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Hydrothermal Reactions in Inorganic Systems

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Abstract.
This paper described what is hydrothermal reactions in inorganic systems.

Introduction

There are many types of hydrothermal reactions in inorganic systems.
There are as follows :

1. Hydrothermal Treatment
2. Hydrothermal Metamorphism (Hydrothermal Alteration)
3. Hydrothermal Crystal Growing
4. Hydrothermal Reaction
5. Hydrothermal Dehydration
6. Hydrothermal Decomposition
7. Hydrothermal Extraction
8. Hydrothermal Reaction Sintering
9. Hydrothermal Hot isostatic Processing
10. Hydrothermal Rrystallization
11. hydrothermal Deposition
12. Hydrothermal Mechanochemical Reaction
13. Hydrothermal Electrochemical Reaction
14. Hydrothermal Corrosion
15. Hydrothermal Etching
16. Testing Under Hydrothermal Condition
17. Phase Equilibria Under Hydrothermal Condition

Why I Study Hydrothermal ?

Because Hydrothermal is one of the interest fields of study.

What is hydrothermal ceramics ? What is the hydrothremal synthesis ? Definition of hydrothermal synthesis by R.Roy [1] is "hydrothermal synthesis" involves H_2O as catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100℃) and pressure (> a few atmosphere).

History of Hydrothermal Experiments

A history of hydrothermal experiments is shown in Table 1 by Rabenau[2]
The first hydrothermal experiment was reported in 1845 by Schafhautl[3] for hydrothermal synthesis of quartz (Fig.1). The second important thing. was by Morey in 1914[4] Morey used the Morey bomb for his experiments. This bomb are able to use up to 300℃ by water vapor of inside volume. The third one was by Tuttle in 1949 [5] .

He used so called test tube type for experiments. We can use two factors indendently, namely pressure and temperature up to the max. 2 bars and 900℃ or 4 bars and 700℃ respectively in a short time.

In 20th centuries, there are many famous scholars, especially Morey[4],Osborn[6],Tuttle[5] Roy[6] , etc. at Geophysical Laboralosy and the Pennsylvania State University for study on phase equilibrium and synthesis of minerals. A stydy on single crystal growth was done by Walker[7] , Laudise[8] , etc. at Bell Laboratories. More recenty Stamburgh [9] of Battlle Memorial Institute was developed to study on hydrothermal experiments for application to mineral technology.

In Europe,Nacken[10] reported for synthesis of quartz at stand point of industrial production. Rabenau[11] published his results,especially hydrothermal synthesis in acidic solution and Frank[12] studied on solutions at high temperature under high pressure.

In the U.S.S.R. and Russia many works for single crystal growth ware done by Lobachev[13] Demianetz,etc. since 1942.

In Japan, Katsurai [15] made a report as early as 1926 for extraction of alumina from aluminous clay and Nagai[16] reported in 1931 to study on hydration of cement. Vapor-phase hydrolysis of esters in 1935 was reportd by Yamazaki [17] .
There were the starting points of hydrothermal works in Japan in early times.

After the world war II, Kunitomi,Ohara and Takeda were studied hydrothermal synthesis of quartz[18].

And then they made synthetic quartz as commercial products.

At present Japan produces a large quantity of synthetic quartz in the world. This is reported by Asahara et al[19] . The other way in Japan after the war, Kiyoura reported decomposition of serpentine [20] .

These were starting points to study hydrothermal experiments in Japan before and after the war.
In korea and China, several paperers appeared in the international conferences and domestic meetings in recently.

Hydrothermal Synthesis

What is the hydrothermal synthesis?
Roy's definition was mentioned above already. Characteristics of hydrothermal synthesis are shown in Table 2.

Application of Hydrothermal Reactions in Ceramics

There are many fields for application of hydrothermal reactions which are shown in Table 3.

Advantages and Disadvantages of Hydrothermal Reactions

There are several points of advantages and disadvantages. As I mentioned before at the previous section, items in Table 2 are advantages. Addition of these items, I would like to add the followings.

1) able to make a high quality and a high purity material
2) able to control purity of the material
3) able to make a good dispersion of the second phase
4) able to make a control of crystal shape
5) able to make a control of particle and grain size
6) able to minimanize the polution problems
7) able to operate low temperature
8) able to make saving energy
9) able to make a small size to a large size of single crystal

Disadvantages of hydrothermal processing are the followings :

1) We need a equipment so called an autoclave for high temperature and high pressure condition.
2) We are not able to watch inside of autoclave in ordinary case.
3) We did not know rate of growth.
   We can estimate the growth rate by experimentally.
4) We do not know chemical factors such as solubility and surface chemistry of solid at hydrothermal conditions.
5) We do not know aging properties of hydroxide.

Pressure and Temperature Ranges of Hydrothermal Processing

Fig.2 shows ranges of pressure and temperature.Hydrothermal reactions need high temperature and high pressure. Temperature is up to 1800℃.
Pressure is up tp 15,000 atm.

Apparatus for Hydrothermal Equipments

Apparatus are one of the important subjects in hydrothermal experiments.
These apparatus are described by Ballman and Laudise[21a), Laudise and Nielson[21b), Givargizov,et al[14), Laudise[8), Rabenau[11abc), Somiya[22), Eitel[23), etc.as a review paper.
Yoshimura, Kubodera, Noma and Sōmiya[24) reported a new type of autoclave, so called mechanochemical reaction bomb which is shown in Fig,3. This apparatus includes steel balls inside of the autoclave.
The balls are effective on grain down sizing, mechanochemical reactions, etc. The second new type autoclave was shown in Fig.4[25) which is included a electrochemical cell inside of the bomb.
The third type is developed by Kumar and Roy[26a)(Fig.5) This is the entirely different from ordinary bomb. A high pressure and a high temperature zone appeared at spark zone in a short time.
Ordinary case for experiments, we use Morey type autoclave(Fig.6) and Tuttle type autoclave (Fig.7). P-T limits for stellite test tube is shown in Fig.8[29)
As for the large volume of autoclave, for industrial scale,Tokyo Communication Co, Ltd. has used the big autoclave of 1005 litter, 8m × 400 ϕ mm. It is shown in Fig.9[19)
Alloys for metals is shown in Table 4-1[21) and Table 4-2[23) . Materials of bombs are very important against high temperature, high pressure and corrosion by chemical attack.

Companies which Produce the Autoclaves

There are famous companies to produce autoclave for hydrothermal reactions.

According to R.Roy [1] there are 3 famous companies, namely.

1. Tem-Pres
   1150 Blanchard Street
   Bellofonte,PA 16823, U.S.A.
   Tel : 814-355-7903
   Fax : 814-355-4089

They are the best source for test tube bombs and gas intensifiers for specialized gases, A, H_2, O_2, NH_3. etc.

2. Autoclave Engineers
   2930 West 22nd Street
   Erie,PA 16512,U.S.A.
   Tel : 814-838-5700
   Fax : 814-833-0145

They are a moderate size company. They make a complete line of lab-scale valves, tubing, collars, all fittings for connections, etc.Also they make very large autoclaves(1m ×3m) for chemical processes.

3. Parr
   211 Fifty-Third Street
   Moline,II 61265,U.S.A.
   Tel : 309-762-7716
   Fax : 309-762-9453

They make simple, low-pressure, low-temperature(300,1000bars)type of autoclaves, 50 ml-1 liter for low- temperature reactions Fig.10 .

Starting Materials

Starting materials are very important for hydrothermal experiments. Requirements for the starting materials are 1) accurate composition, 2) as homogenous as possible, 3) as pure as possible of purity, 4) as fine as possible, etc.

There are 6 types of starting materials which are commonly used in experimemnts : (a) glasses, (b) gels, (c) dry mixtures of oxides, (d) chemical salts such as nitrates,sulphates hydroxids,and carbonate without water, (e) natural minerals and/or natural rocks, (f) pure metal powder and so on.

Concerning powder production, Iwatani's process is shown in Fig.11[26b]. It does not use the autoclave. It is the same of RESA process[26a]. But at the spark point in the water or solutions, it is a place of high temperature and pressure.

Heating Methods and A Batch or A Continuous System

As for hydrothermal process,there are two. One is internal and the other is external heating system. Other way, one is a Batch system and the other is a continuous way[9a,b].
External systems are very common around in the world. Internal heating system is able to pressurize up to 10kb or 1.5kb[27].
They were described by Ballman and Laudise[21a], Laudise and Nielsen[21b], Holloway[27], Edgar[28], Sōmiya[24].

Characteristics of Hydrothermal Processing[9a,b]

Hydrothermal processing has advantages and disadvantages. Characteristics of hydrothermal powders and processing are as follows :

(1) High quality powderds
(2) High purity powders
(3) Reaction rate of powders is high
(4) Dispersion in liquid is good
(5) Shape of powders are able to control
(6) Poluttion for process is the minimum
(7) Process is low temperature operation
(8) Process is energy saving
(9) Volume of equipment is not a big
(10) Able to make a new product

Application of Hydrothermal Products 9a,b)

There are many application by hydrothermal products, namely.

