

## A new materials processing—hydrothermal processing

AHIGEYUKI SŌMIYA, K HISHINUMA\* and TOKUJI AKIBA\*

The Nishi Tokyo University, Uenohara Yamanashi 409-01, Japan

\*Ceramics Division, Chichibu Onoda Cement Corp., 5310 Mikajiri, Kumagaya, Saitama 360, Japan

### 1. Introduction

Hydrothermal processing is one of the processings in fields of materials science and engineering. The word hydrothermal comes from geology since 1850.

In the fields of geology, hydrothermal alteration, hydrothermal metamorphism, hydrothermal state, hydrothermal synthesis, hydrothermal water, etc are used (Gary *et al* 1972, 1974). According to Roy (1994), the definition of hydrothermal synthesis involves H<sub>2</sub>O as catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (> 100°C) and pressure (> a few atmosphere). The word 'hydrothermal' is common in the field of geology, but not so common in the field of materials science and technology.

In the US, Europe and USSR, and/or Russia, many researchers have studied hydrothermal synthesis (for example, Morey 1953; Roy and Tuttle 1956; Walkar 1953; Laudise; Rabenau 1988a, b; Lobachev 1971; Givagirov *et al* 1980; Sōmiya 1990, 1991) and published summary and/or review papers. Recently Stamburgh *et al* (1984, 1987), Stamburgh (1986), Komarneni *et al* (1988), Yoshimura *et al* (1982) and Tani *et al* (1981, 1983) have published their results of powder preparation. This paper is one of review and overview related to hydrothermal processing.

### 2. What reactions are the hydrothermal processing in the field of materials science and technology?

In the field of materials science and technology, there are many types of hydrothermal reactions (Sōmiya 1994), namely (i) hydrothermal treatment, (ii) hydrothermal metamorphism (hydrothermal alteration), (iii) hydrothermal crystal growth, (iv) hydrothermal reactions, (v) hydrothermal dehydration, (vi) hydrothermal decomposition, (vii) hydrothermal extraction, (viii) hydrothermal reaction sintering, (ix) hydrothermal hot isostatic pressing, (x) hydrothermal recrystallization, (xi) hydrothermal electrochemical reaction, (xii) hydrothermal corrosion, (xiii) hydrothermal etching, (xiv) hydrothermal mechanochemical reactions, (xv) testing under hydrothermal condition and (xvi) phase equilibria under hydrothermal condition, and so on.

Some hydrothermal reactions, ultrasonic or microwave, are added in the apparatus of hydrothermal bomb. Acceleration of reaction occurs by using ultrasonic or microwave reactions (Fang *et al* 1992; Komarneni *et al* 1992). An entirely new hydrothermal processing called reactive-electrode submerged-arc process (RESA) was introduced by Kumar and Roy (1988, 1989).

Among these hydrothermal reactions, several are related to earth science and some are related to materials science and technology.

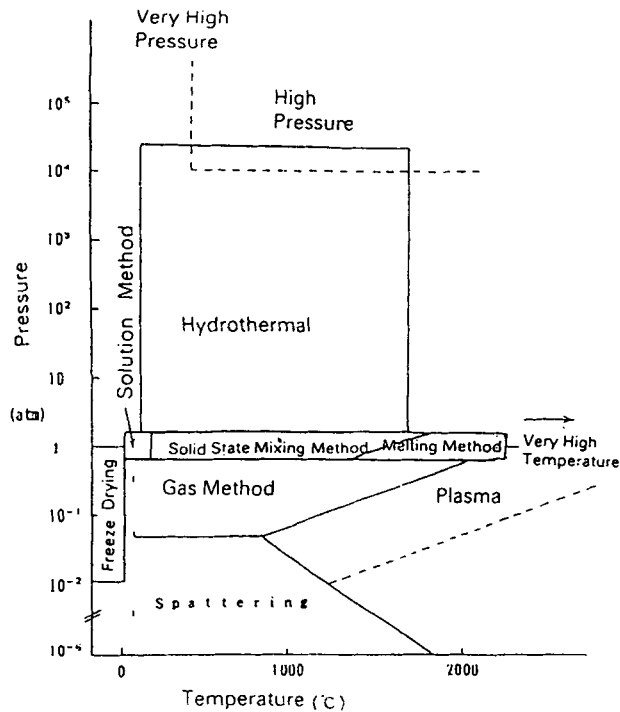


Figure 1. Schematic illustration of temperature and pressure for synthesis of materials.

