A high potential material—zirconia

S SŌMIYA* and T AKIBA†

Department of Materials, Teikyo University of Science and Technology, Uenohara, Yamanashi 409-0133, Japan

†Chichibu Onoda Cement Corp., Kumagaya 360-0843, Japan

Abstract. This is a review as well as an overview of zirconia. Although there are several methods of preparation of zirconia powder, we have described some of the methods of its preparation in this paper, and their application in ceramic bodies.

Keywords. Zirconia; chemical processing; hydrothermal processing; application.

1. Introduction

Powders are very important for ceramic bodies. There are many books and papers related to ceramic powders (Vincenzini 1983; Johnson Jr. 1987; Messing *et al* 1987, 1988, 1990; Hausner *et al* 1989, 1995; Hirano *et al* 1991; Kingery *et al* 1996) etc. A recent book for ceramic powder preparation (Ganguli and Chatterjee 1997) deals with synthetic ceramic powders for all kinds of ceramics.

Concerning science and technology of zirconia, there have been several publications from the First to the Fifth of Proceedings of International Conference on Zirconia (Heuer and Hobbs 1981; Claussen *et al* 1984; Sōmiya *et al* 1988; Heuer 1989; Badwall *et al* 1993). *Zirconia 88* was published by Meriani and Palmonari (1989). Report by Stevens (1986) describes all phases of zirconia. It covers old production processings of zirconia, new methods of processing of zirconia powders, and its uses in ceramics as pigments, refractories, and so on.

Recent review papers by Srinivasan and Davis (1997), Kisi (1998), and Segal (1998) cover aspects in sol-gel chemistry, recent topics in zirconia, and wet chemical processing, respectively.

Developments in zirconia-related studies in Japan are covered in journals of the *New Ceramics* (1992 and 1996) and a text book of zirconia (published by the Ceramic Society, Japan (1984)). High-purity zirconia is finding applications for electric ceramics, optical wave guide, oxygen gas sensors, ceramic parts for engine etc.

2. Mineral resources

Raw materials for zirconia preparation are listed in table 1. These are zircon and baddelyite. Zircon is produced in several countries, but Australia is its

main producer (Yoshiki 1959; Stevens 1986; Suzuki 1998).

3. Methods

In this paper we have described the various methods of zirconia preparation using chemical and hydrothermal processes.

3.1 Chemical processes for zirconia preparation

3.1a *Dry chemical processes:* While Stevens (1986) has described three strategies for zirconia preparation using dry chemical processes, another strategy uses thermal dissociation of zircon.

(i) Chlorination and thermal decomposition

(ii) Alkali oxide decomposition

(iii) Lime fusion

*Author for correspondence

(iv) Thermal dissociation of zircon

Plasma and/or an electric furnace are used for thermal dissociation of zircon. The prevailing condition during dissociation, washing and/or leaching can result in a varied range of properties of the final zirconia powder.

3.1b *Wet chemical processes:* van de Graaf and Burggraaf (1984) have described wet chemical processes for preparation of zirconia as shown in table 2. A description of methods of build up of powders for fine ZrO_2 is listed in table 3.

3.2 Hydrothermal processes for zirconia preparation

Hydrothermal processes for zirconia preparation have been described by Roy (1956), Dawson (1988), Ballman and Laudise (1963), Sheppard (1989), Laudise (1970), Demianets and Lobachev (1984), Brice (1986), Rabenau (1985, 1990), Lobachev (1971), Stambaugh (1983), Sōmiya and Bradt (1987), Sōmiya (1987, 1989, 1990, 1994, 1999), Segal (1989), Byrappa (1991), Kuznetsov (1968), Mupton and Roy (1960), Komarneni *et al* (1986) and Fujiki *et al* (1972).

Major features of powders prepared by hydrothermal processes are listed in table 4. While there are several

Table 1. Mineral resources of zircon and baddelyite.

