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Hydrothermal synthesis of zirconia nanomaterials

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Abstract

Yttria-stabilised zirconia powders and films have been obtained from Zr(IV) peroxides by hydrothermal crystallisation at temperatures in the range 125–200°C. The thermodynamic evaluation evidenced that formation of $Zr(OH)_5^-$ in H_2O_2 solutions increases solubility of Zr (IV) hydrated species and improves the kinetics of the new phase formation by the solubilisation-reprecipitation process. Powders with crystallite sizes in the range 6–22 nm have been obtained. The kinetic parameters for the crystallisation process were calculated using Avrami's approach to control the nanocrystalline structure. Nanocrystalline films consisting of platelet YSZ crystallites were also hydrothermal deposited on alumina substrate of YSZ suggesting a layer to layer growing mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Zirconia ceramic materials are known as important candidates for high tech functional and structural applications. Stabilised Y_2O_3–ZrO_2 ceramics (YSZ) is the most common solid electrolyte used in various applications as oxygen sensors or fuel cells. Their utilisation made automotive and industries more environment friendly due to its adequate level of oxygen ion conductivity and desirable stability in both oxidising and reducing atmospheres. To improve the ionic conductivity in a large temperature range, different ways have been proposed:

(a) Partial or total replacement of Y_2O_3 with Sc_2O_3[1] having a maximum corresponding to the composition $(Y_{0.5}Sc_{0.5})0.3Zr_{0.7}O_{1.85}$. The higher price of dopants and the conductivity decrease observed with holding time due to the structural modifications limit their utilisation.
(b) Reducing the diffusion and transport distances using nanocrystalline membranes and thin films. Kosaki et al.[2] found that nanocrystalline YSZ (16 mol%Y_2O_3) thin films with mean grain sizes in the range 10–200 nm materials exhibited two-three orders of magnitude increase in conductivity compared to polycrystalline and single crystalline materials.
(c) Development of composite ceramic materials with enhanced grain boundary conductivity. It was reported that the grain boundary resistivity may be modified due to the segregated elements.[3]

In order to obtain nanocrystalline zirconia powders different physical, mechanical and chemical methods have been proposed. Among the wet chemical synthesis routes the hydrothermal methods are mentioned to have great potential for the near-room temperature manufacture of both nanopowders and films.[4,5] The main advantages of these routes are related to the homogeneous nucleation processes and very low grain sizes due to elimination of the calcination step. The present paper investigates the hydrothermal synthesis of zirconia nanomaterials from soluble Zr peroxide precursors.

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2. Thermodynamic evaluation

The evaluation of the Gibbs free energy of formation of zirconia has been made considering as starting precursors Zr^{4+}(1), $Zr(OH)^{3+}$ (2), $Zr(OH)_2^{2+}$ (3), $Zr(OH)_3^{+}$ (4) and $Zr(OH)_4$ (5), based on the values of the hydrolisis constants given in[6] and using the HSC soft (Outokumpu Oy, Pori, Finland). The results are presented in Fig. 1.

The calculation has been made considering the general hydrothermal reactions:

$$Zr(OH)_y^{(z-y)+} + (z-y)OH^- = ZrO_2 + \frac{z}{2}H_2O \tag{1}$$

where z is the valency and $y = 1 \ldots z$ is the stoiechiometric coefficient of the hydrated species. It can be observed that increasing the degree of hydration "y" of the initial precursor and the temperature the equilibrium of the hydrothermal synthesis reaction goes toward the formation of ZrO_2. Increasing the addition of hydroxil ions in the system gives rise to the formation of hydrous species $Zr(OH)_5^-$, with higher solubility constant (Fig. 2):

$$\ln K_s = -\frac{1}{RT}\Delta G_y^{\mathrm{sol}} \tag{2}$$

It has been shown that the formation of ZrO_2 (as well as of the most of other oxides) in hydrothermal solutions takes place by a solubilisation-reprecipitation process and a sufficient degree of supersaturation and the presence of nucleation sites are required. Consequently, increasing the solubility of the Zr (IV) hydrated species one may expect to improve the kinetics of the new phase formation. It was also reported that utilisation of peroxo-precursors has important advantages in lowering ZrO_2 synthesis temperature and improving kinetic conditions.[7] This was also explained in terms of an increased solubility of the complex formed in the reaction[8]

$$[Zr_4(OH)_8]^{8+} + 12\ OH^- + 6H_2O_2 \Longleftrightarrow 4[(HOO)Zr(OH)_6]^{2-} + 4\ H^+ \tag{3}$$

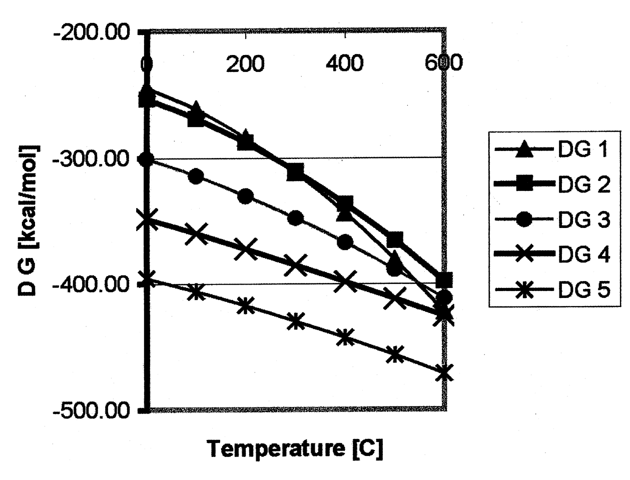

Fig. 1. Evaluation of the Gibbs energy of formation of hydrous zirconia species.

