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ZIRCONIA, PROCESSING AND PROPERTIES

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This paper is a review and on overview of zirconia. Zirconia is one of the important oxide ceramics. This paper describes preparation methods and properties of zirconia fine powders.
There are several methods to make fine zirconia powders such as (1) mechanical, (2) thermal decomposition, (3) precipitation or hydrolysis, (4) hydrothermal, (5) melting and rapid quenching, (6) etc. As for hydrothermal, (1) oxidation, (2) crystallization, (3) decomposition, (4) resa, reactive electrode submerged arc, (5) hydrothermal-microwave,(6) hydrothermal electrochemical, (7) precipitation, (8) etc.

Methods for fine ZrO_2 grains, especially hydrothermal methods

Zirconia is one of the important oxide ceramics. There are many methods to make pure zirconia powders such as (1) chlorination and thermal decomposition, (2) alkali oxide decomposition, (3) lime fusion, (4) thermal dissociation, (5) chemical pure and/or fully and partially stabilized zirconia powders. M.A.C.G.Van de Graaf and A.J. Burggraaf are described chemical zirconia. Properties are different from each method. (Table 1.) Concerning hydrothermal, (1) oxidation, Fig.1, (2) crystallization Fig.2, (3) decomposition, (4) precipitation Fig.3, (5) reactive electrode submerged arc, (6) electrochemical Fig.4, (7) addition of microwave, (8) etc.

Processing of hydrothermal homogeneous precipitation is shown in Fig.5 and properties are shown in Table 2. Microstructure of the sintered zirconia is shown in Fig.6.

Important points of hydrothermal products

Important points of hydrothermal powder are shown in Table 3.

Powders by hydrothermal process are many different points from the other methods. These are shown in Table 3.

Table 3

Major differences of powders and processing between hydrothermal and the other technology based on mainly for powder preparation by W.J. Dawson, by D.L. Segal, by D.W. Jhonson, Jr. and S. Sōmiya

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

Table 1 Methods for Fine ZrO_2 Grain

1) Mechanical (Powder Mixing)	a) Ball Milling
	b) Attrition Milling
	c) Vibration Milling
2) Thermal Decomposition	a) Heating (Evaporation)
	b) Spray Drying
	c) Flame Spraying
	d) Plasma Spraying
	e) Vapor Phase (CVD)
	f) Freeze Drying (Cryochemical)
	g) Hot Kerosene Drying
	h) Hot Petroleum Drying
3) Precipitation or Hydrolysis	a) Neutralization and Precipitation
	b) Homogeneous Precipitation
	c) Coprecipitation
	d) Salts Solution
	e) Alkoxides
	f) Sol-Gel
4) Hydrothermal	a) Precipitation (Coprecipitation)
	b) Crystallization
	c) Decomposition
	d) Oxidation
	e) Synthesis
	f) Electrochemical
	g) Mechanochemical
	h) RESA (Reactive Electrode Submerged Arc)
Hydrothermal + Microwave	
Hydrothermal + Ultrasonic	
5) Melting and Rapid Quenching	

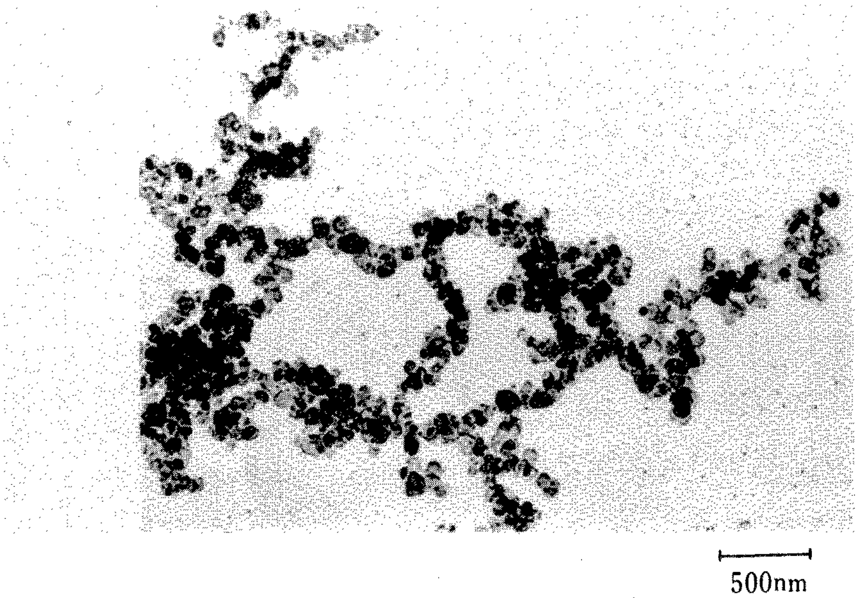

Fig. 1
TEM of Zirconia powder by hydrothermal oxidation, 100 MPa, 500°C, 3h. Zr/O=0.33

