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Historical developments of hydrothermal works in Japan, especially in ceramic science

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Historical developments of hyrothermal works especially hydrothermal synthesis and hydrothermal corrosion in Japan are described. And also, some major activities of important Japanese researchers are given. © *2006 Springer Science + Business Media, Inc.*

1. Beginning of hydrothermal works in the world

Hydrothermal experiments began in 1845 by K. F. E. Schafhalt [1] for synthesis of minerals (Fig. 1). G. Spezia [2] studied the growth of quartz in 1905. These are starting points of hydrothermal works in the World. W. Eitel [3] made a book of "Silicate Science" in 1966 also gives the history of hydrothermal research. He collected a rich source of date in "Volume., Hydrothermal Silicate Systems." A Rabenau [4] gave historical developments of hydrothermal synthesis (Table I). Hydrothermal history has been mentioned in detail in "Handbook of Hydrothermal Technology" by K. Byrappa and M. Yoshimura [5] in 2001.

2. Hydrothermal works in Japan ∼ 1945

Related to Japan, researches are as follows:

(i) The first hydrothermal work was done by T. Katsurai [6] in 1926 and he carried out the decomposition of aluminium ore under hydrothermal conditions (Fig. 2). The autoclave was held at 176°C under 9 atm with aluminum ore and NaOH solution. I don't know why he got the idea of high temperature and high pressure experiments above boiling point of water. One reason may be that he graduated from the Dept. of Metallurgy and Japan had interested in natural resources of aluminium ore in Manchuri, China, at that time.

(ii) The second report by S. Nagai [7] in 1931 was about hydrothermal synthesis of calcium silicates after he returned from study abroad, Germany, with W. Eitel. (W. Eitel was Professor at Kaiser-Willhelm Institut für Silikatforschung, Berlin, Germany at that time.) After the World War II, he went to the U.S., and worked at the Institute for Silicate Research, University of Toledo, Toledo, Ohio, USA) Pressure was up to 20 Kg/cm^2 and temperature was about 210°C. The subject was related to cement chemistry.

(iii) In 1934, S. Yamasaki and T. Titani [8] reported vapor phase hydrolysis. This was one of the original starting point of S. Yamasaki (J. Yamasaki) and N. Yamasaki in hydrothermal work.

(iv) S. Nagai and T. Suzuki [9] in 1935 reported hydrothermal reactions between various clay and 15–50 wt% NaOH solution up to 312°C, 100 atm for 4 h.

One of the reactions is as follows:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + NaOH \rightarrow Al_2O_3 \cdot 2SiO_2 \cdot Na_2O \cdot H_2O$$

(v) In 1944, K. Murakami [10] made a review paper on the Synthesis of Silicates. One of the sections was on hydrothermal. He cited only one Japanese, S. Nagai, of cement compounds in his paper.

3. Between 1946–1965

After the World War II, there were very few research laboratories including Universities which were bombarded (as most part of the Japan was destroyed during the war) on hydrothermal because it was necessary to have equipments for high temperature and high pressure experiments above 100°C and over One atm. And also we have to think of safety requirement of Japanese Government and needed a lot of money for research.

(i) M. Koizumi [11], Kyoto and Osaka University, has studied zeolite since 1945. He was one of the leaders in zeolite research in Japan. He published many reports related to zeolite including synthetic zeolites. One of experiments is described as follows: His laboratory used the bombs of test-tube type up to 800°C, 4000 atm. This covers up to 15 Km depth of the earth. Systems of Na_2O-Al_2O_3-SiO_2-H_2O and Ca O-Al_2O_3-SiO_2-H_2O of gels were studied under the hydrothermal conditions

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TABLE I Hydrothermal Synthesis: Dates

Year	Name	Arrangement	Comments
1845	*Schafhäutl*	Papin's digestor	quartz microcrystals
1848	*Bunsen*	thick-walled glass tubes	carbonates; forerunner or the visual autoclaving
1851	*de Sénarmont*	glass ampoules in autoclave	mineral carbonates, sulfates, sulfides, fluorides; founder of hydrothermal synthesis in geological sciences
1873	*von Chrustschoff*	noble metal lining	protection against corrosive solvents
1914	*Morey*	Morey-type autoclave	''closed'' system; standard
1923	*Smith, Adams*	internally heated autoclave	very high pressures and temperatures: ≥10 kbar, ≥1400°C
1943	*Nacken*	foundation for the industrial quartz growth	introduction of hydrothermal synthesis into solid state physics
1949	*Tuttle*	''cold seal'' or test tube arrangement	external pressure regulation and measurement. More extensive working range than *Morey*, Standard
1973	*Capponi*	modified belt apparatus	extremely high pressures and temperatures: ≥100 kbar, ≥1500°C

After A. Rabenau

of up to 400°C, 2Kb for 16–230 h. Factors of Synthesis are depended on the amount of H_2O, and Na_2O, ratio of Na_2O/Al_2O_3, Na_2O/SiO_2, and Al_2O_3/SiO_2, synthetic temperature, duration of time, etc.