	Zircon ¹				Baddelyite ¹ Brazil		Zircon ²	Baddelyite ²	Zircon ³ Australia	Baddelyite ³ S. Africa	
	Australia	India	Brazil	USA	Favas	Zinkite				Foskor	Purified
SiO_2	32.60	30.00	31.31	35.00	6.36	18.25	34.2	0.4	32.60	1.5	< 0.5
ZrO_2	66.90	66.34	66.31	62.50	82.64	75.35	64.6	98.0	66.90	96.0	> 99.0
TiO_2	0.12	0.26	1.20	1.75	0.58	1.50	0.32	0.3	0.12	1.0	< 0.3
Al_2O_3	0.43	0.90	0.60	0.12	1.29	3.00	0.25	0.04	0.43		
Fe_2O_3	0.04	0.11	0.11	0.10	5.43	3.19	0.28	0.5		1.0	< 0.05
CaO	Tra	0.14	—	0.10	—	—			Tra		
MgO	0.03	0.22	—	0.05	—	—			0.03		
P_2O_5	0.007	0.13	0.22	0.26	0.75	—					
Ig. loss	—	—	0.18	—	2.41	1.17					

After ¹Yoshiki (1959); ²Suzuki (1998); ³Stevens (1986).

Table 2. Survey of powder characteristics by wet chemical processes (van de Graaf and Burggraaf 1984).

Method	Calcining temp. (°C)	Agglomerate size (mm)	Relative agglomerate density (% theor.)	Agglomerate compression strength (MPa)	Tap density (% theor.)	Surface area ($\text{m}^2 \text{g}^{-1}$)
Hot kerosene	600	2–20	—	≥ 100	18	4
Citrate	650	—	—	—	5	58
Sol-gel microsphere	650	1–20	72	> 400	26	32
Peroxide	600	≤ 50	80	> 400	38	82
Acetone-toluene	650	≤ 100	58	—	32	16
Alkoxide	650	—	23	30	12	90
Chloride	650	—	19	30	10	123

Figure 1. Schematic illustration of zirconia powder by hydrothermal oxidation.

advantages of this process, one of the disadvantages is requirement of a high temperature, high pressure equipment. Under hydrothermal processes, there are several approaches for preparation of zirconia powder.

3.2a Hydrothermal decomposition: One of its examples is shown in table 5 (Reynen *et al* 1981). Chemical reaction is as follows.

Table 3. Methods of build up of powders for fine ZrO_2 (Revised Sōmiya 1999).

- 1) Thermal decomposition
 - a) Heating (evaporation)
 - b) Spray drying
 - c) Flame spraying
 - d) Plasma spraying
 - e) Vapour phase (CVD)
 - f) Freeze drying (cryochemical)
 - g) Hot kerosene drying
 - h) Hot petroleum drying
- 2) Precipitation or hydrolysis
 - a) Neutralization and precipitation
 - b) Homogeneous precipitation
 - c) Coprecipitation
 - d) Salts solution
 - e) Alkoxides
 - f) Sol-gel
- 3) Hydrothermal
 - a) Precipitation (coprecipitation)
 - b) Crystallization
 - c) Decomposition
 - d) Oxidation
 - e) Synthesis
 - f) Electrochemical
 - g) Mechanochemical
 - h) RESA (reactive electrode submerged arc)
 - i) Hydrothermal + microwave
 - j) Hydrothermal + ultrasonic
- 4) Melting and rapid quenching

Figure 2. Schematic illustration of the processes in the hydrothermal oxidation for monoclinic ZrO_2 powder under 1000 kg/cm^2 in Pt capsule and hydrothermal reaction sintering for ZrO_2 .

3.2b Hydrothermal oxidation: Starting materials are zirconium metal chip and/or powder and water or solution of Ca, Mg, Y, etc of nitrate, chloride etc (Sōmiya 1987, 1989, 1990, 1994). Schematic illustration is shown in figures 1 and 2.

Below 200°C , there is no reaction between Zr metal and water. At 300°C , there is formation of hydride. Above 400°C , Zr hydride decomposes to oxide and hydrogen. Microstructure of zirconia powder by this method is shown in figure 3. Solution of Y, Ca, Mg, etc of nitrate are used to stabilize zirconia.

Reaction of zirconium and water is as follows:

3.2c Hydrothermal crystallization: Starting materials are hydrous zirconia prepared from ZrCl_4 solution with 3 N NH_4OH , filtered, dispersed in distilled water and refiltered. The precipitate dried at 120°C for 48 h. Distilled

Table 4. Major features of hydrothermal processes (After Dawson 1988; Segal 1989; Johnson Jr. 1987; Sōmiya 1999).

