Nonisothermal Synthesis of Zirconia and Zirconia-Based Nano-Powder Through Oxalate Processing

Oleg Vasylkiv[*], Yoshio Sakka[*], Hanna Borodians'ka[**] and Keijiro Hiraga[*]

[*]National Research Institute for Metals, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan
Fax: 81-298-59-2401, e-mail: sirius@nrim.go.jp
[**]Institute for Problems in Material Science, Krzhizhanivs'kogo Str. 3, Kiev, 01142, Ukraina

Abstract

A nontraditional rout for controlling the particle size distribution and morphology of yttria stabilized zirconia (3Y-TZP) and zirconia-titania composites is explained. Nano-powders with a narrow size distribution of primary particles and aggregates were produced. The obtained powder had a particle size of 8–15 nm, and it is weakly agglomerated, with a narrow agglomerates size distribution of 60–120 nm.

Characteristics of morphology evolution and crystallization during decomposition were investigated to optimize the heating mode of decomposition. Changes in heating rates cause changes in the path of synthesis. This includes the rate of several processes: complete decomposition of oxalate with formation of amorphous resulting product, crystallization of product, and coalescence of particles at elevated temperatures. These processes are superimposed with elevating of heating rates. High rates shift the process into other temperature ranges in comparison with slow heating. Consequently there are two synthesis schedules differing both in fineness of the final product, degree of its agglomeration, and temperatures of synthesis and crystallization. Nonlinear heating processing avoids hard agglomeration of super-active primary particles, and avoids agglomeration, which results from the relatively high temperature synthesis and crystallization.

Keywords: Nanopowder, nonisothermal, zirconia, oxalate

1. INTRODUCTION

Controlled density and microstructure of ceramic materials are largely dependent on the characteristics of the green material, [1,2] and also dependent on the secondary-particle size distribution.

Nano-powders with small primary particle size obtained by wet chemical processing are as usual heavily agglomerated. Particle agglomeration occurs when the precipitated precursors, or gels, are dried and milled and when the precursor materials are calcined at temperatures over 650 °C. [3-7] It is desirable to produce a precursor powder at such conditions which allow avoiding hard agglomeration of the final powder.

Zirconia ceramic, stabilized by the addition of oxides Y_2O_3, MgO and its composites with titania are an important material due to its many applications. Its properties depend strongly on the crystal structure and microstructure.

The most commonly used methods for the synthesis of mixed oxides are the various sol-gel, hydrothermal and hydroxide methods for nano-size powder production.[3-7]

However, the oxalate route for obtaining nano-sized zirconia powders has not been popular. It is well known that other oxides, and mixed oxide systems, such as barium titanate, yttrium doped ceria, neodynium doped barium cerium oxides, and yttrium-barium systems with precise stoichiometry, have been successfully produced using the oxalate process.[8-14]

With these objectives we have studied the processing of zirconia nano-powder using the oxalate precursor method. It was expected that homogeneous mixing could be achieved, and that oxalate precursor-derived oxides would consist of nano-sized, weakly agglomerated primary-particles with narrow secondary particles size distribution.

2. EXPERIMENTAL PROCEDURE

The starting reagents were zirconium (VI) oxychloride, hydrous $ZrOCl_2$ $10H_2O$ (98%), oxalic acid dehydrous $C_2H_2O_4$ $2H_2O$ (>99.5%), $MgCl_2$ $6H_2O$ and $TiCl_4$ (99%) (all produced by High Purity Chemicals, Japan). Yttrium oxide grains (>99.99%) (High Purity Chemicals, Japan) were dissolved in aqueous solution of hydrochloric acid with subsequent mixing for 48 hours to obtain the $2YCl_3$ solution. Aqueous solutions of different compositions with concentration of 0.01 – 1 mol/l were prepared. The stream of sol droplets after contact with the oxalic acid solution, transformed to a gel or precipitate consisting of the agglomerates of 3mol% yttrium zirconium oxalate. Spraying of extremely diluted chlorides solution into reaction zone was used for promotion of a highest possible degree of dispersion.

Two technological routes of post-synthesis treatment were used to obtain fine weakly agglomerated oxalate powder. In the first route the ending oxalate powders were washed 8 – 10 times to separate the precipitate from the hydrochloric acid and centrifuged to remove the free water. Subsequent freeze drying was used. Freeze Dryer (FDS500 Shimadzu, Japan).