1) High purity materials : ZrO_2, HfO_2 , Al_2O_3 , CeO_2 , Cr_2O_3 , Fe_3O_4 , ZnO , etc.
2) Abrasive powders : Fe_2O_3 , Al_2O_3 , ZrO_2, Cr_2O_3
3) Glaze : ZrO_2
4) Cutting tools : Al_2O_3 , Al_2O_3-ZrO_2 , Al_2O_3-HfO_2 , Al_2O_3-ZrO_2-HfO_2
5) Magnetic materials : Fe_3O_4 , $BaFe_{12}O_{19}$
6) Pigments : TiO_2 , Fe_2O_3
7) Catalysis : TiO_2 containing materials , zeolite
8) Electronics : SiO_2 , $BaTiO_3$, ZnO , ZrO_2
9) Building materials : $CaSiO_3$
10) Gemstones : SiO_2 , ZrO_2
11) Spacer : Al_2O_3
12) Sintered bodies : Iron oxides , ZrO_2 , Cr_2O_3

Shape and Size of the Products

Shape and size of hydrothermal products are
1) Fine powders as single crystals or amorphous materials

2) A large or a small size of single crystal
3) Fiberous material
4) Sintered body
5) Thin film
and so on.

What is ideal powders ?

There is no an ideal powder in the world. But there is a powder which is very close to the ideal powder. Concerning the ideal powder, we have to think the items. They are shown in Table 5.

Fine Powder Products by Hydrothermal Reactions

There are many reports concerning hydrothermal synthesis of inorganic materials.
It is shown in Fig.12. They are elements, hydroxides, single oxides, complex oxides, and many compounds.

Industrial Products by Hydrothermal Reactions

As for industrial products, they are shown in Table 6. They are a bulk body and single crystals.

Hydrothermal Powder Preparations

Powder is very import for cermaics.
Hydrothermal powder is one of the powders which is very close to the ideal powder. What is the ideal powder ? The items are shown in Table 7.

Real Hydrothermal Powder

Real hydrothermal powder has many characteristic points. They are close to the ideal powder. Real powders are 1) less aggromaration, 2) fine less than 1 μm, 3) chemical compositions are pure as possible, 4) sphere as possible, 5) homogeneous as possible, 6) narrow particle size distribution, 7) and so on.

Hydrothermal powder is one of the excellent powders among the real powders. Schubert and Petzow show star diagrams which are produced various processes. These are shown in Fig.13. [30]

Industrial Products of Powders in Japan

There are several companies to produce in Japan the hydrothermal powders as follows :

Chichibu Cement Co.,Ltd.	ZrO_2 6-5 ton/M
Sakai Chemical Industries Co.,Ltd.	perovskites 10ton/ M~17ton/M
Showa Denko Co.,Ltd.	Al_2O_3 1ton/M
Ube Industries Co.,Ltd.	Ba Ferrite 3~5ton/M
Co-op Chemical Co.,Ltd.	Smectite 50ton/Y
Kumimine Industries Co.,Ltd.	Sponite
Res. Union for Kaolinite	Kaolinite
Iwatani Chem. Inds Co.,Ltd.	Al_2O_3 , MgO , Spinel , Al_2O_3 , ZrO_2

The product by Chichibu Cement Co.,Ltd.[31] are shown in Fig.14. Properties of products are also shown in Table 8. Schematic processing is shown in Fig. 15.

Powders by Sakai Chemical Industries Co.,Ltd.[32] Showa Denko K.K.[33] , Ube Industrie[34] ,Iwatani Chemical Industries Co.,Ltd.[26b], and Co-op Chemical Co.,Ltd.[35] , are shown in Fig.16,17,18 and 19,and Table 9.

Hydrothermal Reaction Sintering and Hydrothermal Oxidation

Metal powders are oxidized by high temperature and high pressure water. Then metal is changed to oxide powder. More high temperature, oxide powder is going to sinter.
Schematic illustration is shown in Fig.20 and 21 for ZrO_2.
In the case of ZrO_2, between 400℃ and 800, at about 100bars, monoclinic ZrO_2 powders appeared and at 100bars and 1000℃, they became a sintered body.
Characteristics of hydrothermal reaction sintering are shown in Table 10.

Process of hydrothermal reaction sintering is shown in Table 11. And it is divided 4 groups. It is shown in Table 12. Examples of the hydrothermal reaction sintering are shown in Table 13.

High Oxygen Pressure Experiments

Sōmiya[37] was reported high oxygen pressure experiments for study on phase relations

between CrO_2 and Cr_2O_3. White[38] was described one chapter for high oxygen pressure experiments. One of disadvantages is burning of oganic materials in oxygen gas. Cleaning of equipment is one of important things. In the first place, the equipment is washed by acetone and in the second place, it is washed by destiled water.
A summery reported by White[38] .

Summery

This paper is a overview and a review paper for hydrothermal reactions in inorganic system.

Acckowledgements
I wish to express my appreciation to the staff,students, research fellows at my laboratory and also professor R.Roy who gave good advices.

Table 1 History of Hydrothermal Experiments after Rabenau[2)]

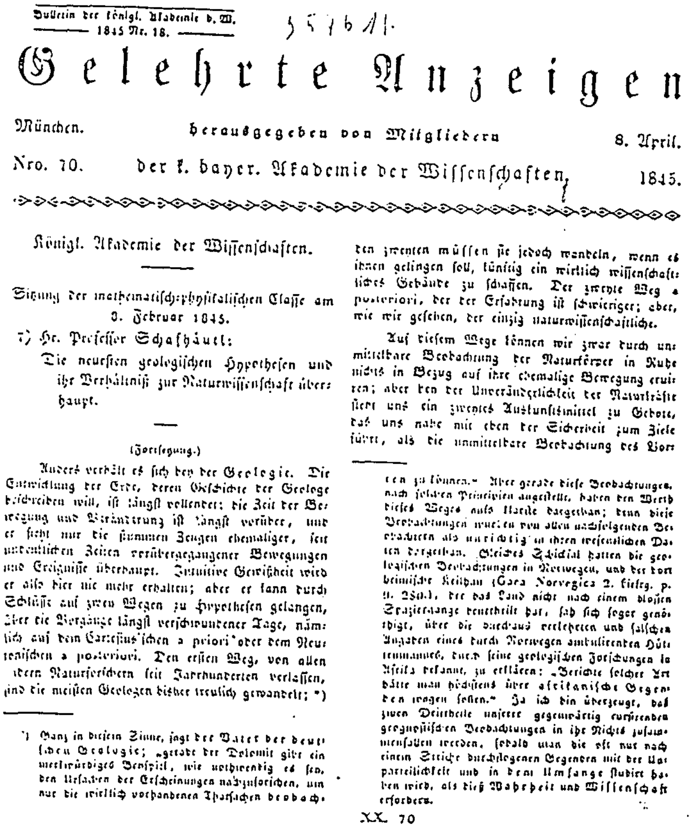
Year Name	Arrangement	Comments
1845 Schafhautl	Papin's degestor	quartz microcrystals
1948 Bunsen	thick-walled glass tubes	carbonates; forerunner of the visual autoclav-ing
1851 de Sénarmont	glass ampoules in autoclave	mineral carbonates, sulfates,sulfides,fluo-rides; founder of hy-drothermal synthesis in geological sciences
1873 von Chrustschoff	noble metal lining	protection against cor-rosive solvents
1914 Morey	Morey-type autoclave	"closed"system;stand-ard
1923 Smith,Adams	internally heated autoclave	very high pressures and temperatures : ≧10kbar,≧1400℃
1943 Nacken	Foundation for the industrial quartz growth	introduction of hydro-thermal synthesis into solid state physics
1949 Tuttle	"cold seal" or test tube arrangement	external pressure regu-lation and measure ment. More extensive working range than Morey.Standard
1973 Capponi	modified belt apparatus	extremely high pressres and temperatures: ≧10kbar,1500℃

Table 2 Chararistics of Hydrothermal Synthesis

1) able to synthesis low temperature form
2) able to make metastale form
3) able to make a composite like organics and inorganic mixture
4) able to make a material which has a very high vapor

Table 3 Application of Hydrothermal Reactions in Ceramics

1) Study on phase equilibrium
2) Preparation of ultrafine single crystalls
3) Preparatin of ultrafine amorphous materials
4) Single crystal growth
5) Hydrothermal reaction sintering
6) Hydrothermal sintering
7) Hydrothermal crystallization
8) Disolving-corrosion
9) Etching
10) Preparation of composites....Inorganic+ Organic
11) Testing under hydrothermal condition
12) Making thin films
13) Radio-active waste management



Bulletin der königl. Akademie d. W.
1845 Nr. 18.

55761.