(ii) S. Nagai and M. Sekiya [12], University of Tokyo, reported in 1948 preparation of gypsum plaster by hydrothermal method. They produced $CaSO_4 \cdot \frac{1}{2}H_2O$ from $CaSO_4 \cdot 2H_2O$ by heating at 123°C under 2 atm of water vapor pressure.

Gelehrte Anzeigen

München. herausgegeben von Mitgliedern 6. April.

Nro. 70. der k. bayer. Akademie der Wiſſenſchaften. 1845.

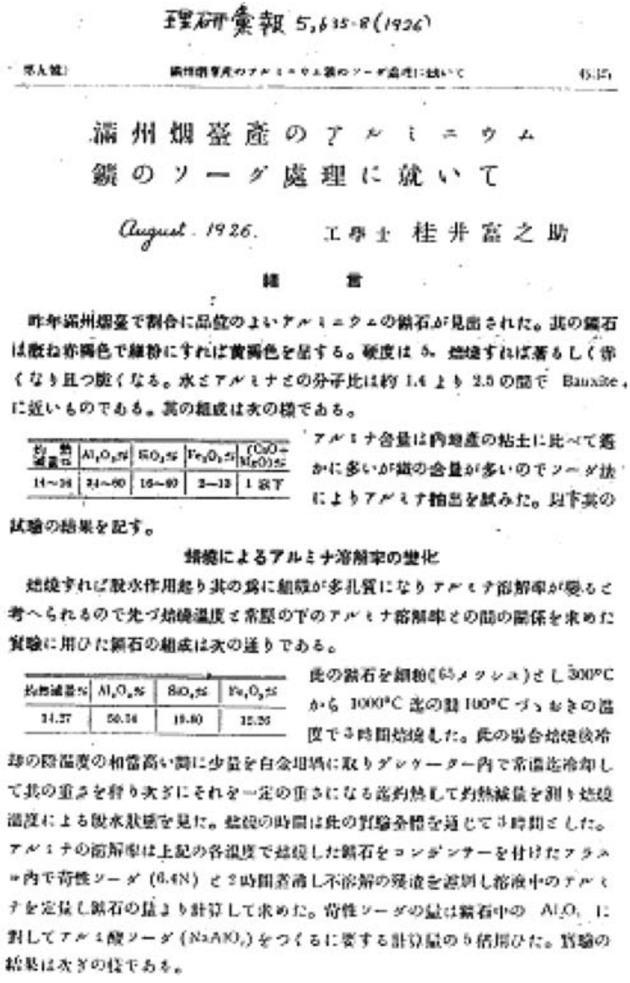
Königl. Akademie der Wiſſenſchaften.

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

1) Hr. Profeſſor Schafhäutl:

Die neueſten geologiſchen Hypotheſen und ihr Verhältniß zur Naturwiſſenſchaft überhaupt.

Figure 1 The first report on Hydrothermal Reactions.



理研彙報 5, 635-8 (1926)

滿州烟臺產のアルミニウム
鑛のソーダ處理に就いて

August. 1926. 工學士 桂井富之助

緒言

昨年滿州烟臺で割合に品位のよいアルミニウムの鑛石が見出された。其の鑛石は概ね赤褐色で細粉にすれば黄褐色を呈する。硬度は5、燒焼すれば著しく脆くなり且つ脆くなる。水とアルミナとの分子比は約1.4より2.5の間で Bauxite に近いものである。其の組成は次の樣である。

灼熱減量%	Al_2O_3%	SiO_2%	Fe_2O_3%	$(CaO+MgO)$%
14~24	24~60	16~40	3~13	1以下

アルミナ含量は内地產の粘土に比べて遙かに多いが鐵の含量が多いのでソーダ法によりアルミナ抽出を試みた。以下其の試驗の結果を記す。

燒焼によるアルミナ溶解率の變化

燒焼すれば脱水作用起り其の爲に組織が多孔質になりアルミナ溶解率が變ると考へられるので先づ燒焼溫度と常壓の下のアルミナ溶解率との間の關係を求めた。實驗に用ひた鑛石の組成は次の通りである。