In the second route the resulting oxalate powder was washed without centrifuging and dried in an oven at 120 °C for 48 hours to evaporate the water and the hydrochloric acid. In the case of gel formation the direct oven drying was employed.

Oxalates with different surface area were tested for decomposition using thermogravimetric and differential thermal analysis (TG-DTA) (Thermo Plus 2 Rigaku, TG8120, Japan). Linear heating rates of 40 – 600 °C /h, and nonlinear heating programs were used. Subsequent holdings were applied to remove the contaminations and residual chlorides from the powders surface. The TG-DTA data were used to optimize nonlinear heating regimes for controlled decomposition, and to chose the temperature and time of holding.

Phase identification of the oxide powders after decomposition was determined by X-ray diffractometry (XRD) (JEOL JDX-3500). The surface area was studied using the BET method (Coulter SA 3100). TEM (JEM-100-CX, Japan), 500 keV was used for studying of powder morphology.

The secondary particles size was analyzed using a Laser Particle Size Analyzer (LSPZ-100, Otsuka Electronics). Micro tip ultrasonication (Shimazu, USP-600) was used to destroy powder agglomerates in suspension. A range of ultrasonication time of 0.5 – 10 min, using 20 kHz and 160 W, was used to determine the effect on agglomerate size.

3. RESULTS AND DISCUSSION

The influence of the precursor solution concentration on the oxalate processing, and on its final surface area, primary and secondary particle size distribution of resulting oxides, was investigated.

A graph of the influence of the initial reagents concentration on the surface area of oxalate powders obtained using the second technological rout is given in Fig. 1. The results show that by changing the reagent concentration, oxalate powders with very different surface area can be produced.
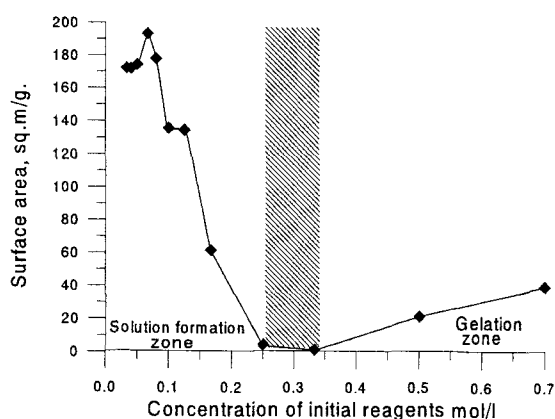

Fig. 1. Zirconia oxalate powders surface area dependence on concentration of initial reagents in aqueous solution

If the content of reagents in solution is more than 0.35 mol/l the process causes the formation of gel, which consists of the circuits of synthesized oxalate powders with different density. The usual processing steps such as filtration of resulting oxalate powder and washing for removing the chloride ions are impossible. HCl can be removed by washing for an extended time with subsequent centrifuging no less than 8 - 10 times. Such a

procedure is very inefficient. This problem is reduced if solution is more diluted and the content of reagents is 0.3 – 0.01 mol/l. Fig. 1 shows that below the gelation zone, an intermediate zone, and a zone of solution formation exist. Oxalates can be precipitated from very diluted aqueous solutions, though it takes 48 – 120 hours in duration because the particle size is very fine. Using of centrifuging is effective for separation of oxalate powder from the aqueous solution of hydrochloric acid. In the same time centrifuging, which was operated at 2000 – 8000 rpm, extremely decreased the surface area of the oxalate powder.

There is the strong dependence of oxalate powders surface area on the concentration of reagents and post-synthesis treatment (Table I). Concentration of 0.1 – 0.02 mol/l and the second technological rout allowed producing of the best oxalate powder with surface area of 140 – 196 sq. m/g.

Table I. Surface area of zirconium oxalate powders prepared using different technological routes

Reagents concentration, mol/l	Surface area of the oxalate powders washed, centrifuged and freeze dried, m^2/g	Surface area of the oxalate powder dried in a furnace, m^2/g
1	20.9	4.2
0.8	24.5	6.3
0.2	8.6	18.2
0.125	33.6	134.7
0.1	41.4	138.4
0.02	39.7	195.8