Gelehrte Anzeigen

München. herausgegeben von Mitgliedern 8. April.
Nro. 70. der k. bayer. Akademie der Wissenschaften. 1845.

Königl. Akademie der Wissenschaften.

Sitzung der mathematisch-physikalischen Classe am 8. Februar 1845.

7) Hr. Professor Schafhäutl:

Die neuesten geologischen Hypothesen und ihr Verhältniß zur Naturwissenschaft überhaupt.

(Fortsetzung.)

Anders verhält es sich bey der Geologie. Die Entwicklung der Erde, deren Geschichte der Geologe beschreiben will, ist längst vollendet; die Zeit der Bewegung und Veränderung ist längst vorüber, und er sieht nur die stummen Zeugen ehemaliger, seit undenklichen Zeiten vorübergegangener Bewegungen und Ereignisse überhaupt. Intuitive Gewißheit wird er also hier nie mehr erhalten; aber er kann durch Schlüsse auf zwey Wegen zu Hypothesen gelangen, über die Vorgänge längst verschwundener Tage, nämlich auf dem Cartesius'schen a priori oder dem Newtonischen a posteriori. Den ersten Weg, von allen andern Naturforschern seit Jahrhunderten verlassen, sind die meisten Geologen bisher treulich gewandelt; *) den zweyten müssen sie jedoch wandeln, wenn es ihnen gelingen soll, künftig ein wirklich wissenschaftliches Gebäude zu schaffen. Der zweyte Weg a posteriori, der der Erfahrung ist schwieriger; aber, wie wir gesehen, der einzig naturwissenschaftliche.

Auf diesem Wege können wir zwar durch unmittelbare Beobachtung der Naturkörper in Ruhe nichts in Bezug auf ihre ehemalige Bewegung eruiren; aber bey der Unveränderlichkeit der Naturkräfte steht uns ein zweytes Auskunftsmittel zu Gebote, das uns nahe mit eben der Sicherheit zum Ziele führt, als die unmittelbare Beobachtung des Vor-

*) Ganz in diesem Sinne, sagt der Vater der deutschen Geologie; „gerade der Dolomit gibt ein merkwürdiges Beyspiel, wie nothwendig es sey, den Ursachen der Erscheinungen nachzuforschen, um nur die wirklich vorhandenen Thatsachen beobachten zu können.“ Aber gerade diese Beobachtungen, nach solchen Principien angestellt, haben den Werth dieses Weges aufs klarste dargethan; denn diese Beobachtungen wurden von allen nachfolgenden Beobachtern als unrichtig in ihren wesentlichen Daten dargethan. Gleiches Schicksal hatten die geologischen Beobachtungen in Norwegen, und der dort heimische Keilhau (Gaea Norvegica 2. Liefrg. p. u. 250.), der das Land nicht nach einem bloßen Spaziergange beurtheilt hat, sah sich sogar genöthigt, über die durchaus verkehrten und falschen Angaben eines durch Norwegen ambulirenden Hüttenmannes, durch seine geologischen Forschungen in Afrika bekannt, zu erklären: „Berichte solcher Art hätte man höchstens über afrikanische Gegenden wagen sollen.“ Ja ich bin überzeugt, daß zwey Dritttheile unserer gegenwärtig cursirenden geognostischen Beobachtungen in ihr Nichts zusammenfallen werden, sobald man die oft nur nach einem Striche durchflogenen Gegenden mit der Unpartheilichkeit und in dem Umfange studirt haben wird, als dieß Wahrheit und Wissenschaft erfordern.

XX. 70

Fig.1 The First Report on Hydrothermal Reactions

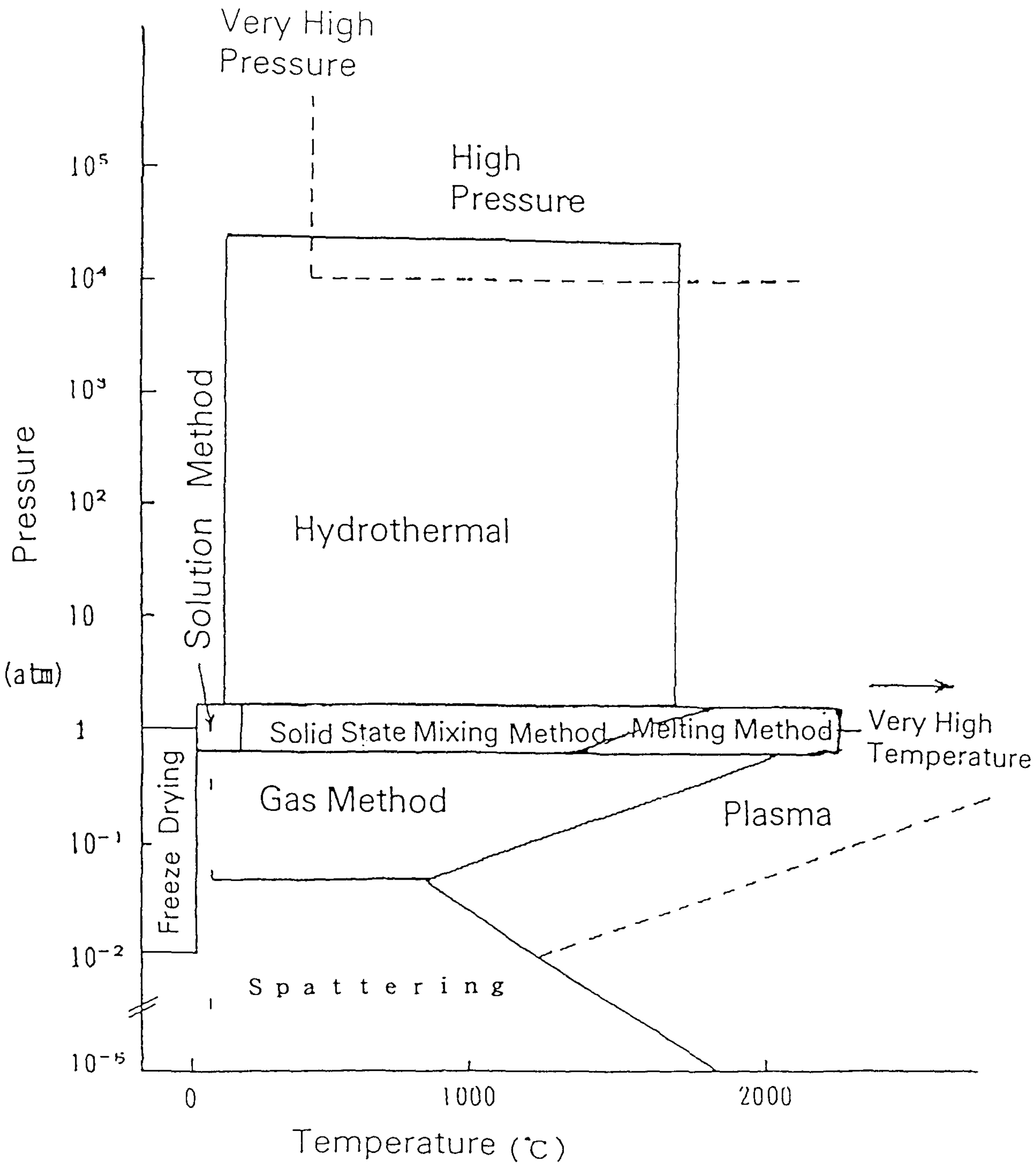


Fig.2 Schematic Illustration of Temperature and Pressure for Synthesis of Materials

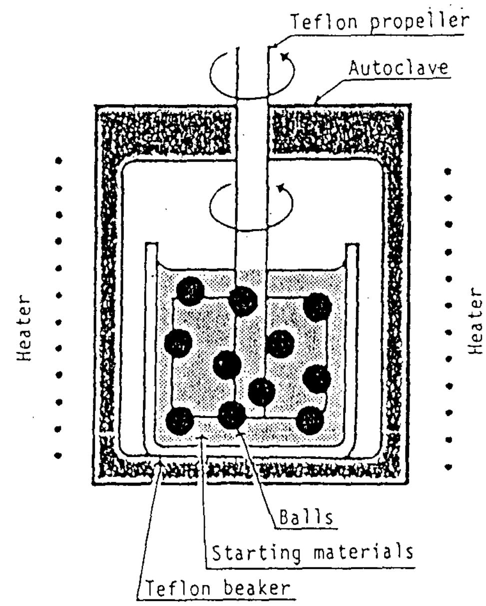


Fig. 3 Experimental apparatus with steel balls.