灼熱減量%	Al_2O_3%	SiO_2%	Fe_2O_3%
14.27	50.34	19.80	15.26

此の鑛石を細粉(65メッシュ)とし300°Cから1000°C迄の間100°Cづゝ各溫度で3時間燒焼した。此の場合燒焼後冷却の際溫度の相當高い間に少量を白金坩堝に取りデシケーター内で常溫迄冷却して其の重さを秤り次ぎにそれを一定の重さになる迄灼熱して灼熱減量を測り燒焼溫度による脱水狀態を見た。燒焼の時間は此の實驗全體を通じて3時間とした。アルミナの溶解率は上記の各溫度で燒焼した鑛石をコンデンサーを付けたフラスコ内で苛性ソーダ(6.4N)と2時間煮沸し不溶解の殘渣を濾別し溶液中のアルミナを定量し鑛石の量より計算して求めた。苛性ソーダの量は鑛石中の Al_2O_3 に對してアルミン酸ソーダ($NaAlO_2$)をつくるに要する計算量の5倍用ひた。實驗の結果は次ぎの樣である。

Figure 2 The first research paper of Hydrothermal Reactions in Japan (1926).

TABLE II Formation of Single Crystal of Beryl Hydrothermally [After H. Saito, H. Kubota, and M. Kunitomi (1958)]

200 atm	330–360°C
300	330–360
400	320–340
500	320–360
600	315–330

(iii) After the World War II, S. Yamasaki returned from China, he got a position of Professor at the Kochi University and started the hydrothermal works again. During his stay in China, he had done great researches. He, however, did not able to bring his papers to Japan. He carried out excellent hydrothermal research at the University. One of his research activities [13] is as follows:

He reported the hydrothermal decomposition and extraction on Li from Lithiamica or Kaolin-feldspar at 175° to 400°C with NaOH and $Ca(OH)_2$ solutions under saturated water vapor. Above the critical temperature, reaction finished nearly 100% after 40 min. with OH- ion.

(iv) R. Kiyoura and R. Itoh [14] reported the hydrothermal reactions of silicates such as perlite and muscovite with Na_2CO_3 solution up to 370°C, 200 atm. They used Morey type bomb. The reaction products were sericite, etc. This was in 1952. They also synthesized talc ($3MgO{\cdot}4SiO_2{\cdot}H_2O$) and serpentine ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$) under hydrothermal conditions below 500°C and 300 atm. Sericite was also synthesized from silica gel, aluminium hydroxide, and NaOH solution.

(v) Y. Otsubo and C. Kato [15] of Waseda University in 1952 studied the hydrothermal synthesis of acid clay from silica gel, alumina gel and $MgO{\cdot}SiO_2$: Al_2O_3:MgO = 4:1:0.2 mol ratios. Materials were synthesized at 300°C, 85 atm for 20 h and at 500°C, 85 atm for 20 h. Then the reaction products were tested. They also studied hydrothermal synthesis of montmorillonite $Al_2Si_4O_{14}(OH)_2{\cdot}nH_2O$ at 300°C and 35 atm. These were reported during 1952 to 1956.

(vi) M. Kunitomi, H. Saito, and T. Kunugi [16] of Yamanashi University studied the synthesis of quartz and other minerals. As for the synthetic quartz, I will explain it later. One of the experimental treatments (hydrothermal separation) of asbestos to remove glassy material from mother rock. He operated the autoclave at 300–350°C for 4 to 20 h to obtain useful materials (in 1952). The second example is the hydrothermal synthesis of beryl ($Be_3Al_2(SiO_3)_6$), from glass composition under 320–360°C with 3% NaOH solution. The results are shown in Table II (in 1958).

(vii) T. Noda of Nagoya University and H. Saito of Yamanashi University, *et al.* [17] reported in 1956 the hydrothermal treatment of synthetic phlogopite ($KMg_3(AlSi_3O_{16})(OH)_2$) to remove glassy phase from synthetic phlogopite bodies and also exchange OH^- ion to F^-. Hydrothermal treatment was at 350°C, for 24 to 48 h, 2N NaOHaq or ½ and 10N KOH solution. Over ¼N KOH solution was better than weak solution.