TG-DTA analysis was applied to determine the characteristics of decomposition of oxalates with different surface areas, and the decomposition with different heating rates to give the minimum primary particle size of oxide. Fig. 2 shows the DTA data for the thermal decomposition of 3mol% yttrium zirconium oxalates with different surface areas.
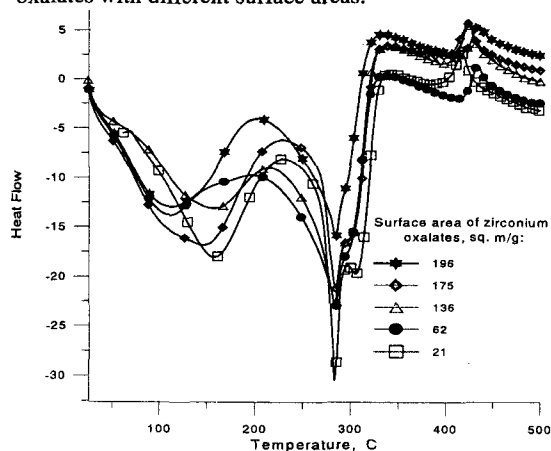

Fig. 2. DTA curves for thermal decomposition of oxalates (Heat flow values are in μV).

There are two endothermic peaks and one exothermic peak. The endothermic peaks represent the stage of water removal and oxalate decomposition. The exothermic peak is the stage of zirconia crystallization.

Oxalates having the finest primary particles began to decompose earlier than the coarser powders, and finished their decomposition at slightly higher temperatures. The temperature intervals of crystallization

increase to higher temperatures with decreasing initial oxalate surface area, but the thermal effect of crystallization was nearly the same 70±2 μV·s/mg for all oxalates. The temperature at which crystallization was completed for all oxalate-derived zirconia powders was not more than 490 °C (DTA and X-ray analysis data).

Thermal decomposition of zirconium oxalates having different surface areas was used to obtain zirconia powders with different properties. Experiments for the decomposition of oxalate powders with different surface areas at an optimized heating regime determined that the best primary and secondary particle size of zirconia powder corresponded to the finest oxalate powder.
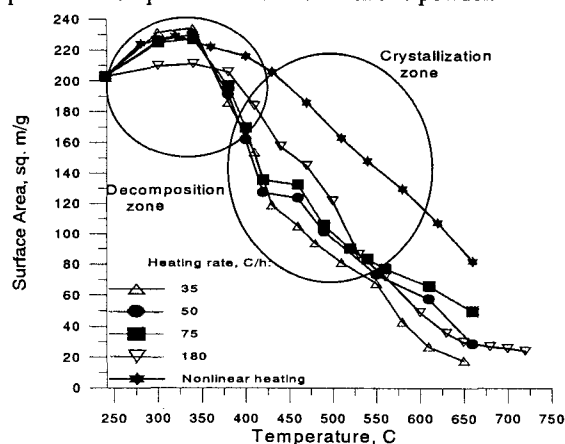

Fig. 3. Evolution of surface area during oxalate decomposition under the nonisothermal conditions.

Surface area evolution during zirconium oxalate decomposition under nonisothermal conditions is shown in Fig. 3. Heating rate 600 °C/h was used up to the temperature of 240 °C. It is clear that low heating rates of 35-75 °C/h produce the maximum surface area. After decomposition was completed at the optimal temperature-time conditions, the surface area began to decrease sharply. This decomposition route is optimal to obtain the finest, weakly agglomerated, amorphous zirconia powders. The crystallization temperature is higher than the temperature for the maximum surface area. For slow heating of yttria stabilized zirconia, the zone of crystallization is 440 – 470 °C, and the maximal surface area zone is 300 - 375 °C. For heating rates of 180 – 600 °C/h, the completion temperature of zirconia synthesis is higher, and the time for oxalate decomposition is shorter. In such heating regimes, the powder surface area has no time to develop and the temperature become reasonable for appearance of the aggregates of coarser primary particles. The temperature of crystallization in such heating regimes is 470 – 530 °C. This high temperature of synthesis completion can be used to obtain nano-size powder. However primary particles are deeply agglomerated. Table II shows the primary particle size distribution and powder agglomerates size (secondary particle size). Zirconia powders obtained from coarse and agglomerated oxalates are also coarse.

The finest primary zirconia can be obtained by decomposition of the oxalate produced by synthesis in

very diluted (0.05 – 0.01 mol/l) precursor solution.