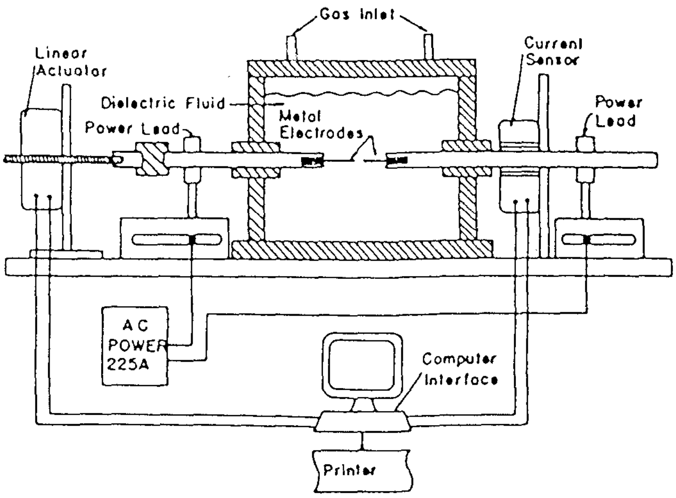


Fig.5 Schematic of microprocessor-controlled RESA apparatus for fine-powder preparation.

26a)
A. Kumar and R. Roy
J.Am. Ceram. Soc 72 (1989) 354-356
and J. Mat.Res 3[6] (1988) 1373-1377

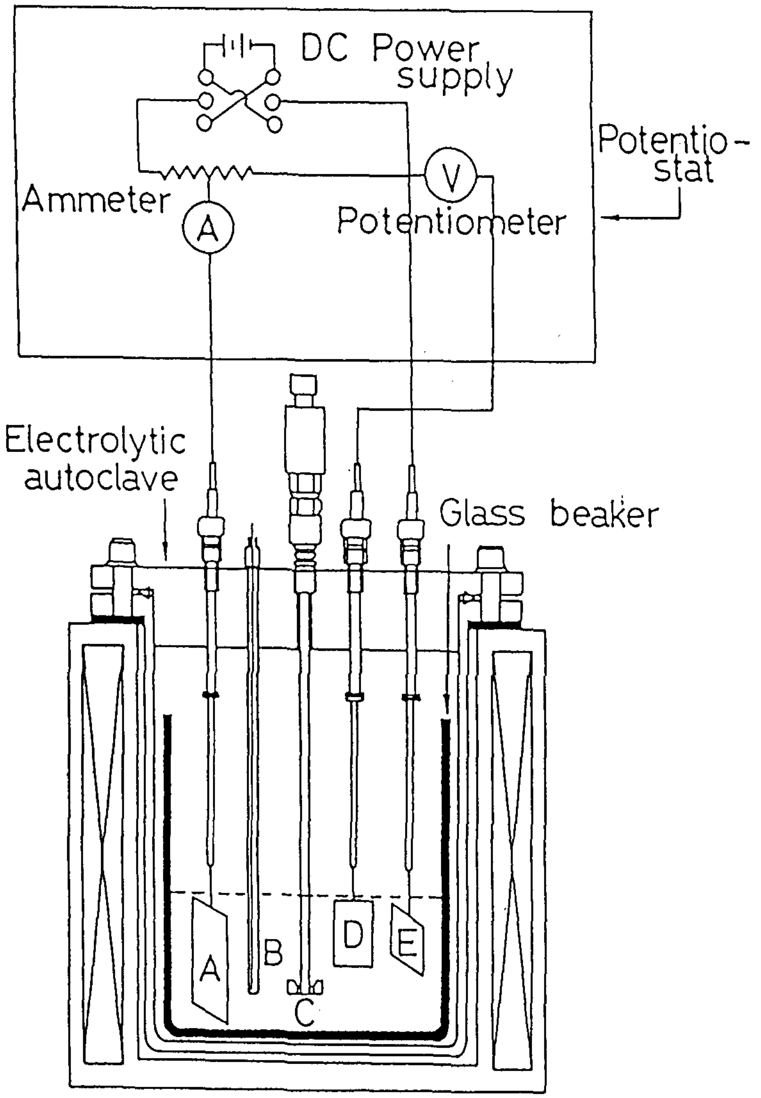


Fig. 4 Schematic illustration of the electrochemical cell and circuit arrangments for anodic oxidation of Zr metal plate under hydrothermal conditions.[34]
(a) Counter electrode (Pt plate) ; Cathode, (b) Thermocouple, (c) Stirrer, (d) Reference electrode (Pt plate), (e) Working electrode (Zr plate); Anode.

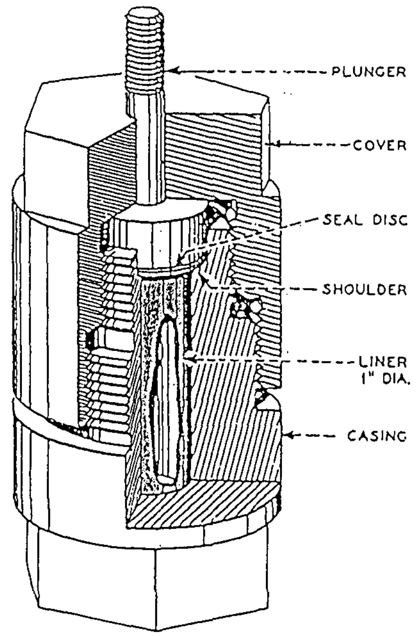


Fig.6 Autoclave with flat plate closure(after Morey)[4)]

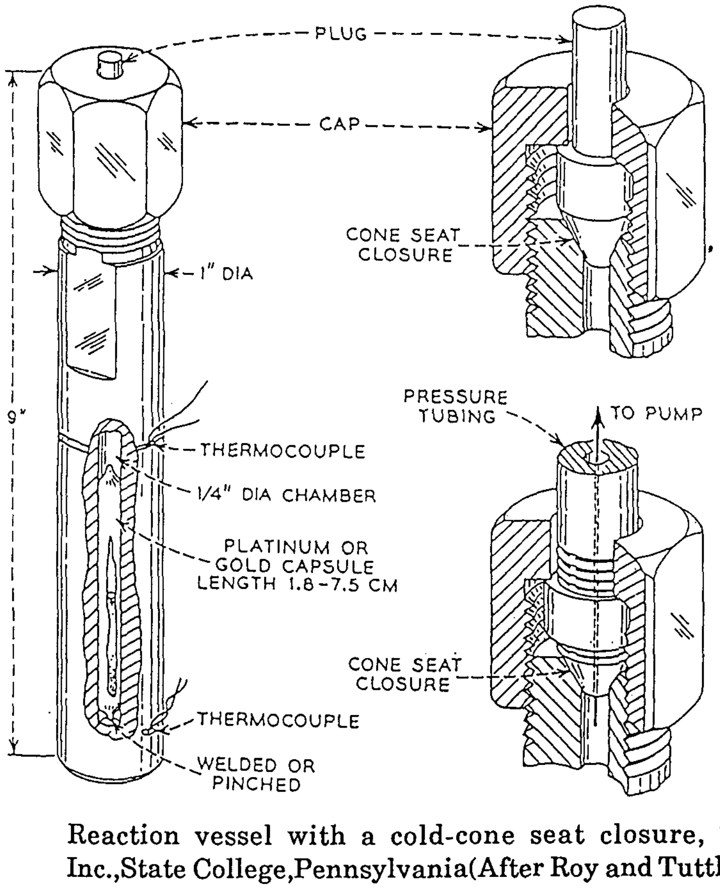


Fig.7 Reaction vessel with a cold-cone seat closure, Tempress Inc.,State College,Pennsylvania(After Roy and Tuttle,1956)[6)]

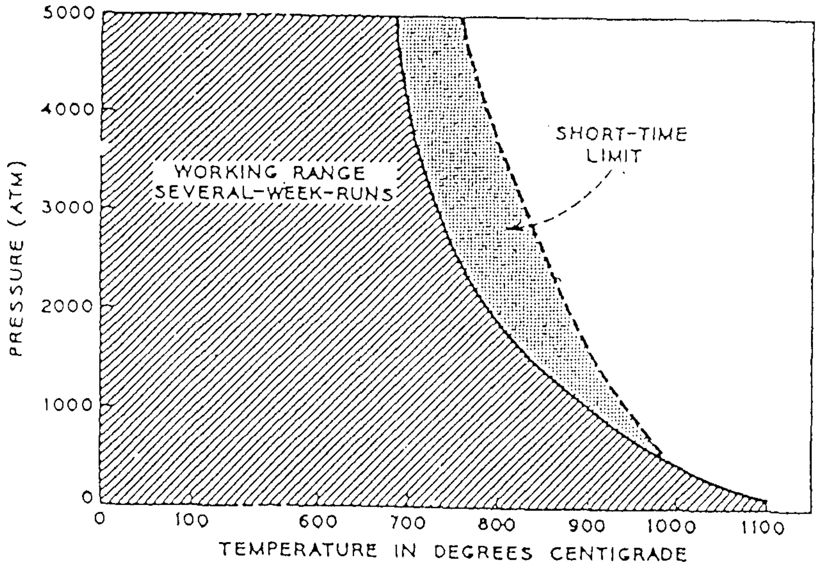


Fig.8 P-T limits for stellite vessel,Catalog Information,Tempress Inc.,State College,Pennsylvania.[29a]