- 1) Powders are formed directly from solution.
- 2) Powders are anhydrous, crystalline or amorphous. It depends on producing of hydrothermal powder temperature.
- 3) It is able to control particle size by hydrothermal temperature.
- 4) It is able to control particle shape by starting materials.
- 5) It is able to control chemical composition, stoichiometry etc.
- 6) Powders are highly reactive on sintering.
- 7) In many cases, powders do not need calcination.
- 8) In many cases, powders do not need milling process.

Table 5. Hydrothermal decomposition (After Reynen *et al* 1981).

ZrSiO_4	18.43 wt%
$\text{Ca}(\text{OH})_2$	14.9 wt%
NaOH	4.67 wt%
H_2O	62 wt%
Liquid/solid ratio	2
NaOH concentration in the solution	7 wt%
Mol. ratio $\text{Ca}(\text{OH})_2/\text{ZrSiO}_4$	2
Temperature	350°C
Vapour pressure	$170 \times 10^5 \text{ Pa}$
Reaction time	8 h

Table 6. Phases present and crystallite size produced by hydrothermally crystallized powders at 100 MPa for 24 h.

Mineralizer	Temperature (°C)	Average crystallite size (nm)	
		Tetragonal ZrO ₂	Monoclinic ZrO ₂
KF (8 wt%)	200	Not detected	16 nm
KF (8 wt%)	300	Not detected	20 nm
NaOH (30 wt%)	300	Not detected	40 nm
H ₂ O	300	15 nm	17 nm
LiCl (15 wt%)	300	15 nm	19 nm
KBr (10 wt%)	300	13 nm	15 nm

Figure 3. Zirconia powders by hydrothermal oxidation. **a.** Starting material of Zr metal powder. **b.** ZrO₂ powder at 500°C, under 100 MPa after 3 h. **c.** ZrO₂ powder at 500°C under 100 MPa after 24 h. **Figure 4.** TEM of tetragonal ZrO₂ (70%) and monoclinic ZrO₂ (30%) powders prepared by hydrothermal crystallization at 300°C under 100 MPa for 24 h using 15 wt% of LiCl solution.

water and solution of salts are used as mineralizers (Tani 1981, 1983; Yoshimura *et al* 1984). Figure 4 shows the TEM of powders (tetragonal and monoclinic), prepared by hydrothermal crystallization at 300°C under 100 MPa for 24 h using 15 wt% of LiCl solution. Table 6 lists the phases present and crystallite size produced by hydrothermally crystallized powders at 100 MPa for 24 h.

3.2d Hydrothermal homogeneous precipitation: This has been described by Sōmiya *et al* (1986). Chichibu Cement Co. now Chichibu Onoda Cement Corp. (1992) adopted hydrothermal homogeneous precipitation method to produce fine zirconia powders. Schematic representation of this method of processing is shown in figure 5. Figure 6 shows the TEM of powders obtained by this process. Both single crystals and/or soft agglomerated powders can be obtained.

Characteristics of Y₂O₃ containing ZrO₂ by hydrothermal homogeneous precipitation powders are shown in table 7. Microstructure and characteristics of sintered body are shown in figure 7 and table 7, respectively. Grain size of the sintered body produced from hydrothermal homogeneous precipitation is as small as 2–5 nm and contains no pores.

3.2e Hydrothermal electrochemical method: Zirconium metal plate is used as a working electrode (anode). Anodic oxidation was conducted in 200 ml of Y(NO₃)₃ solution using platinum plate as counter electrode and reference electrode. ZrO₂ film forms on Zr metal plate. As low as 250°C, 4.5 V or less, and pH < 5, result in the formation of ZrO₂ on the surface of Zr metal (Yoshimura *et al* 1989).

Table 7. Typical characteristics of Y_2O_3 containing ZrO_2 obtained by hydrothermal homogeneous precipitation.