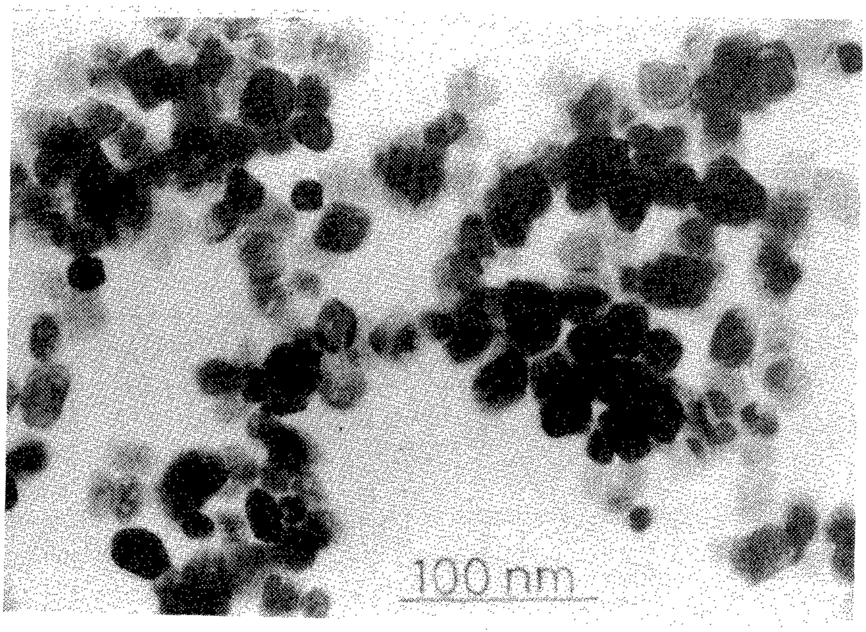

Fig. 2
TEM of Zirconia, (mono) powder by hydrothermal crystallization, 400°C, 100MPa, 24h. using 8 wt % KF sol.

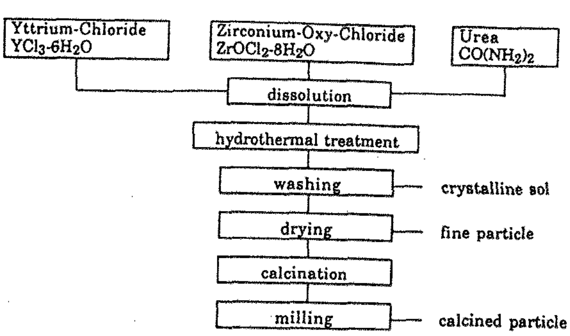

Fig. 5 Hydrothermal ZrO_2 process by Chichibu Onoda

Table 2 Hydrothermal ZrO_2 powders by Chichibu Onoda

Typical characteristics

Powder		ZY30	ZY80	ZP20
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
Crystallite size	(nm)	22	22	20
Average particle size *1)	(μm)	0.5	0.5	1.5
Specific surface area *2)	(m^2/g)	20	25	95
Sintered specimens		1400°C×2hs	1500°C×2hs	
Bulk density	(g/cm^3)	6.05	5.85	
Bending strength *3)	(MPa)	1000	300	
Fracture toughness *4)	($MPam^{1/2}$)	6.0	2.5	
Vicker's hardness	(GPa)	12.5	11.0	
Thermal expansion 20–1000°C	($\times 10^{-6}/°C$)	11.0	10.6	

*1) Photo Sedimentation Method *2) B.E.T. Method(N_2)
*3) 3-Point Bending Method *4) M.I. Method