The second main condition of obtaining the finest oxalate powder is the maximizing of the reaction volume during the synthesis. Using of the high rate mixing provides an extremely high liquid flow. Spraying of extremely diluted chlorides solution into reaction zone with applying the previous condition promotes a high degree of dispersion, large local water excess and large reaction volume for the limited amount of reagents. Applying of such synthesis conditions provided the finest and low agglomerated oxalate powder. Applying of spraying is unreasonable if concentration of the reagents is more than 0.05 mol/l.

Initial oxalate processing plays the main role in the creation of the resulting ceramic powder properties. Limitation of the agglomeration of the primary oxalate powders during formation, washing, and drying steps allowed avoiding or limitation of the formation of hard agglomerates during thermal decomposition. Such requirements are more necessary for the final properties of the ceramic powders than the requirement of the lowest temperatures of synthesis and the shortest time of exposition into the high temperature region.

Decomposition at a linear heating rate of 50-75 °C/h allows obtaining of the primary zirconia particles (6 – 8 nm). However this heating rate is very slow and directly after synthesis the agglomerates of finest particles begin to consolidate (Table III). As a result, such powder is non-uniform with wide size distribution. Further technological application of this powder is doubtful. Heating at the highest rates leads to zirconia powder with a coarser primary particle size and strongly agglomerated. This decomposition schedule resulted in the formation of relatively coarse agglomerated powder, because synthesis and crystallization occur simultaneously and hard agglomerates of nano-size particles were formed.

Table II. The primary and secondary particle size range of zirconia obtained from the oxalates.

Surface area of the oxalate powders	Primary particle size	Secondary particle size range
21 m²/g	70±10 nm	300 - 700 nm
62 m²/g	25 ± 5 nm	90 - 500 nm
136 m²/g	17 ± 5 nm	90 - 230 nm
196 m²/g	8 ± 3 nm	70 - 120 nm

Table III. The primary particle size and powder size range of zirconia obtained from oxalate in different heating regimes

Heating regimes	Primary particle size	Secondary particle size range
35 °C/h	8 ± 2 nm	150 - 430 nm
50 °C/h	10 ± 2 nm	70 - 120 nm
180 °C/h	30 ± 5 nm	150 - 550 nm
Nonlinear heating	10 ± 2 nm	60 - 120 nm

Heating with rates, which are most advantageous for decomposition of oxalate in low-temperature region, allowed separate regions for synthesis and crystallization. However, as mentioned above, a dense intermediate phase appeared in the initial stages of decomposition (100–250 °C). The second problem of such a

decomposition-synthesis schedule is the fact that the finest zirconia amorphous particles are very active. Because these primary particles are "dense-packed", their activity before and during crystallization also leads to the formation of agglomerates.

Changes in heating schedule cause changes in the path of synthesis. This includes the several processes: complete decomposition of oxalate with formation of amorphous resulting product, crystallization of product, and coalescence of particles at elevated temperatures. All these processes are superimposed with elevating of heating rates. The rates of 180 – 600 °C/h shift the process into other – highest temperature ranges in comparison with 40 – 120 °C/h heating. Heating with such rates introduced the system into the zone of zirconia synthesis, and immediately into the crystallization zone. As a result, the temperature region of decomposition completing and crystallization region imposes. This schedule resulted in the formation of coarse, agglomerated powder. Consequently there are two synthesis schedules differing both in fineness of the final product, degree of its agglomeration, and temperatures of synthesis and crystallization.

None of the linear heating schedules are in fact the optimum. Only nonlinear heating of the finest oxalate useful for obtaining zirconia powder with a narrow primary particle size distribution of 8 – 10 nm, and with a secondary particle size of 60 – 120 nm. Most of the advantages of the linear regimes were considered, and the drawbacks were avoided in optimized nonlinear heating regime. In the first stage of decomposition, maximum heating rate of 600 °C/h produces a highly porous intermediate product. On the stage of decomposition completion, such heating schedule provides the best temperature-time conditions for formation of finest amorphous product at the lowest temperatures (Fig. 3). The crystallization stage is separated from the synthesis stage, and also occurs at the lowest possible temperature region. This nonlinear heating processing avoids hard agglomeration of super-active fine powders, and avoids aggregation, which results from the relatively high temperature of synthesis and crystallization.