Figure 1 shows temperature and pressure ranges for hydrothermal processing (Sōmiya 1994). The temperature range is between 1800°C and 100°C and the pressure is less than 15 kb atms and above 1 bar.

### 3. Advantages of hydrothermal processing

Some advantages of the hydrothermal processing are (Sōmiya 1994): (a) higher quality products from impure raw materials, (b) waste materials to change the marketable products, (c) we can use a wide variety of raw materials, (d) less polluting, (e) less capital intensive, (f) less energy intensive and (g) reduced operating costs, etc.

### 4. Equipments of hydrothermal processing

To keep the high temperature and pressure, we need a bomb and a furnace. As for experimental equipmental works, Morey bomb and Tuttle test tube are the most famous. These are shown in figures 2 and 3 (Sōmiya 1994). Relating to metals, there are many heat resistant alloys. We have to select the alloys due to temperature and pressure.

As for heating system, one is external and the other is internal (Holloway 1971; Edgar 1973). Above the pressure of 10 kb, we used internal heated pressure vessel. As for limitation of temperature and pressure, this is shown in table 1 (Laudise and Nielsen 1991). There are three famous companies which produce the bombs in the US (Roy 1994). They are Tem-Pres (they are the best source for test tube bombs and gas

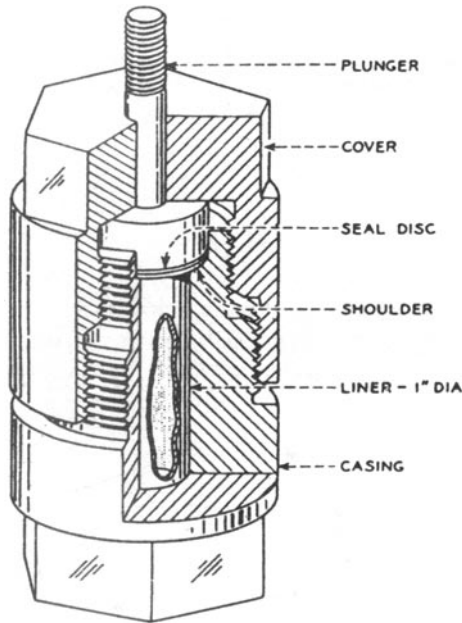


Figure 2. Welded closure vessel (after Morey 1937).

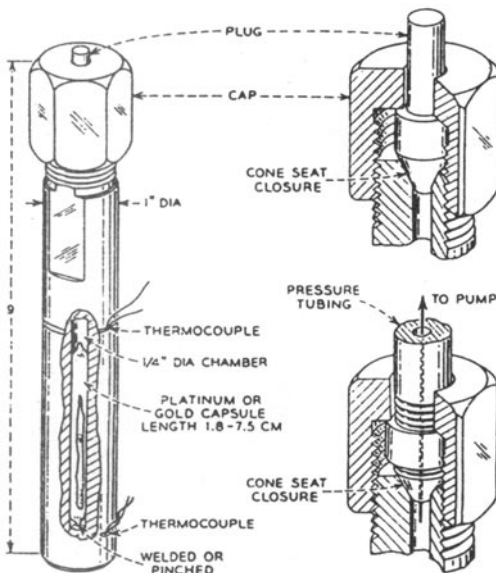


Figure 3. Reaction vessel with a cold-cone seat closure, Tempress Inc., State College, Pennsylvania (after Roy and Tuttle 1956).

intensifiers for specialized gases. A, H<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub> etc.), Autoclave Engineers (this being a moderate sized company, they make a complete line of lab-scale valves, tubing, collars, all fittings for connections, etc. They also make very large autoclaves (1 m 3 m) for chemical processes) and Parr.