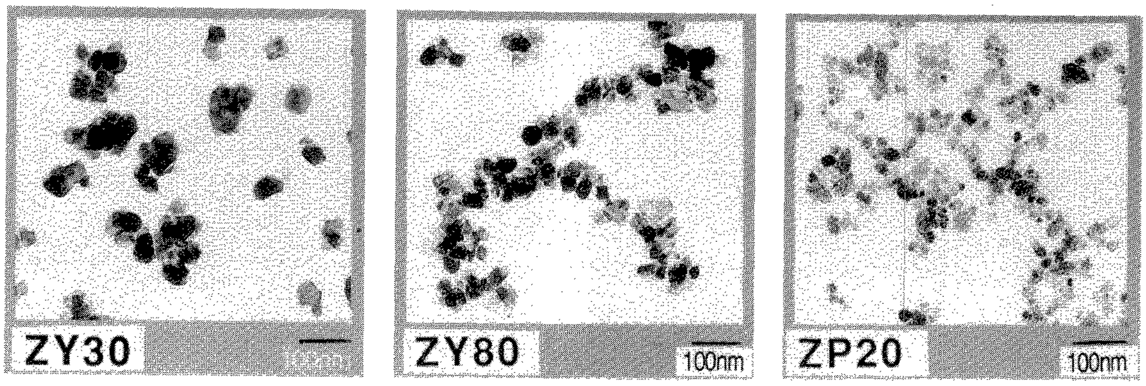

Fig. 3 TEM of hydrothermal homogeneous precipitation zirconia powder (Chichibu Onoda Cement Corp.)

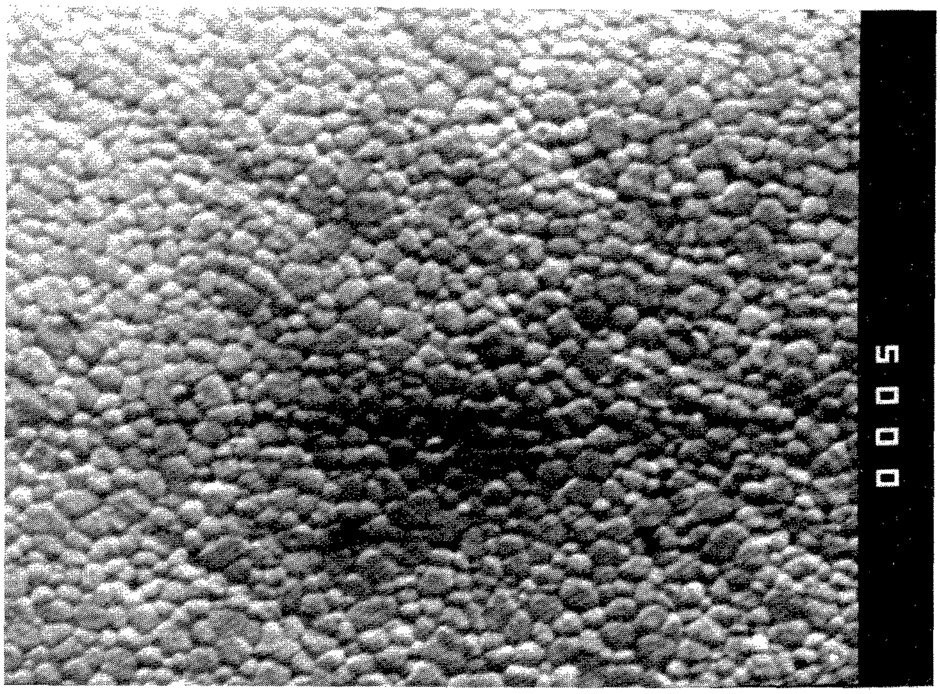

Fig. 6 TEM of the zirconia sintered at 1400°C. for 1h.

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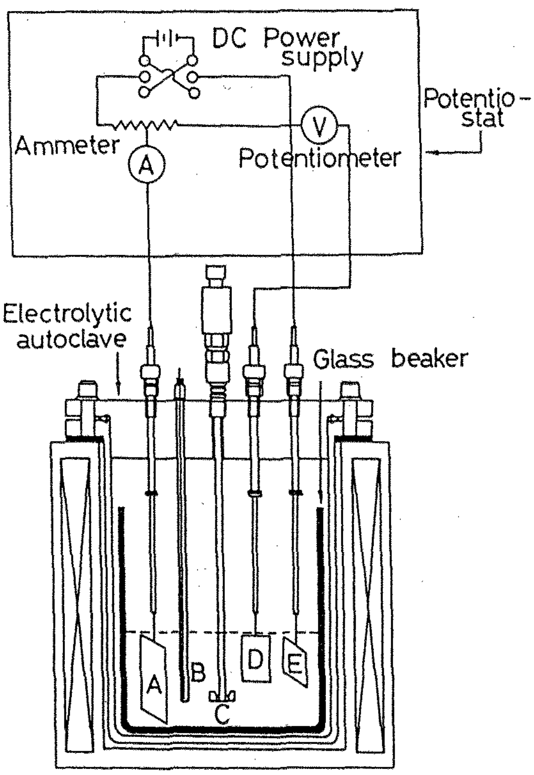
Fig. 4 Schematic illustration of the electrochemical cell and circuit arrangements for hydrothermal electrochemical method

(a) Counter electrode (Pt plate); Cathode, (b) Thermocouple, (c) Stirrer, (d) Reference electrode (Pt plate), (e) Working electrode (Zr plate); Anode.



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