(viii) T. Noda *et al.* [18] of Nagoya University reported hydrothermal synthesis of fluor—hydroxyl muscovite in 1966. They used test tube type autoclaves containing silica gel and alumina gel, KHF_2 and K_2CO_3 as starting materials. Temperatures were 500 to 600°C under 500 to 900 atm.

4. Synthesis of quartz

1) At present, Japan is the leading country to produce synthetic quartz in the world. Table III shows world production. Table IV shows application of synthetic quartz in Japan.

After the paper by A. C. Walker and E. Bueher (1950) [19] and A. C. Walker (1954) [20], K. Kunitomi of Yamanashi University wanted to grow quartz in 1952 because:

a. During the World War II, there was a quartz oscillator factory in his area, Yamanashi.

b. He wanted to contribute industry of his area, Yamanashi Prefecture.

TABLE III Synthetic Quartz in the World

Jpan	1200 ton/year
USA.	330
China	800
East Europe	150
UK, France	40
Korea	30
Brazil	20
Belgium	20
South Africa	20
Russia and the others	1000
Total	3610

Handbook of Hydrothermal Chemistry, p. 252, Gihodo Shuppan K.K. (1997).

TABLE IV Production of Quartz Oscillator (unit: million yen)

	2000	2001	2002
1. Industrial Quartz Oscillator	29,158	13,656	13,175
2. Tunning Fork Type	34,789	27,105	28,516
3. Quartz Oscillator for Automobile	6,228	7,233	8,589
4. Quartz Oscillator for TV, VTR	10,191	6,133	5,502
5. Quartz Oscillator for Public Welfare	42,552	31,729	28,598
Public Welfare Subtotal $(3 + 4 + 5)$	58,971	45,095	42,689
6. Quartz Oscillator for Industry	95,176	69,609	56,363
7. Quartz Oscillator for Clocks	39,194	26,894	22,539
8. Quartz Wave Filter	23,011	15,312	11,996
Total	280,299	197,671	175,278

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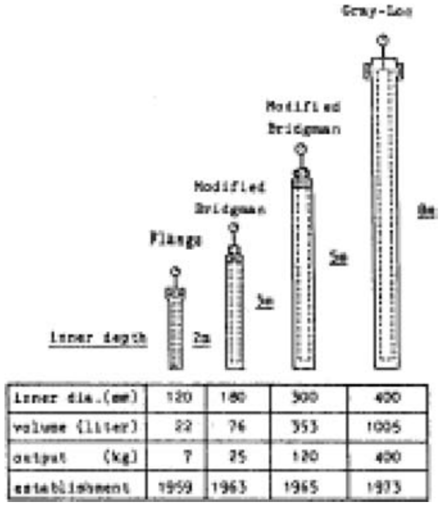
c. He read the papers on synthesis of quartz by A. C. Walker.

d. He was one of leaders in his University and very active in his research field.

The first hydrothermal bomb at Yamanashi University was 35 mm in diameter, 50 cm in depth and 465 cc of volume. It was vertical type and able to use up to 1000°C. They used 5% Na_2CO_3 solution. First report by S. Taki, M. Kunitomi, J. Asahara, and T. Ozawa [24] appeared in 1956. Study on the synthesis of quartz in Toyo Communication Inc. started in 1955.

Yamanashi University was cooperated with Toyo Communication. In 1959, Toyo Communication had mass production equipments. Toyo Communication [26] produced quartz and amount of production increased year after year. Figs 3 and 4 was volume and sealing method of autoclave. You are able to imagine how big the autoclave is! The method to produce synthetic quartz is so called "hydrothermal temperature difference method." The operating conditions are shown in Table V [26].



Inner dia.(mm)	120	180	300	400
volume (liter)	22	76	353	1005
output (kg)	7	25	120	400
establishment	1959	1963	1965	1973

Figure 3 Historical trend of which output capacity from one autoclave-batch gradually increased by larger autoclaves.

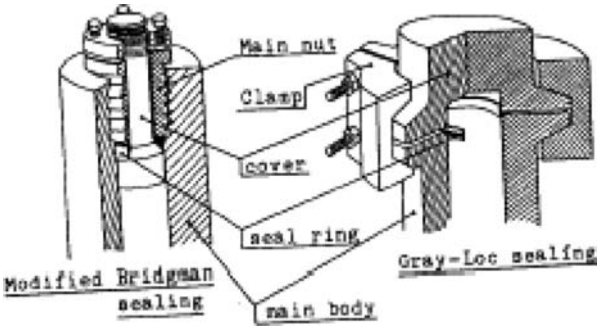


Figure 4 Comparison for self- and pressure-energized sealing systems applied to larger autoclaves. (Modified Bridgman seal and Gray-Loc seal.)