## 5. ZrO<sub>2</sub> preparation

There are several methods by which to produce ZrO<sub>2</sub> powder (Sōmiya 1984; Stevens 1986), namely (i) chlorination and thermal decomposition, (ii) alkali oxide decomposition, (iii) plasma decomposition, (iv) fusion method and (v) chemical processing (a. sol-gel, b. hot-kerosene, c. citrate, d. peroxide, e. acetone-toluene, f. alkoxide, g. chloride, h. hydrothermal and i. the others. Each processing has its own advantages and disadvantages.

The following are the characteristics of hydrothermal powders: (i) very fine particles as low as 100–10 nm size, ordinary average is 20 nm, (ii) narrow particle size distribution, (iii) little or no macroscopic agglomeration—if there is any agglomeration of the powders, it is very soft, (iv) homogeneous—distribution dopant is well and it is similar to chemical route of sol-gel powder, (v) chemical composition and purity is control-

**Table 1.** Limits of pressure and temperature of autoclave\*.

	Pressure (MPa)	Temperature (°C)
Pyrex (5 mm inside diameter, 9 mm outside diameter)	0.6	250
Quartz (5 mm inside diameter, 9 mm outside diameter)	0.6	300
Morey type	40	400
Welded Walker-Buehler	200	480
Delta Ring	230	400
Bridgman seal	370	500
Modified Bridgman seal	370	500
Cold-seal test-tube	400	200
Stellite 25	200	800
Rene 41	100	740
TZM	300	1100

\*Modified from Sōmiya (1994)

**Table 2.** Ideal powder.

1) Fine powder less than 1 μm	8) Free flowing
2) Soft or agglomeration	9) Less defects dense particle
3) Narrow particle size distribution	10) Less stress
4) Morphology, sphere	11) Reactivity, sinterability
5) Chemical composition controllable	12) Crystallinity
6) Microstructure controllable	13) Reproducibility
7) Uniformity	14) Process controllable

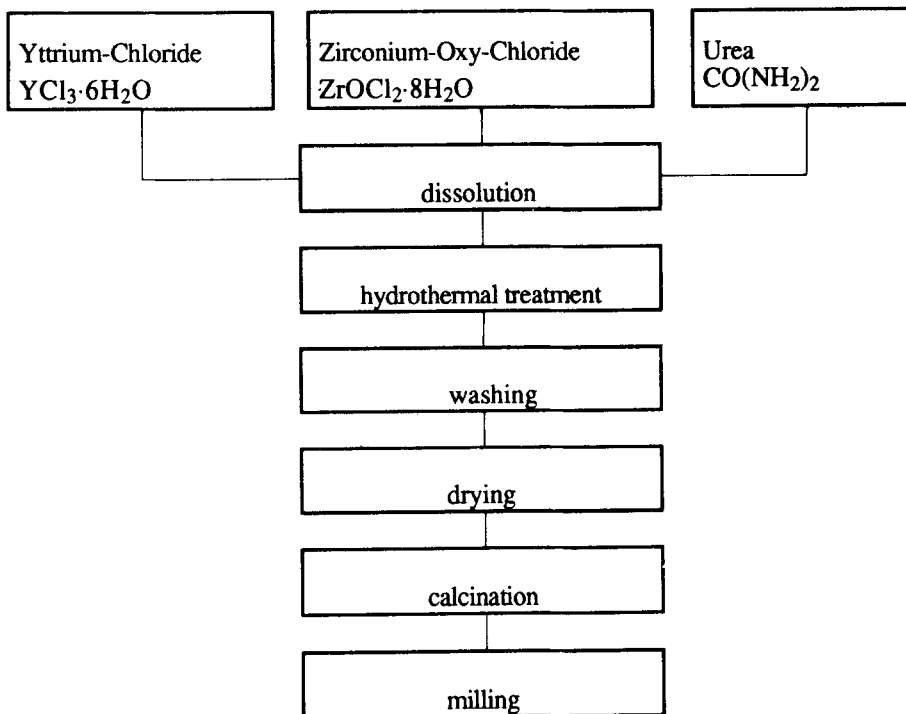
**Table 3.** Characteristics of hydrothermal powders.

