – I.10. – P.2303-2312

12. Matsui K., Ohgai M. Formation Mechanism of Hydrous Zirconia Particles Produced by Hydrolysis of ZrOCl<sub>2</sub> Solutions: IV, Effects of ZrOCl<sub>2</sub> Concentration and Reaction Temperature // *J. Am. Ceram. Soc.* – 2002. – Vol.85. – I.3. – P.545-553.

13. Clearfield A. Crystalline hydrous zirconia // *Inorg. Chem.* – 1964. – Vol.3. – I.1. – P.146-148.

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## STRUCTURE FORMATION OF NANOSCALE SCANDIA STABILIZED ZIRCONIA POWDERS OBTAINED BY CO-PRECIPIATION METHOD

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*We analyzed the physicochemical processes of nanostructure formation of stabilized zirconia powders prepared by co-precipitation method. It has been established that scandium (III) precipitates in the same pH range as that of zirconium (IV). When preparing ZrO<sub>2</sub> from co-precipitated zirconium scandium hydroxides, through their thermal dehydration two types of water molecules and two types of OH groups are formed in intermediate compounds. The number of high-temperature OH groups correlates with the number of additive ions which are localized near additive ions and form bridge OH groups. On the basis of a concept on zirconium (IV) tetrameric structure in solutions, a physicochemical model of nanoparticles formation in scandium (III) stabilized zirconia powders prepared by co-precipitation method has been proposed.*

**Keywords:** scandium stabilized zirconia; solid oxide fuel cells; co-precipitation; NMR study; structure formation of nanoparticles.

## REFERENCES

1. Vereschak V., Brychevskiy M., Vasylyev O. *Mechanicheskie i elektrofizicheskie svoystva elektroliticheskoi keramiki na osnove dioksida tsirkoniya, stabilizirovannogo oksidom skandiya* [Mechanical and electro-physical properties of electrolyte ceramics based on zirconia stabilized with Scandia]. *Voprosy khimii i khimicheskoi technologii*, 2008, vol. 2, pp. 135-138. (in Russian).
2. Pasenko O.O., Vereshchak V.G., Nikolenko N.V. *Termodynamichnyi analiz protsesu osadzhennya gidroksydu tsyrkoniyu* [Thermodynamic analysis of zirconium hydroxide precipitation process]. *Voprosy khimii i khimicheskoi technologii*, 2009, vol. 3, pp. 155-157. (in Ukrainian).
3. Pasenko O.O., Vereshchak V.G., Nikolenko N.V., Nosov K.V. *Termodynamichnyi analiz protsesu sumisnogo osadzhennya tsyrkoniyu i ridkozemel'nykh elementiv* [The thermodynamic analysis of the process of joint deposition of zirconium and rare earth elements]. *Voprosy khimii i khimicheskoi technologii*, 2009, vol. 5, pp. 107-109. (in Ukrainian).
4. Veyland A., Dupont L., Pierrard J.-C., Rimbault J., Aplincourt M. *Thermodynamic stability of zirconium(IV) complexes with hydroxyl ions*. *European Journal of Inorganic Chemistry*, 1998, vol. 11, pp. 1765-1770.
5. Aveston J. *Hydrolysis of scandium(III): ultracentrifugation and acidity measurements*. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1966, pp.1599-1601.
6. Wasserman I.M., *Khimicheskoe osadzhdenie iz rastvorov* [Chemical precipitation from solutions]. *Khimiya*, Leningrad, 1980. 208 p. (in Russian).
7. Vereshchak V.G., Nosov K.V., Baskevich O.S., Brychevsky N.N., Vasylyev O.D., *Sintez nanodispersnyh poroshkov dioksida tsirkoniya, stabilizirovannykh skandiem* [Synthesis of nanodispersed powders of zirconium dioxide stabilized by scandium]. *Voprosy khimii i khimicheskoi technologii*, 2007, vol. 5,

pp. 80-84. (in Russian).

8. Vereshchak V.G., Gomza U.P., Pasenko O.O., Suhoi K.M. Issledovanie fraktal'noi struktury nanorazmernogo poroshka chastichno stabilizirovannogo dioksida tsirkoniya [Investigation of fractal structure nanosized powders partially stabilized zirconia]. *Voprosy khimii i khimicheskoi tehnologii*, 2007, vol. 6, pp. 80-84. (in Russian).

9. Matsui K., Ohgai M. Formation mechanism of hydrous-zirconia particles produced by hydrolysis of  $ZrOCl_2$  solutions. *Journal of the American Ceramic Society*, 1997, vol. 80, no. 8, pp. 1949-1956.

10. Matsui K., Ohgai M. Formation mechanism of hydrous-zirconia particles produced by hydrolysis of  $ZrOCl_2$  solutions: II. *Journal of the American Ceramic Society*, 2000, vol. 83, no. 6, pp. 1386-1392.

11. Matsui K., Ohgai M. Hydrolysis of  $ZrOCl_2$  solutions: III, Kinetics study for the nucleation and crystal-growth processes of primary particles. *Journal of the American Ceramic Society*, 2001, vol. 84, no. 10, pp. 2303-2312.

12. Matsui K., Ohgai M. Formation mechanism of hydrous zirconia particles produced by hydrolysis of  $ZrOCl_2$  solutions: IV, Effects of  $ZrOCl_2$  concentration and reaction temperature. *Journal of the American Ceramic Society*, 2002, vol. 85, no. 3, pp. 545-553.

13. Clearfield A. Crystalline hydrous zirconia. *Inorganic Chemistry*, 1964, vol. 3, no. 1, pp. 146-148.