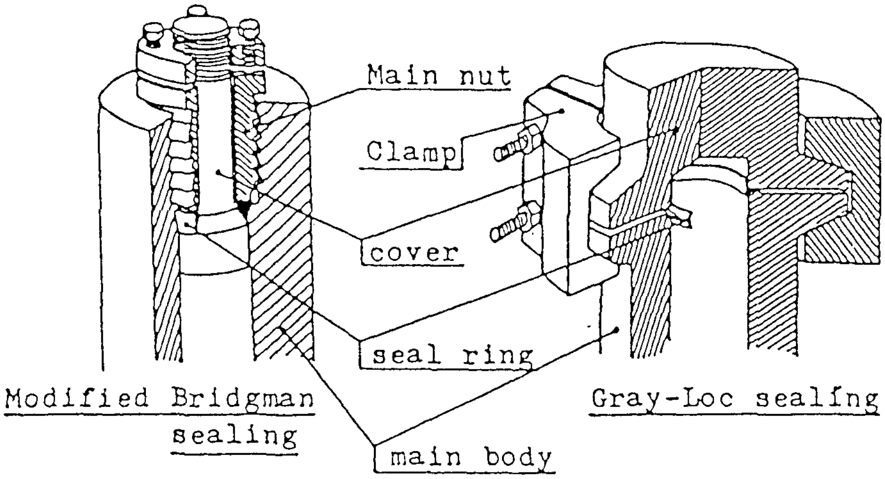


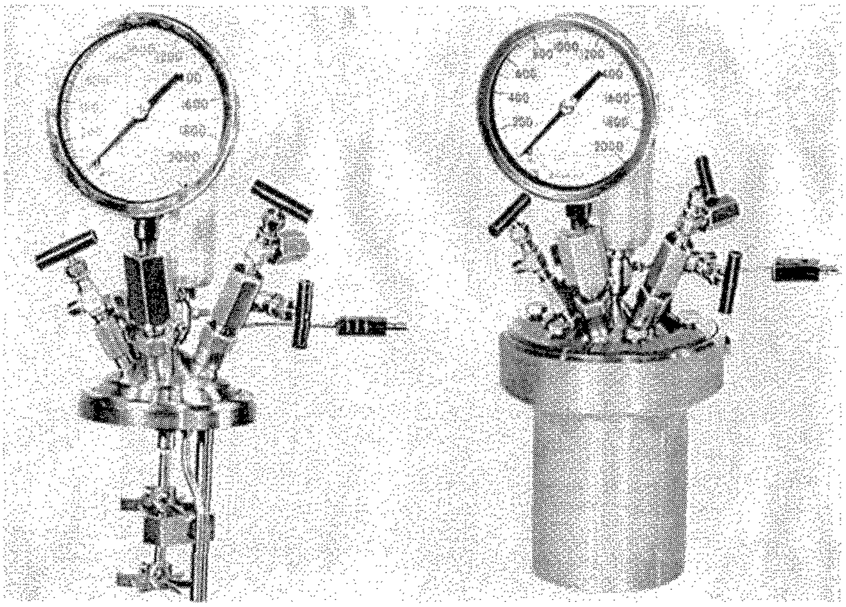
Fig.9 Comparison for self-and pressure-energized sealing systems applied to large autoclaves.(Modified Bridgman seal and Gray-Loc seal) (After Asahara,et al)[19]

Table 4-1 Alloys for Autoclave(1)[21)]

	C	Mn	Si	Cr	Ni	Co	Mo	W	Nb	Ti	Al	
Low carbon steel	0.15	0.5										
4140 Steel	0.4	0.9	0.2	1			0.2					
Stainless Steel 301	0.08	0.06	0.6	15	9							
19-9-DL	0.3	1.1	0.6	19	9		1.2	1.2	0.4	0.3		
Croloy 15-5-N	0.10	1.5	0.5	15	15		1.5	1.5	1.0			N0.12
Timken 17-22-A	0.30	0.59	0.66	1.25	0.25		0.51				0.22	Cu 0.14
Inconel X	0.05	0.5	0.4	14.5	Bal	1.0				2.5	0.8	Fe ?
Udimet 500	0.08	0.2	0.2	20	Bal	15	3.5			3	3	
Stellite 25				19-21	9-11			14-16				
Renè 25				19	Bal	11	10					
TZM							Bal			0.5		Zr 0.08

Table 4-2 Nominal Chemical Composition of Pressure Vessel Materials (2)[29b)]

	Major Elements — Percent					
Material	Fe	NI	Cr	Mo	Mn	Other
T316 Stainless Steel	65	12	17	2.5	2.0	Si 1.0
Alloy 20CB	35	34	20	2.5	2.0	Cu 3.5, Cb 1.0 max
Alloy 400	1.2	66				Cu 31.5
Alloy 600	8	76	15.5			
Alloy B-2	2	66	1	28	1	Co 1.0
Alloy C-276	6.5	53	15.5	16	1	W 4.0, Co 2.5
Nickel 200		99				
Titanium Grade 4		Commercially pure titanium				Ti 99 min
Zirconium Grade 705		Zr 95.5 min, Hf 4.5 max, Co 2.5				



Head Assembly for 1000 ml Bomb *1000 ml Bomb Assembly with Magnetic Drive*

Fig. 10 Parr bomb

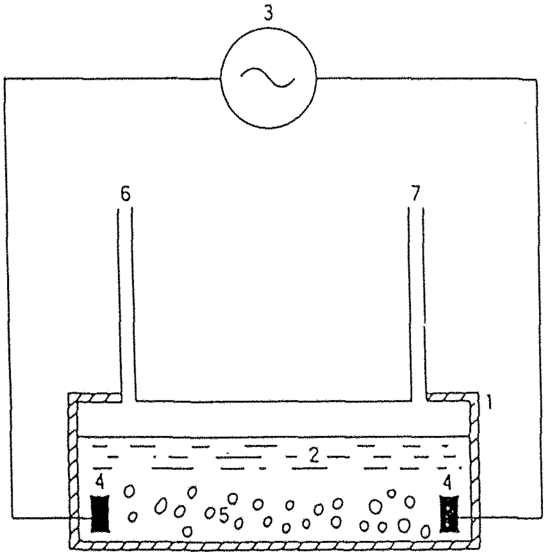


Fig. 11 Schematic Illustration of Iwatani process
1. Reaction vessel
2. Water
3. Spark generator
4.Electrodes
5. Metal Pellots
6. Metal and water supply
7. Discharge of powder and gas