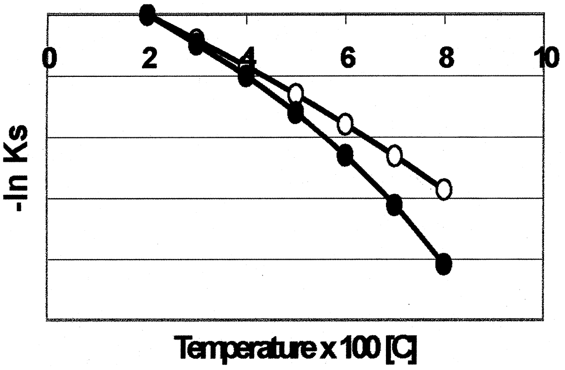

Fig. 2. Solubility of $Zr(OH)_4$ (■) and $Zr(OH)_5^-$ (○) species vs. temperature of hydrothermal solutions.

3. Experimental procedure

A feedstock Zr (IV) solution has been prepared by solubilisation of pure $ZrCl_4$ into distilled water. The precursor was then prepared by mixing this solution with the appropriate amount of sodium hydroxide containing H_2O_2 solution according to reaction (3). Yttria has been dissolved in the zirconia solution in the appropriate amount corresponding to 9.5 mol% ratio. YSZ powders were then precipitated by controlled decomposition of the Zr (IV) complex in Teflon autoclaves in the temperature range 125–200°C and times from 1 to 4 h. The precipitates have been filtered, washed with distilled water to remove the soluble chlorides and ethanol to reduce agglomeration and dried for several hours in air at 110°C. In some experiments sintered alumina tapes were immersed in the solution in the autoclave. Phase composition of powders was investigated by XR diffraction. The degree of crystallisation of cubic ZrO_2 phase (x_c) has been calculated from the ratios between the areas of the characteristic [111] peaks of samples and standard samples obtained by ammonia coprecipitation. The mean crystallite sizes were calculated according to the Sherrer formula from the broadening of the [111] characteristic peak of the crystalline phases. Scanning electron microscopy (Cambridge SM 250) was performed on powders and films after gold deposition in vacuum.

Table 1
Cubic zirconia crystallisation[a]

Temperature (°C)	Cubic phase		Monoclinic phase		Kinetic constants	
	X_c (%)	D_{111} (nm)	X_m (%)	D_{111} (nm)	k	n
125	21	7	–	–	1.65×10^{-9}	2.09
150	47	17	20	14	3.47×10^{-8}	1.871
175	69	19	26	22	1.285×10^{-6}	1.241
200	56	22	25	23	2.698×10^{-5}	1.308

[a] Crystallisation degree and mean crystallite sizes for 2 h hydrothermal reaction.

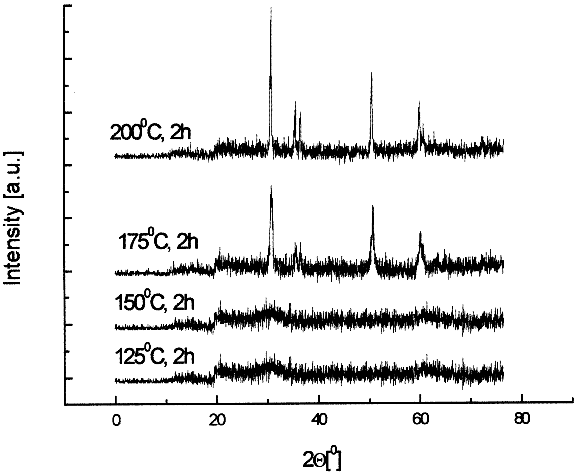

Fig. 3. XRD patterns of YSZ powders obtained from soluble Zr(IV) peroxide precursors.

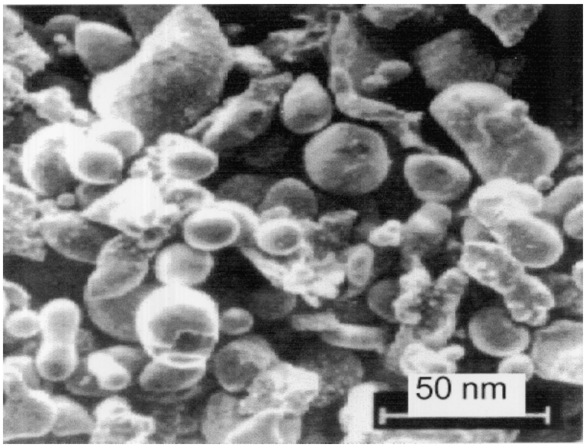

Fig. 4. SEM micrograph of YSZ powders obtained via hydorthermal process from soluble Zr(IV) peroxide precursors (2 h at 200°C).