		ZY30	ZY80	ZP20
<i>Powder</i>				
Chemical composition	ZrO_2 (wt%)	94.7	86.0	> 99.9
	Y_2O_3	5.2	13.9	—
	Al_2O_3	0.010	0.010	0.005
	SiO_2	0.010	0.010	0.005
	Fe_2O_3	0.005	0.005	0.005
	Na_2O	0.001	0.001	0.001
	Cl^-	< 0.01	< 0.01	< 0.01
	Ignition loss	1.5	1.5	8.0
<i>Sintered Body</i>				
Sintered specimens		$1400^\circ\text{C} \times 2 \text{ h}$	$1500^\circ\text{C} \times 2 \text{ h}$	
Bulk density (g/cm^3)		6.05	5.85	
Bending strength ³ (MPa)		1000	300	
Fracture toughness ⁴ ($\text{MPam}^{1/2}$)		6.0	2.5	
Vicker's hardness (GPa)		12.5	11.0	
Thermal expansion		11.0	10.6	
	$20 \sim 1000^\circ\text{C}$ ($\times 10^{-6}/^\circ\text{C}$)			

¹Photo sedimentation method; ²BET method (N_2); ³3-Point bending method; ⁴MI method.

Figure 5. Hydrothermal ZrO_2 process by Chichibu Onoda Cement Corp. **Figure 6.** TEM of ZrO_2 powders produced by hydrothermal homogeneous precipitation (Chichibu Onoda Cement Corp.).

Table 8. XRD analyses of zirconia powders produced by microwave-hydrothermal and conventional hydrothermal techniques (After Komarneni *et al* 1992).

Concentration of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (M)	Temperature ($^{\circ}\text{C}$)	Duration (h)	Reaction products in order of abundance as determined by XRD
Microwave-hydrothermal			
0.5	164	0.5	Poorly crystalline monoclinic ZrO_2 (m- ZrO_2)
0.5	164	2.0	Same as above
1.0	164	2.0	Very poorly crystalline m- ZrO_2
1.0	194	2.0	m- ZrO_2
Conventional-hydrothermal			
1.0	195	2.0

Figure 7. Microstructure of TZP (3 mol% Y_2O_3) sintered at 1400°C for 2 h washed by $\text{C}_2\text{H}_5\text{OH}$ and calcined at 1000°C for 1 h.

3.2f Reactive electrode submerged arc: This process is used for making fine oxide and nonoxide powders (10–1000 nm) (Kumar and Roy 1988, 1989). At the region of arc, in the shortest time, high temperature and high pressure develop.

3.2g Microwave-hydrothermal method: Komarneni *et al* (1992) reported microwave-hydrothermal synthesis of ceramic powders. They used concentration of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ such as 0.5 and/or 1.0 mol, temperature 164°C and 194°C , and very short duration time. Thus they obtained crystalline powder of monoclinic ZrO_2 (table 8).

4. Ideal powder and hydrothermal powder

Tables 9 and 10 show characteristics of an ideal powder and hydrothermal powder. The hydrothermal powder is close to the ideal powder.

Figure 8. Schematic illustration of the electrochemical cell and circuit arrangements for anodic oxidation of Zr metal plate under hydrothermal conditions. (A) Counter electrode (Pt plate), cathode; (B) thermocouple; (C) stirrer; (D) reference electrode (Pt plate); (E) working electrode (Zr plate), anode.**Table 9.** Characteristics of ideal powders.

No agglomeration
Fine powder
Controllable chemical composition
Sphere as far as possible
Homogeneous as far as possible
Narrow particle size distribution
High crystallinity
Good sinterability
Good forming property
Reproducible
Less defects
No stress

Figure 9. Schematic of microprocessor-controlled RESA apparatus for fine powder preparation.

Figure 10. Commercial products of zirconia (After Nikkato and Toray).

Table 10. Characteristics of zirconia powder obtained by hydrothermal homogeneous precipitation.

Homogeneity: good
Grain size: fine grain, less than 1 μm
Coagulation not agglomeration and/or single crystals
Crystallinity: good
Flow ability: forming is good
Sinterability: good
Pores in grain: absent

5. Application

One of the applications of zirconia is shown in figure 10.