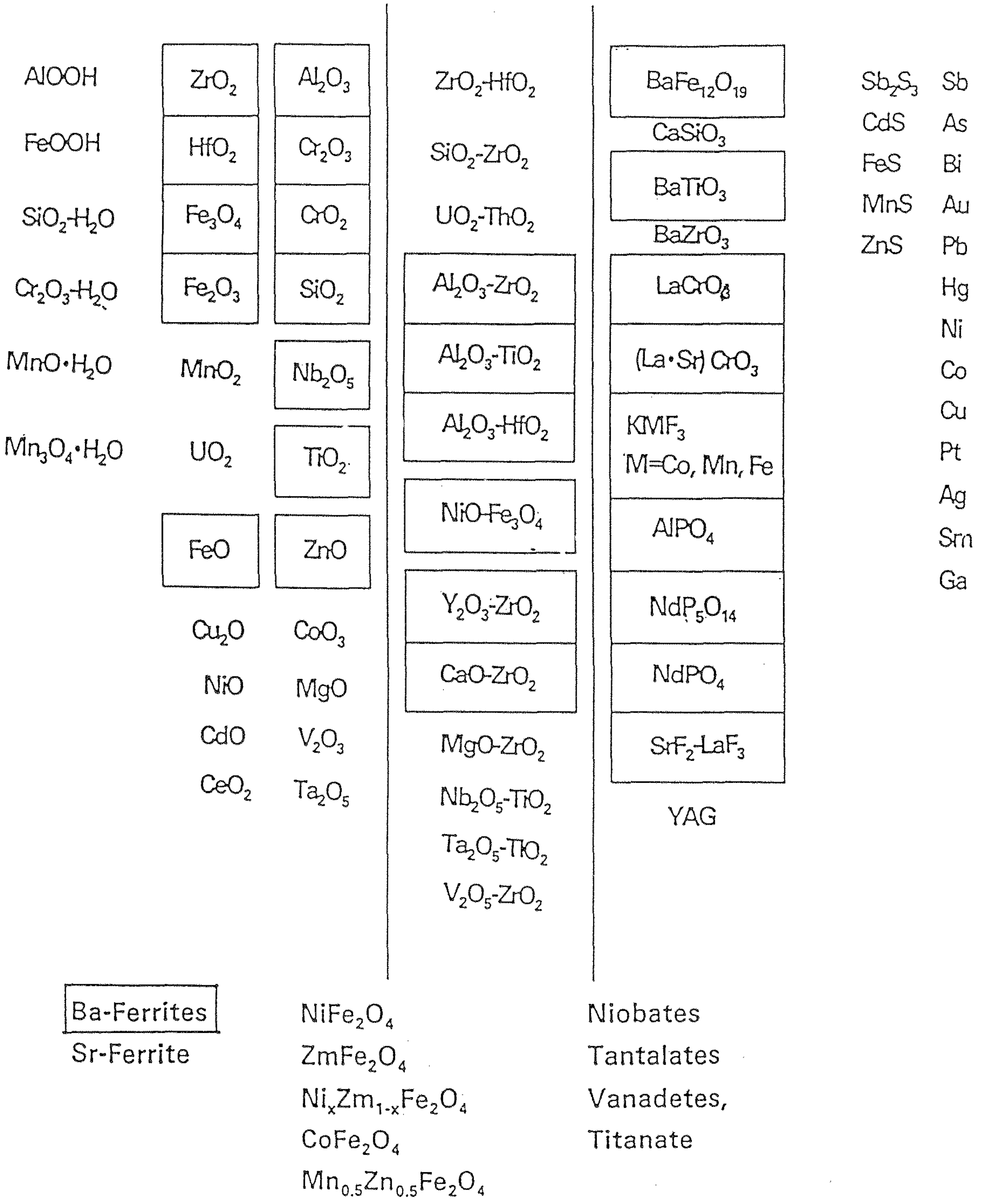


Fig. 12 Fine powders Synthesized Under HydrothermalCondition.
[ ]: We have studied in my 1ob.

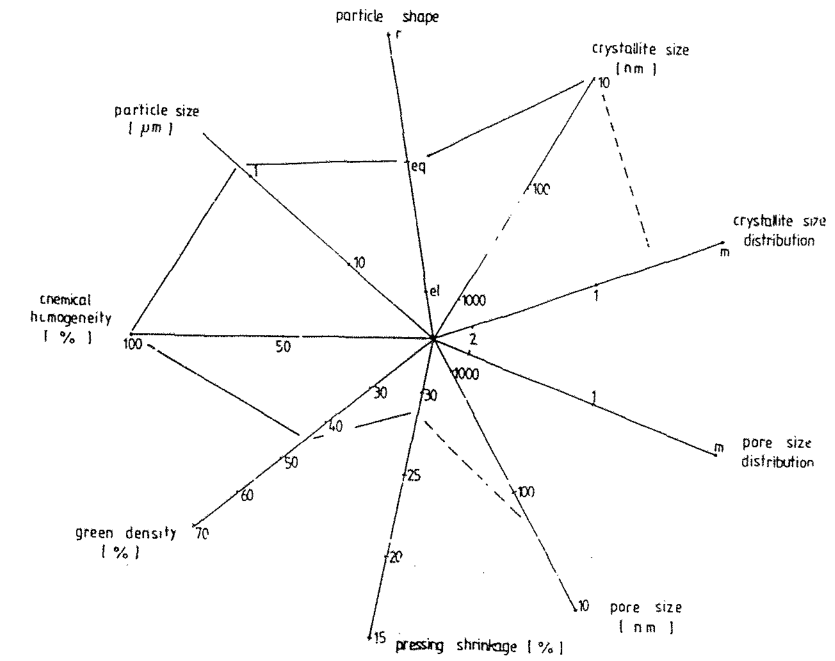


Fig. 13a[30)] Star diagram of different powder properties. Alkoxide powders are chemically homogeneous and have very fine crystallites but their technical handleability is difficult. After Schubert and Petzow.[30)]

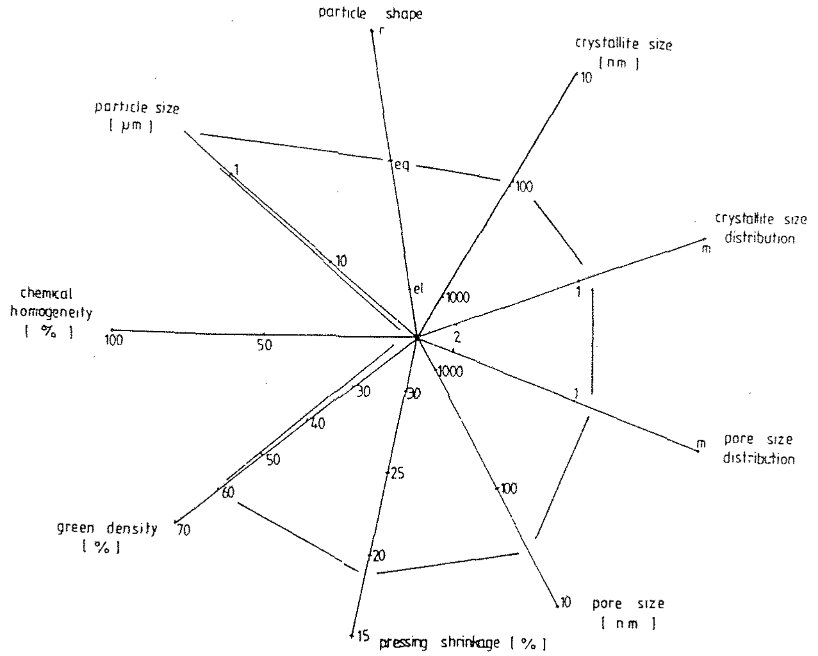


Fig. 13b[30)] Star diagram of different powder properties. Oxide mixtures are chemically completely inhomogeneous but they can be handled easily. After Schubert and Petzow.[30)]

Table 8. Hydrothermal ZrO2 Powders by Chichibu Cement Co.,Ltd.

特　性/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^-	<0.010	<0.010	<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	28	95
Sintered specimens		1400°C×2hs	1500°C×2hs	
Bulk density	(g/cm^3)	6.02	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	9.0	

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

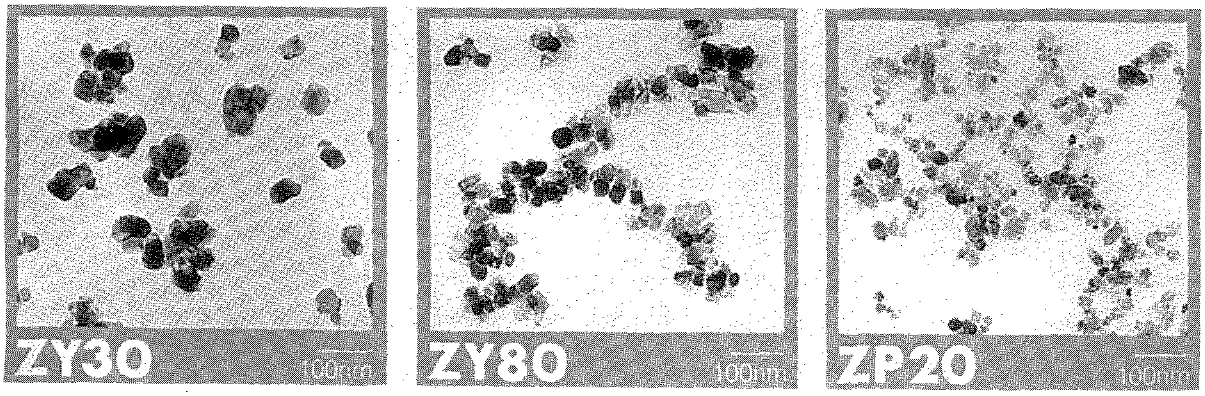


Fig. 14 Industrial Products of Hydrothermal ZrO2 Powders by Chichibu Cement Co.,Ltd. Japan.