TABLE V Growth Conditions of Synthetic Quartz(26)

Filling Conditions	
Solution	: 0.5–1.0 N NaOH or Na_2CO_3
Degree of fill	: 75–85%
Baffle closure	: 80–90%
Seed crystal	: Z-plate or Y-bar Quarts Crystal
Nutrient	: Natural Quarts
Operating condiitons	
Crystallizing temperatures	: 330–340°C
Dissolving temperature	: 360–370°C
ΔT	: 20–35°C
Pressure	: 800–1500 kg/Cm^2
Duration	: 20–100 days
Growth rate	: 0.5–1.5 mm/day (Z-axis)

Why Japan wants to produce synthetic quartz? Because:

a. Good quality of natural quartz occurs in Brazil.
b. Quantity to supply is not stable.
c. Demand is increasing year after year.
d. Natural quartz has twins and also the defects.
e. Industry in Japan wants to grow good quality quartz.
f. Quartz industry in Japan is developing since 1950.

These are reasons why synthetic quartz in Japan was used increasingly rapidly.

There are good papers to know historical developments of synthetic quartz, namely by Noda [21] Ohara [22], Taki [23, 24], and Iwasaki and Iwasaki [25]. According to these papers, Kunitomi has established the bomb inside a small building at the roof for safety.

The second group was the Kobayashi Institute of Physical Research of Hagiwara, Yamamoto, Fujimura, and Akita [27]. They reported their paper in 1956. This group made operation with Kinsekisha.

The third group was Ohara [22] of Tohoku University and Nippon Dempa Kogyo.

5. Between 1966–1982

Hydrothermal work by Kunitomi's group, by Noda's group, by Koizumi's group, etc., was still active and when new comers appeared in this field.

(i) Kunitomi's Laboratory [28] was working on colored quartz and new compound such as VO_2 at 350–400°C under 450–800 Kg/cm^2.

(ii) Noda *et al.* [29], Nagoya University, worked on fluor-hydroxyl muscovite. $KAl_3Si_3O_{10}F_x(OH)_{2-x}$ compositions, where $X = 0$ to 2.0 were synthesized hydrothermally within the temperature range 500–600°C, and pressure range of 500–900 atm. Starting materials were gel composition and chemicals.

(iii) Saito and Takei [30] of Keio University studied ferrite and published their results in 1966. Nickel ferrites

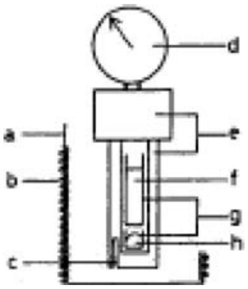


Figure 5 Apparatus for the hydrothermal dehydration method: (a) furnace; (b) heater; (c) thermocouple well; (d) pressure gauge; (e) autoclave; (f) nutrient; (g) Pt-tube; (h) dehydration reagent.

were synthesized at 330°C for 3 h. Above 200°C, rate of ferrite formation was good. These works were not much different from changing the temperatures.

(iv) Nobuoka and Ando [31] of Government Research Industrial Institute, Osaka has studied iron oxides and iron hydroxides under hydrothermal conditions. One of the results is as follows: α-Fe_2O_3 was formed at 290–300°C and magnetite was formed 450–500°C from $FeSO_4$ aq and NaOH aq.

(v) Mitsuda [32] Laboratory has studied the hydrothermal reactions for calcium silicate industry since 1969. His group published their reports such as tobermorite, xonotlite, etc., in the system of CaO-Al_2O_3-SiO_2-H_2O system.

(vi) Saito [33] moved from Yamanashi University to Nagoya University. One of the most interesting studies in 1979 was hydrothermal dehydration for the synthesis of crysotile fibers, $Mg_6{\cdot}(OH)_8Si_4O_{10}$ from Mg $(OH)_2$, $MgBr_2$ and SiO_2 and of potassium hexatitanate, $K_2Ti_6O_3$ from TiO_2 in KOH solution. For dehydration, part of water in the autoclave, metals such as Mg, and/or Zn which with higher ionization tendency that of hydrogen was used. Fig. 5 is show the apparatus.