1) Very fine particles, 10 ~ 30 nm	6) Controlled morphology
2) Narrow particle size distribution	7) Many cases, single crystals
3) Little or no macroscopic agglomeration	8) Well crystallized particles
4) Homogeneous	9) Low temperature synthesis
5) Chemical composition is controllable	10) Low stress
	11) Free flowing

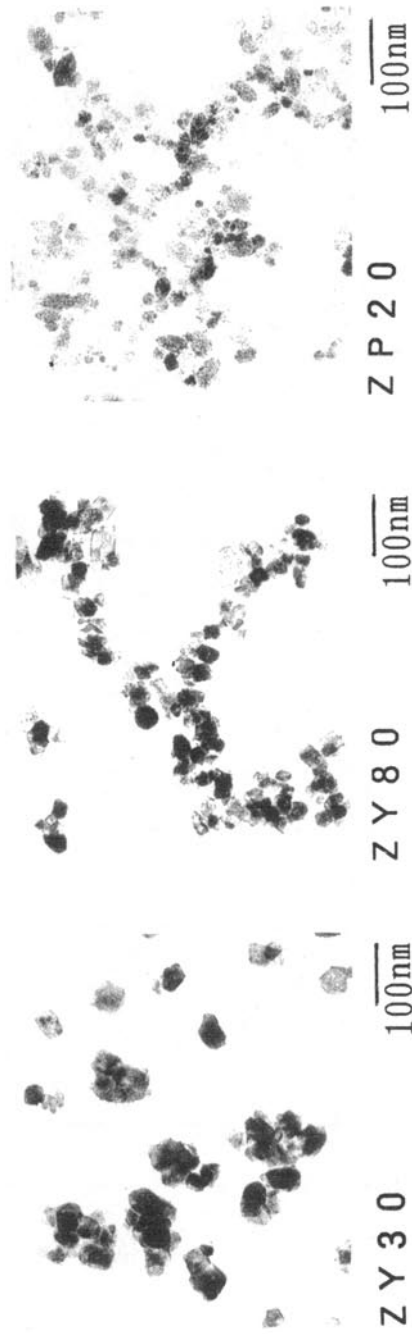
**Table 4.** Typical characteristics.

Powder		ZY30	ZY80	ZP20
Chemical composition	ZrO <sub>2</sub> (wt%)	94.7	86.0	> 99.9
	Y <sub>2</sub> O <sub>3</sub>	5.2	13.9	--
	Al <sub>2</sub> O <sub>3</sub>	0.010	0.010	0.005
	SiO <sub>2</sub>	0.010	0.010	0.005
	Fe <sub>2</sub> O <sub>3</sub>	0.005	0.005	0.005
	Na <sub>2</sub> O	0.001	0.001	0.001
	Cl <sup>-</sup>	< 0.01	< 0.01	< 0.01
	Ignition loss	1.5	1.5	8.0
Crystallite size	(nm)			
Average particle size*	( $\mu$ m)			
Specific surface area**	(m <sup>2</sup> /g)			
Sintered specimens		1400°C × 2h	1500°C × 2h	
Bulk density	(g/cm <sup>3</sup> )			
Bending strength <sup>†</sup>	(MPa)			
Fracture toughness <sup>††</sup>	(MPa <sup>1/2</sup> )			
Vicker's hardness	(GPa)			
Thermal expansion	20 ~ 1000 C ( $\times 10^{-6}$ /C)			

\*Photo sedimentation method; \*\*B.E.T. method (N<sub>2</sub>); <sup>†</sup>3-Point bending method; <sup>††</sup>M.I. Method

**Figure 4.** Hydrothermal process--- schematic flow.

lable. We are able to obtain high purity products, (vi) controlled morphology, (vii) many cases, single crystals, it depends on hydrothermal temperature, (viii) well crystallized particles, (ix) low temperature synthesis and (x) low stress etc.



**Figure 5.** Microstructure of hydrothermal ZrO<sub>2</sub> powders.

According to Schubert and Petzow (1990), hydrothermal powder of  $ZrO_2$  is one of the powders which is close to the ideal powder. As for items for ideal powder, they are shown in table 2. The characteristics of hydrothermal powder are shown in table 3. The Chichibu Onoda Cement Corp. has produced hydrothermal  $ZrO_2$  powder. The process, properties and microstructures are shown in figure 4, table 4 and figure 5, respectively.