Hydrothermal process schematic flow

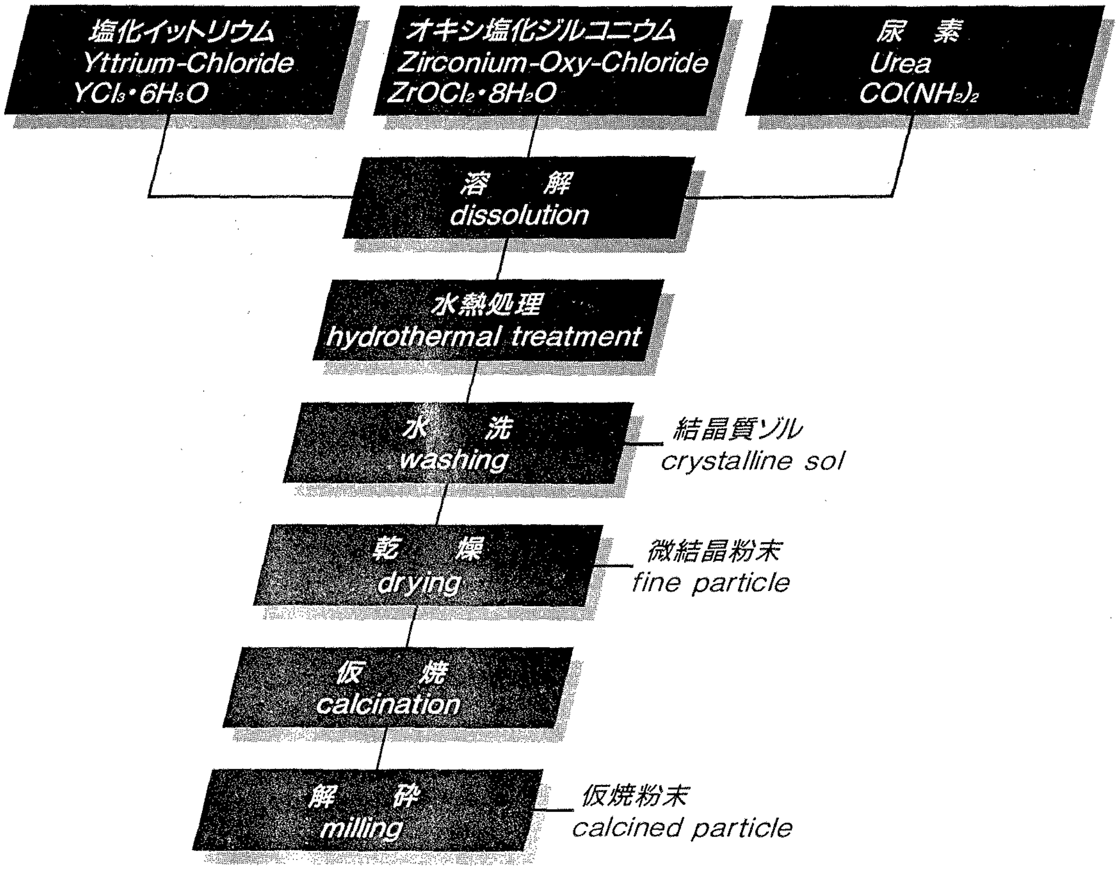


Fig. 15 Hydrothermal ZrO_2, Process by Chichibu Cement Co.Ltd.

BT－01　(No. 800201)

1. Compound : $BaTiO_3$

2. TEM micrograph (×20,000)

3. Physical properties

Ave. particle size (μm)	0.11	TEM micrograph
Sp. surface area (m^2/g)	11.6	BET method
Bulk (ml/100g)	125	JIS K5101-18
Moisture (wt%)	0.3	at 105℃
Ignition loss (wt%)	1.3	at 1200℃

Fig. 16　Hydrothermal $BaTiO_3$ by Sakai Chem. Ind. Co.Ltd.

4. Purity

Ba/Ti (atomic ratio)	0.999
SrO (wt%)	0.01
CaO (wt%)	0.001
Na_2O (wt%)	0.001↓
SiO_2 (wt%)	0.01↓
Al_2O_3 (wt%)	0.01↓
Fe_2O_3 (wt%)	0.002

5. Sintering properties

Molding (20φ)	
Pressure (kg/cm^2)	1000
Green Density (g/cm^3)	3.35
Sintering Properties	
Firing Condition	1200℃×2h
Density (g/cm^3)	5.65
Shrinkage (%)	16.5

6. Dielectric properties (1200℃×2hrs)

K 20℃	4050
TanD 20℃ (%)	1.3
Curie Point (℃)	125
Resistivity (Ω・cm)	3.5×10^{11}

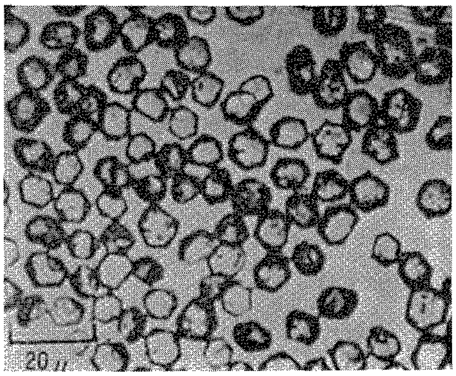


Fig. 17 Alfit, α-Al_2O_3 Single Crystals Produced by Showa Denko K.K.

Table 9 Characteristics of Ba-ferrite fine particles
Ube Industries Ltd.

● Particle properties

Particle diameter (μm)	0.05～0.1
Aspect ratio	3～10
Density (g/ml)	5.25
Specific surface area (m'/g)	20～60

● Magnetic properties

Coercivity (Oe)	200～1500
Saturation magnetization (emu/g)	>55

Particle diameter and coercivity can be controlled arbitrarily.

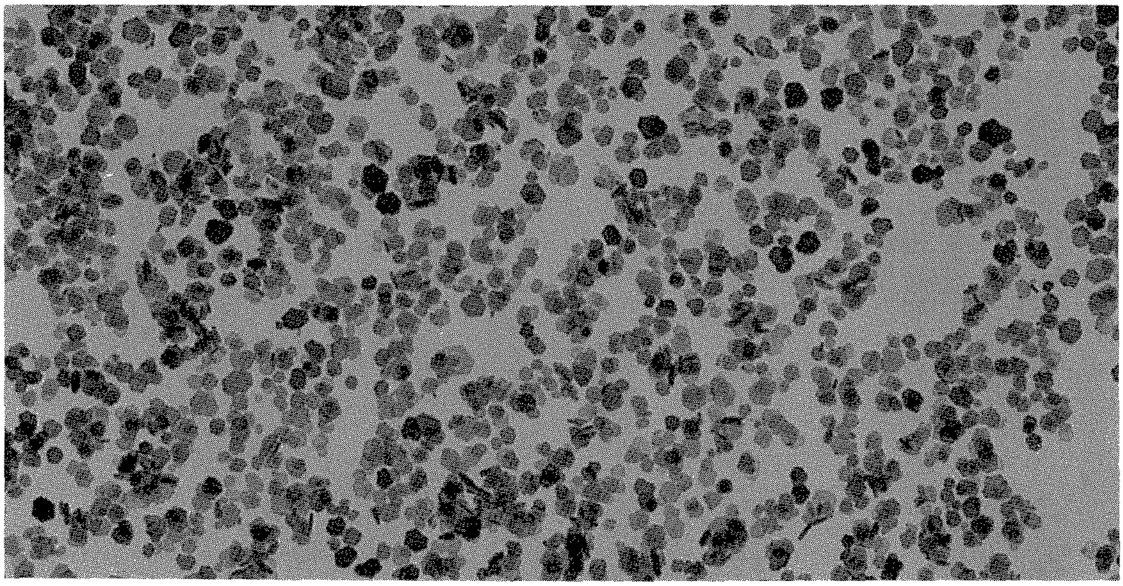


Fig. 18 Hydrothermal Ba-ferrite produced by Ube Industries Ltd.

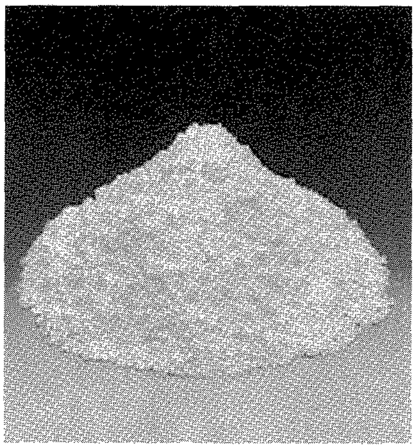
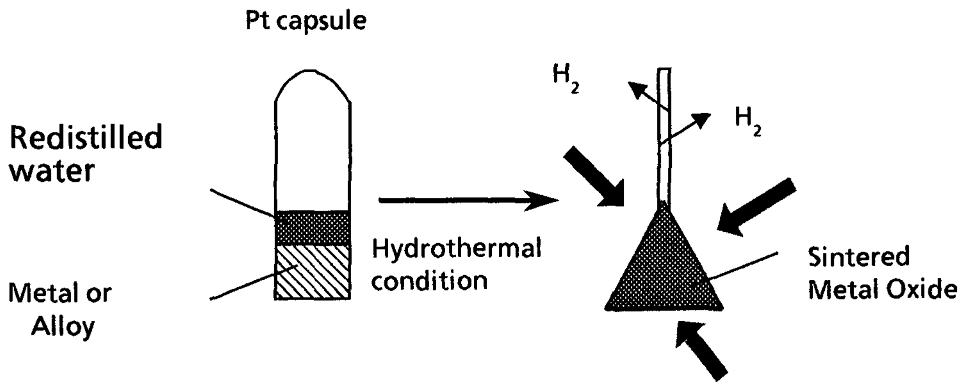


Fig. 19 α-Al_2O_3 Power by Iwatani Chem. Ind.Co.Ltd.

$$M + xH_2O \rightarrow MOx + xH_2$$



Pure and dense sintered oxide
Relatively low temperature
without additives. Homogeneous and Isotropic
Unstable oxides at high temperatures by transformation, decomposition and/or vaporization

Example: m-ZrO_2, Cr_2O_3, $LaCrO_3$, HfO_2, etc.