The rate of the primary particles growing is inappreciable when temperature is lower than 800 °C. The uniform, weakly agglomerated, fully stabilized tetragonal (Fig. 4) zirconia powder can be obtained by nonlinear decomposition of the finest oxalate. It is impossible to avoid the agglomeration of finest primary particles. Only obtaining the most uniform agglomerates with the minimum size without milling procedure can be achieved.
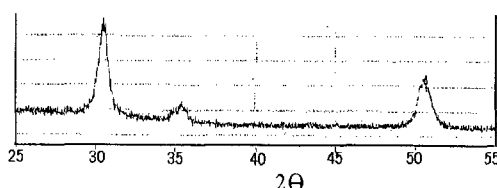

Fig. 4. X-ray diffraction pattern of synthesized 3Y-TZP.

Zirconia-based composite powders with compositions of 3mol% $(0.95Y_2O_3+ 0.05MgO) \cdot 97mol\%$

$(0.95ZrO_2 + 0.05TiO_2)$ and 3mol% $(0.9Y_2O_3+ 0.1MgO) \cdot 97mol\%$ $(0.9ZrO_2 + 0.1TiO_2)$ were synthesized using the produced methodology. The primary particle size and powder agglomerates size distribution of composite powders are same as for the yttria-stabilized zirconia.

The possibility of agglomerates destruction using micro-tip ultrasonic treatment was also studied. Such treatment is important for obtaining a uniform colloid required for slip casting to obtain a green compact with uniform particle distribution. The conclusion was that a treatment of 10 – 15 min is optimal for dispersion, and that longer treatment times are not effective.

4. CONCLUSIONS

A methodology of nano-size 3Y-TZP synthesis through oxalate processing has been explained. The process of zirconium oxalate synthesis was optimized. Fine oxalate powder with the primary particles size of 8–10 nm has been obtained and analyzed for decomposition. The methodology of producing of the nano-powder with narrow secondary particle size distribution has been discussed. The conclusion that initial processing of oxalate as far as powder post-synthesis treatment and decomposition regime plays the equal role in the creation of the resulting ceramic powder properties was made. The requirements for the wet chemical processing are more necessary for the final properties of the ceramic powders than the requirement of the lowest temperatures of synthesis and the shortest time of exposition into the high temperature region.

Controlled non-linear heating schedule was developed and optimized to obtain zirconia nano-powder and yttria-magnesia stabilized zirconia-titania composite powder.

REFERENCES

(1) F. F. Lange J. Am. Ceram. Soc., 72 [1] 3-15 (1989).
(2) T. Uchikoshi, Y. Sakka, K. Ozawa, and K. Hiraga, J. Euro. Ceram. Soc., 18 [6] 669-674, (1998).
(3) K. Lee, A. Sathyagal, P. Carr, and A. McCormick, J. Am. Ceram. Soc., 82[2] 338-42 (1999)
(4) P. Rivas, J. Martines, M. Caracoche, A. Rodriguez, and A. Lopez Garcia, J Am. Ceram. Soc., 81 [1] 200-204 (1998).
(5) C. L. Ong, J. Wang, S. C. Ng, and L. M. Gan, J. Am. Ceram. Soc., 81 [10] 2624-28 (1998).
(6) E. Tani, M. Yoshimura, and S. Somiya, J. Am. Ceram. Soc., 66 [1] 11-14 (1983).
(7) C.L. Ong, J. Wang, L.M. Gan, and S.C. Ng, J. Mater. Sci. Lett., 15, 1680-83 (1996).
(8) S. Gijp, L. Winnubst, and H. Verweij, J. Am. Ceram. Soc., 82 [5] 1175-80 (1999).
(9) O. Vasylkiv, Ph.D. Thesis, Kiev, Ukraine (1997).
(10) A. Ragulya, O. Vasylkiv, and V. Skorokhod, Powder Metallurgy and Metal Ceramics, 3/4 [389] 56-63 (1997).
(11) O. Vasylkiv, A. Ragulya, and V. Skorokhod, Powder Metallurgy and Metal Ceramics, 5/6 [390] 48-55 (1997).
(12) K. Higashi, K. Sonoda, H. Ono, S. Sameshima and Y. Hirata, J. Mater. Res., 14 [3], 342-48 (1999).
(13) N. Kuschevskaia, Powder Metallurgy and Metal Ceramics, 7/8 [402] 47-50 (1998).
(14) J. Van Herle, T. Horita, T. Kawada, N. Sakai, H. Yokokawa, and M. Dokiya, J. Am. Ceram. Soc., 80 [4] 933-40 (1997).
(15) W. Luan, L. Gao, and J. Guo, Nanostructured Materials, 10 [7] 1119-1125 (1998).