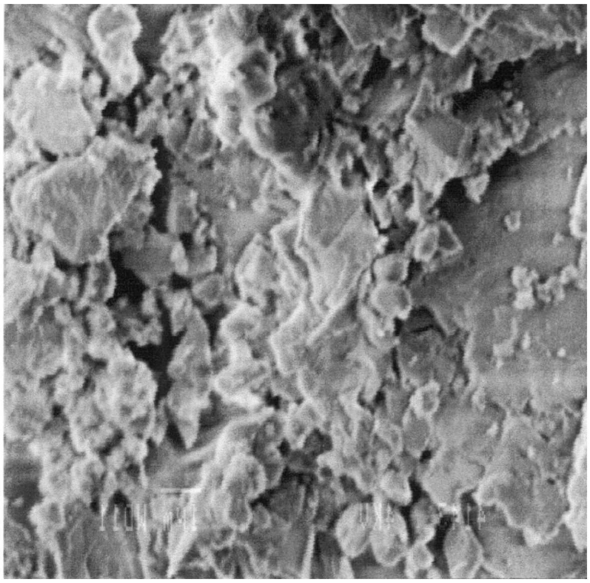

Fig. 5. SEM micrograph of YSZ film hydrothermal deposited on Al_2O_3 substrate.

4. Results and discussions

In the temperature range 125–200°C cubic zirconia phase has been formed, the degree of crystallisation increasing with time and temperature of hydrothermal treatment (Table 1). Powders with large peaks, typically for the nanopowders have been prepared (Fig. 3). Increasing temperature and time monoclinic zirconia phase has also been formed. The calculated mean crystallite sizes increases from about 6 nm to a maximum of 22 nm. The SEM micrographs shows that powders with homogeneous size distribution have been formed (Fig. 4). Some agglomerates can also be observed.

The kinetic constants of the crystallisation process have been studied using the equation proposed by Avrami

$$\ln\ln\frac{1}{1-x_c} = \ln k - n\ln t \tag{4}$$

where x_c is the fraction of the crystalline phase crystallised at the given time, k is the kinetic factor and n is the time exponent. The calculated values are presented in Table 1. The values obtained correspond to a diffusion-controlled crystallisation process.

The proposed hydrothermal route allowed the direct synthesis of nanocrystalline films by deposition on alumina substrate. The SEM of the deposited films (Fig. 5) showed that it consists from platelate crystallites of YSZ, their morphology suggesting a layer to layer growing mechanism.

According to the well known brick-layer model, one could expect the grain boundary ionic conductivity of YSZ ceramics decrease with decreasing grain size. In the case of YSZ–Al_2O_3 nanocomposits and films however, the first preliminary results indicate an important enhancement of the grain boundary conductivity. This could be explained if we consider the phase limits as short-circuits for the conduction of oxygen vacancies.

5. Conclusions

Yttria stabilised zirconia powders can be obtained at low hydrothermal temperatures from Zr (IV) peroxide precursors. The determination of the kinetic constants allows to control the crystallisation process to obtain powders with crystallite sizes in the range 6–22 nm. Preliminary tests make us expect that materials obtained starting from this precursors could contribute to significantly improve the ionic conductivity of the solid state conductor.

Acknowledgements

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References

1. Ciachi, F. T. and Badwal, S. P., The system Y_2O_3–Sc_2O_3–ZrO_2: phase stability and ionic conductivity studies. *J. Eur. Ceram. Soc.*, 1991, **7**, 197–206.
2. Kosacki, I., Colomban, P. and Anderson, H. V., *Proceedings of the US–Japan Workshop on Electrically Active Ceramic Interfaces*. MIT, USA, 1998, pp. 180–188.
3. Miyayama, M. and Yanagida, H., Dependance of grain boundary density in yttria-stabilized zirconia. *J. Am. Ceram. Soc.*, 1984, **67**, C194–C195.
4. Kriygsman, P., *The Hydrothermal Synthesis of Ceramic Powders*. Chemical Eng. Comp. AG, Niederscherli, Switzerland, 1992.
5. Tsukuda, T., Venigalla, S., Morrone, A. A. and Adair, J. H., Low-temperature hydrothermal synthesis of yttrium-doped zirconia powders. *J. Am. Ceram. Soc.*, 1999, **82**(5), 1169–1174.
6. Baes, C. and Mesmer, E., *The Hydrolisis of Cations*. Wiley, New York, 1976.
7. Zhitomirsky, I., Electrolytic deposition of oxide films in the presence of hydrogen peroxide. *J. Eur. Ceram. Soc.*, 1999, **19**, 2581–2587.
8. Piticescu, R., *Wet chemical synthesis of ultradisperse ceramic powders*. PhD thesis, University Politehnica Bucharest, 1998.