Fig. 20 Hydrothermal Reaction Sintering

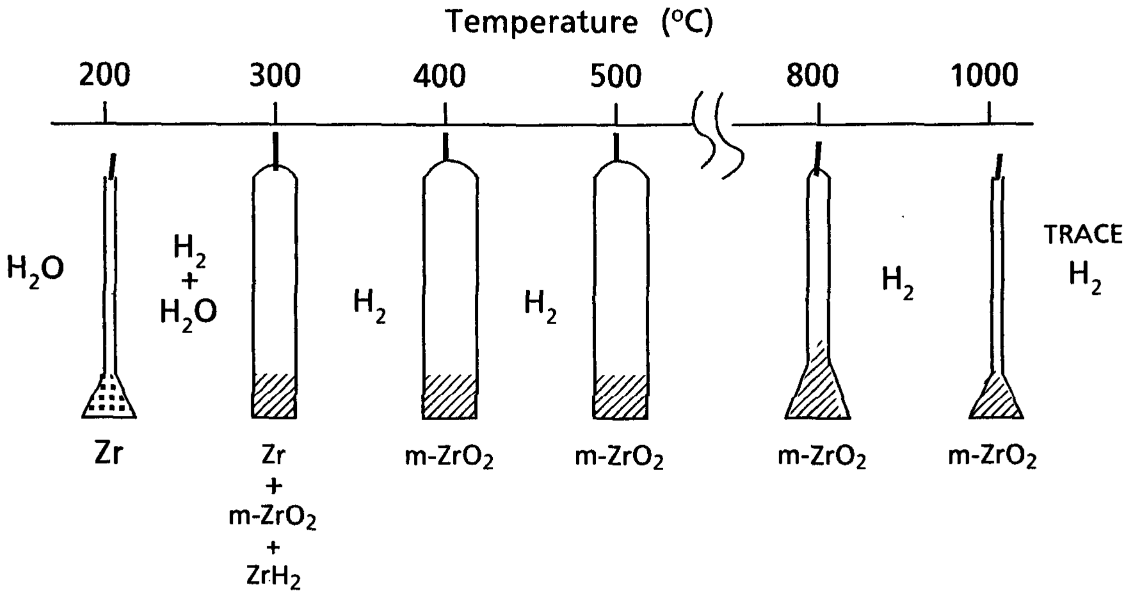


Fig. 21 Schematic illustration of the processes in the hydrothermal reaction sintering of monoclinic ZrO_2 under 1000kg/cm^2 in Pt capsule.

Table 13 Examples of Hydrothermal Reaction Sintering

Products	Press.	Starting Temp. & Press. for Formation of Oxide		Solution	Temp.	Press.	Time	Average Grain Size		Relative Density	Starting Temp. of Sintering
								Start. Mat.	Sintered Body		
	Mpa	°C	MPa		°C	MPa	h	m	m	(%)	°C
Wüstite "FeO"	49 ~ 490	650	98	Pure water	900		24				
Magnetite "Fe_3O_4"	~ 196	250	98	10 m NaOH KOH NH_4Cl	550	98	1				
Chromia "Cr_2O_3"	~ 98	500	98	Pure water	1000	98	3	50	10±3	>99.2	
					850	98	3	50		>99	
	~ 693			Pure water	1000	100	3	20 ~ 40		>90	
				0.01 m HCl							
				0.01 m HNO_3	1000	100	3	20 ~ 40	2 ~ 3	~95	
					1100	100	3	20 ~ 40	2 ~ 3	~95	
					1400	100	3	20 ~ 40	30 ~ 40	~95	
Monoclinic Zirconia Mon.-ZrO_2	98 ~ 686	300	98	Pure water	1000 ~	98	3	1 ~ 20	0.1 ~ 3	> 95	700
Monoclinic Hafnia Mon.-HfO_2				Pure water	900	100		0.2x0.02 (mm)	average 73 nm	92	900
					1000	100			average 89 nm	94	
									0.2 0.5		
					1200	100		average	110 nm		
									0.5 ~ 1.0	94	
$LaCrO_3$		700	100	Pure water	1000~1400	100	3				

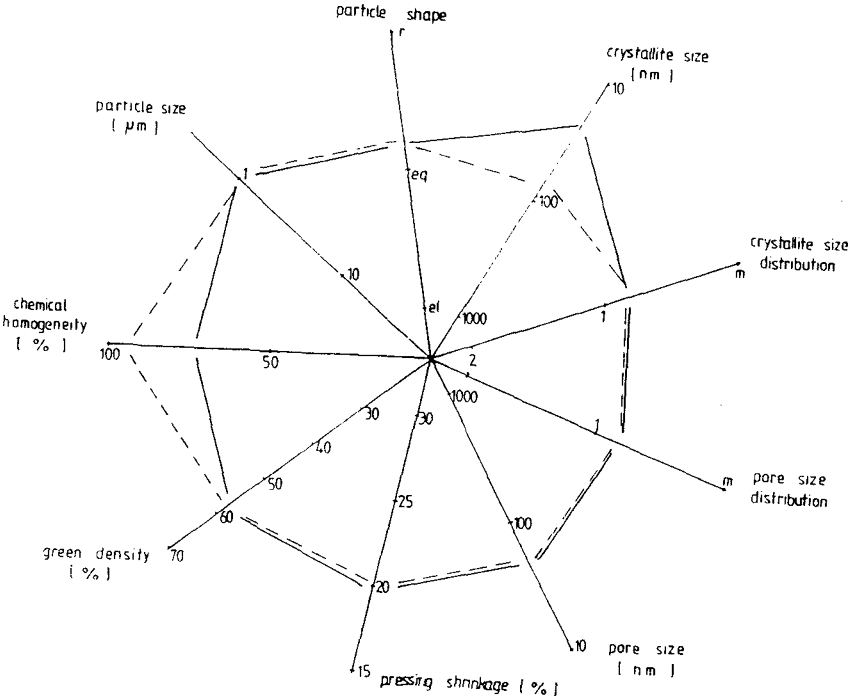


Fig. 13c[30] Star diagram of different powder properties for co-precipitated (solid line) and hydrothermal crystallized powder (broken line) are characterized by a well-balanced set of properties, but none of the properties is ideal. They are the fovorable compromise at present. After Schubert and Petzow.[30]

Table 5 Ideal Powder

1) Fine Powder Less Than 1 μ m
2) Soft or No Agglomeration
3) Narrow Partiele Size Distribution
4) Morphology, Sphere is Better
5) Chemical Composition Controllable
6) Microstructure Controllable
7) Uniformity
8) Free Flowing
9) Less Defects, Dense Particle
10) Less Stress
11) Reactivity, Sinterability
12) Crystallinity
13) Reproducibility
14) Process Control

Table 6 Industrial Products by Hydrothermal Reactions in Japan

1) Large Size
   Autoclaved light weight concrete

2) Small Size
   Single crystals
   - (a) Quartz
   - (b) Zeolite
   - (c) Gemstone
   - (d) Powders
     - (1) Al_2O_3
     - (2) ZrO_2
     - (3) Perovskite
     - (4) Ba-Ferrite
     - (5) Al_2O_3-TiO_2
     - (6) Kaolinite
     - (7) Smectite

Table 7 What is Ideal Powders ?

The items are as follows :
1) No agglomaration
2) Fine Powder
3) Controllable chemical composition
4) Sphere as possible
5) Homogeneous as possible
6) Narrow particle size distribution
7) High crystallinity
8) Good sintability
9) Good forming property
10) Reproducible
11) Less defects
12) No stress

Table 10 Characteristics of Hydrothermal Reaction Sintering

1) It is lower temperature sintering.
2) It is able to sinter the material which has transition, decomposition,and high vapor pressure.
3) It is a very fine grain body.
4) It is able to get a high density sintered body.
5) It is a uniform sintered body for microstructure.
6) It is energy saving process.

Table 11 Hydrothermal Reaction Sintering

1) Cracks appear
2) Oxde Thin Film Formation
3) Hydride Formation
4) Hydroxide Formation
5) Oxide Particle Formation by
Decomposition from Hydride, Hydroxide
6) Hydrogen
7) Hot Isostatic Process

Table 12 Reaction Process of Hydrothermal Oxidation Examined

1) Direct Oxidation	Fe_3O_4,Cr_2O_3,ZnO,SiO_2,etc.
2) Via Hydroxide	Al_2O_3,HfO_2,TiO_2,Nb_2O_5,etc.
3) Via Hydride	ZrO_2,HfO_2,TiO_2,Nb_2O_5,etc.
4) Hydrid(Mixed)	ZrO_2-Al_2O_3,HfO_2-Al_2O_3,etc

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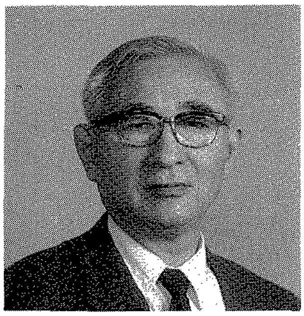

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