References

Badwall S P S, Bannister M J and Hannink R H J (eds) 1993 *Science and technology of zirconia* (Basel, Switzerland: Technomic Publishing Co. Inc.) Vol. V, p. 862

- Ballman A A and Laudise R A 1963 *Hydrothermal growth in the art and science of growing crystals* (ed.) J J Gilman (New York: John Wiley) p. 231
- Brice J C 1986 *Crystal growth processes, hydrothermal growth* (New York: John Wiley) p. 194
- Byrappa K (ed.) 1991 *Hydrothermal growth of crystals* (Oxford: Pergamon Press) p. 363
- Anonymous 1992 *Catalogue of hydrothermal zirconia* (Tokyo: Chichibu Onoda Cement Corp.)
- Claussen N, Rühle M and Heuer A H (eds) 1984 *Science and technology of zirconia* (Am. Ceram. Soc.) Vol. II, p. 842
- Dawson W J 1988 *Am. Ceram. Soc. Bull.* **67** 1673
- Demianets L N and Lobachev V N 1984 in *Modern crystallography* (ed.) A A Chernov (Berlin: Springer Verlag) Vol. III, p. 380
- Fujiki Y, Mitsuhashi T and Suzuki Y 1972 *J. Am. Ceram. Soc.* **55** 223
- Ganguli D and Chatterjee M 1997 *Ceramic powder preparations: A handbook* (Dordrecht: Kluwer) p. 221
- Hausner H, Messing G L and Hirano S (eds) 1989 *Ceramic powder processing science* (Köln: Deutsche Keramische Gesellschaft) p. 960
- Hausner H, Messing G L and Hirano S (eds) 1995 *Ceramic processing science and technology* (Ohio: Am. Ceram. Soc.) p. 820
- Heuer A H 1989 *Am. Ceram. Soc. Bull.* **68** 1658
- Heuer A H and Hobbs L W (eds) 1981 *Science and technology of zirconia* (Ohio: Am. Ceram. Soc.) p. 477
- Hirano S, Messing G L and Hausner H (eds) 1991 *Ceramic powder science* (Ohio: Am. Ceram. Soc.) Vol. IV, p. 758
- Ikegami T et al 1992 *New Ceram.* 60
- Ipponmatsu M 1992 *New Ceram.* 79
- Itoh K and Kakita S 1996 *New Ceram.* 8
- Johnson D W Jr 1987 *Advances in ceramics: ceramic powder science* (Japan: Ceramic Soc.) Vol. 21, p. 3
- Kankawa Y 1992 *New Ceram.* 48
- Kingery J J, Schilling C H and Adair J H (eds) 1996 *Science, technology, commercialization of powder synthesis and shape forming process* (Ohio: Am. Ceram. Soc.) p. 331
- Kisi E (ed.) *Zirconia engineering ceramics old challenges—new ideas* (Switzerland: Trans. Tech.) p. 325
- Komarneni S, Roy R and Adier J A 1986 *Adv. Ceram. Mater.* **1** 87
- Komarneni S, Roy R and Li Q H 1992 *Mater. Res. Bull.* **37** 1393
- Kumar A and Roy R 1989 *J. Am. Ceram. Soc.* **72** 354
- Kuznetsov V A 1968 *J. Cryst. Growth* **3,4** 405
- Laudise R A 1970 *The growth of single crystals* (New Jersey: Prentice-Hall) p. 275
- Lobachev A N (ed.) 1971 *Hydrothermal synthesis of crystals* (New York: Consultant Bureau)
- Meriani S and Palmorari C 1989 *Advances in zirconia science and technology, Zirconia '88* (London: Elsevier Applied Science) p. 379
- Messing G L, Fuller E R Jr and Hausner H (eds) 1988 *Ceramic powder science* (Ohio: Am. Ceram. Soc.) p. 1207
- Messing G L, Hirano S and Hausner H (eds) 1990 *Ceramic powder science* (Ohio: Am. Ceram. Soc.) Vol. III, p. 995
- Messing G L, Mazdiyasn K S, McCauley J W and Haber R A (eds) 1987 *Ceramic powder science* (Ohio: Am. Ceram. Soc.) p. 825