## 6. Summary

The hydrothermal processing has emerged as the new materials processing for powder preparation. This describes definition, history, advantages, characteristics of the powder, ideal and hydrothermal powder.

## Acknowledgements

I appreciate MRS-Taiwan for inviting me to present this paper at IUMR-ICA-94 and Chichibu Onoda Cement Corp. for adopting our results for producing  $ZrO_2$  powder by hydrothermal processing.

## References

- Edgar A 1973 *Experimental petrology* (Oxford: Clarendon Press) pp 217
- Fang Y, Agrawal D K, Roy D M, Roy R and Brown P W 1992 *J. Mater. Res.* **7** 2292
- Gary M, McAfee Jr R and Wolf C L (eds) 1972, 1974 *Glossary of geology* (Washington DC: Am. Geological Institute) pp 344–345
- Givagirov E, Bagdasaroy K S, Kuznetsov V A, Demianets L N and Lobachev A N 1980 The growing of crystals, in *Modern crystallography III* (Springer Verlag) pp 380–406
- Holloway J B 1971 *Internal heated pressure vessels* (ed.) G C Ulmer (Springer Verlag) pp 217–258
- Komarneni S, Fregeau E, Breval E and Roy R 1988 *J. Am. Ceram. Soc.* **71** C26
- Komarneni S, Roy R and Li Q H 1992 *Mater. Res. Bull.* **27** 1393
- Kumar A and Roy R 1988 *J. Mater. Res.* **3** 1373
- Kumar A and Roy R 1989 *J. Am. Ceram. Soc.* **72** 354
- Laudise R A *The growth of single crystals* (New Jersey: Prentice Hall Inc.)
- Laudise R A and Nielsen J W 1991 Hydrothermal crystal growth, in *Solid State Physics* (eds) F Seitz and D Twinbull pp 149–222
- Lobachev A N (ed.) 1971 *Hydrothermal synthesis of crystals* (Consultants Bureau) pp 153
- Morey G W 1953 *J. Am. Ceram. Soc.* **36** 379
- Rabenau A 1988a *Angew Chem. Int. Ed.* **24** 1026
- Rabenau A 1988b *J. Mater. Edu.* **10** 543
- Roy R and Tuttle O F 1956 *Phys. Chem. Earth* **1** 138
- Roy R 1994 Personal Communication: *Trans. MRS-Japan* **B19** 1106
- Schubert H and Petzow G 1990 Preparation and characterization of ceramic powders, in *Advanced ceramics III* (ed.) S Sōmiya (Elsevier) pp. 45–56
- Sōmiya S 1984 *Nippon Kinzoku Gakkaiho* **23** 97
- Sōmiya S (ed.) 1990 Hydrothermal preparation of fine powders, in *Advanced ceramics III* (Elsevier) pp 207–243
- Sōmiya S 1991 Powders: Hydrothermal preparation, in *Concise Encyclopedia of advanced ceramic materials* (ed.) R J Brook (Pergamon Press) pp 375–377
- Sōmiya S 1994 *Trans. MRS Japan* **193** 1105
- Stamburgh E P 1986 *Hydrothermal processing for advanced ceramic oxides. Proceeding ICTTE 86, Technology shaping our future.* pp 71–75

- Stamburgh E P *et al* 1984 *Technology for new/improved hydrothermal process, Handbook 1* pp 293
- Stamburgh E P *et al* 1987 *Technology for new/improved hydrothermal process, Handbook 2* pp 411
- Stevens R 1986 An introduction to zirconia, in *Zirconia and zirconia ceramics* (Magnesium Electron Ltd.) pp 9–11
- 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
- Walker A C 1953 *J. Am. Ceram. Soc.* **36** 250
- Yoshimura M, Kikugawa S and Sōmiya S 1982 Preparation of zirconia fine powders by reaction between zirconium metal and high temperature–high pressure solutions, in *High pressure in research and industry* pp. 793–796