- Mori M 1992 *New Ceram.* 73
- Moriwaki M and Arashi H 1996 *New Ceram.* 37
- Mupton F A and Roy R 1960 *J. Am. Ceram. Soc.* **43** 234
- Nishida H and Nimura I 1996 *New Ceram.* 15
- Ogai M 1992 *New Ceram.* 43
- Ohnishi H and Sakuda M 1996 *New Ceram.* 31
- Ohno M 1996 *New Ceram.* 46
- Rabenau A 1985 *Angew. Chem. Int. Ed. Engl.* 1026
- Rabenau A 1990 *Advanced ceramics* (ed.) S Sōmiya (London: Elsevier Science) Vol. III, p. 163
- Reynen P, Bastins H, Pavlovski B and von Mallinckrodt D 1981 *Advances in ceramics* (Ohio: Am. Ceram. Soc.) Vol. 3, p. 464
- Roy R 1956 *J. Am. Ceram. Soc.* **4** 145
- Sakuma T 1992 *New Ceram.* 55
- Segal D 1989 in *Chemical synthesis of ceramic powder* (Cambridge: Cambridge University) p. 114
- Segal D 1998 in *Zirconia engineering ceramics, old challenges—new ideas* (ed.) E Kisi (Switzerland: Trans. Tech.) p. 241
- Sheppard L M 1989 *Am. Ceram. Soc. Bull.* **68** 979
- Sōmiya S (ed.) 1989 *Hydrothermal reactions for materials science and engineering: An overview of research in Japan* (Amsterdam: Elsevier) p. 505
- Sōmiya S (ed.) 1990 *Advanced ceramics* (London: Elsevier Applied Science) Vol. III, p. 252
- Sōmiya S 1994 *Hydrothermal reactions in inorganic systems* (eds) S Sōmiya, M Doyama and R Roy (Amsterdam: Elsevier) p. 1105
- Sōmiya S 1996 *New Ceram.* 1
- Sōmiya S 1999 *J. Eur. Ceram. Soc.* **19** 81
- Sōmiya S and Bradt R C (eds) 1987 *Fundamental structural ceramics* (Tokyo: Terra Scientific) p. 464
- Sōmiya S, Yoshimura M, Nakai Z, Nakai K, Hishinuma K and Kumaki T 1986 *Ceramic microstructural development of hydrothermal powder and ceramics microstructure* (eds) J A Pask and A Evans (New York: Plenum)
- Sōmiya S, Yamamoto N and Yanagida N (eds) 1988 *Science and technology of zirconia* (Ohio: Am. Ceram. Soc.) p. 1148
- Srinivasan R and Davis B H 1997 *A review of super ceramic material: Synthesis and characterization* (ed.) D L Perry (New York: Plenum) p. 147
- Stambaugh E P 1983 Paper presented at the 85th annual meeting of American Ceramic Society
- Stevens R 1986 *Introduction to zirconia: Zirconia and zirconia ceramics* p. 51
- Sugita E 1992 *New Ceram.* 65
- Suzuki T 1998 *Zirconia: Annual review '98/99* (in Japanese) (Tokyo: Arumu Publishing Co. Ltd.) p. 45
- Takami A 1992 *New Ceram.* 69
- Tani E, Yoshimura M and Sōmiya S 1981 *J. Am. Ceram. Soc.* **64** C181
- Tani E, Yoshimura M and Sōmiya S 1983 *J. Am. Ceram. Soc.* **66** 11
- Van de Graaf M A C G and Burggraaf A G 1984 in *Science and technology of zirconia* (eds) N Claussen, M Rühle and A Heuer (Ohio: Am. Ceram. Soc.) p. 744
- Vincenzini P (ed.) 1983 *Ceramic powders* (Amsterdam: Elsevier Scientific) p. 1025
- Yamamoto T 1996 *New Ceram.* 25
- Yoshimura M and Sōmiya S 1984 *Report of the Lab of Eng. Mat. Tokyo Inst. Technology No. 9* p. 53
- Yoshiki B 1959 *Mineral technol.* (Tokyo: Gi ho do Publishing Co. Ltd.) p. 297
- Yoshimura M, Yoo S E and Sōmiya S 1989 *Report of the Lab. Eng. Mat. Tokyo Inst. Technology No. 14* p. 23