(vii) W. Ishibashi [34] of Iwatani Industry Co., Ltd. reported to produce fine ceramic powders by spark discharge method in 1977. It is similar to method by Kumar and Roy [34] of RESA (Reactive Electrode Submerge Arc (1988, 1989)). Area of spark was high temperature and high pressure in a short time. Electrodes were metallic Cu, Al and Fe of 7 mm in diameter. Vessel was 200 mm × 500 mm × 1000 mm and water was 40 L. Fig. 7 shows schematic illustration of the apparatus. Average grain size was 0.15 μm and 0.05 μm for Al and Fe respectively, at 610 KH_2.

(viii) Kondo, Daimon, Lee *et al.* [35] of Tokyo Institute of Technology reported hydrothermal reactions in the system CaO-SiO_2-H_2O. Starting materials were quartz as SiO_2 and $Ca(OH)_2$ as CaO at 181°C, under saturated water vapor for 3–8 days. They measured solubility of solid in the liquid.

(ix) Yamasaki, Matsuoka, Mitsushio, Yamasaki *et al.* [36] established a Research Laboratory of Hydrothermal Chemistry attached to the Kochi University in April, 1973. One of the reports was hydrothermal formation of $BaTiO_3$ by K. Matsuoka from $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 in 1978. $Ba(OH)_2{\cdot}8H_2O$ liberated water at 180°C. $Ba(OH)_2$ was fully dissolved in the liberated water under hydrothermal condition. Operating temperature was 110 to 370°C. Reaction rate was increased increasing operating temperature. For examples, at 200°C, reaction needed by 10 min and at 300 and 370°C , reaction finished instantly.

(x) Mitsushio and Matsuoka [37] reported hydrothermal changes of silica gels in 1978 under 100 to 400°C, 500 Kg/m^2 for 168 h. After the treatments, gels were changed to .-cristobalite, silica K, α-quartz.

(xi) At "the International Symposium on Hydrothermal Reactions" in 1982 [38], there were many Japanese papers for hydrothermal synthesis:

K. Asaga, *et al.*, Tokyo Institute of Technology, Kinetics of hydrothermal reactions in the CaO-SiO_2 system
Y. Fujiki, *et al.*, NIRIM, Hydrothermal leaching of Cs and Sr in titanate
Y. Harita, Hokkaido University, Hydrothermal synthesis of (Ca, Mn)SiO_3 clino-bustamite, and (Mg, Mn)SiO_3 kanoite
N. Hara and N. Inoue, Government Industrial Research Institute, Kyushu Formation of jennite
J. T. Iiyama Lab., University of Tokyo, Phase equilibria in the system $CaSiO_3$-$MgSiO_3$-(Mg, Fe) Cl_2-H_2O
S. Kaneko, *et al.*, Shizuoka University, Phase Transformation of CdS
S. Hirano, *et al.*, Nagoya University, Synthesis of $Na_{0.70}MnO_{2.25}$ crystal
M. Koizumi Lab., Osaka University Crystallization of zeolite Y
T. Mitsuda Lab., Nagoya Institute of Technology Cement related compounds
H. Mitsushio, *et al.*, Kochi University, Hydrtothermal synthesis of dolomite
K. Nagashima Lab., University of Tsukuba Sulfosalts study
A. Sugaki, Tohoku University, Hydrothermal synthesis of sulfides
K. Takai, *et al.*, Mizusawa Industrial Chemicals, Ltd., Hydrothermal synthesis of $PbTiO_3$
K. Matsuoka Lab. and Yamasaki Lab. Kochi University, Crystallization and transformation of zirconia, and dolomite formation
J. Asahara and K. Nagai, Toyo Communications, Synthetic quartz
S. Taki and M. Hosaka, Yamanashi University, Synthetic quartz
I. Sunagawa, Tohoku University Hydrothermal growth
N. Kishima and H. Sakai, Okayama University, Measurement of Hydrogen Concentration
K. Watanabe Lab., Keio University Thermodynamic behavior of pure water

Y. Suzuki Lab., Tsukuba University, Reactions serpentine and quartz
H. Muraishi Lab., Fukuoka University of Education, Hydrothermal crystallization of silica gel
K. Hasegawa, *et al.*, Toyo Communication, Synthesis of aluminum phosphate
K. Hasegawa, *et al.*, Chichibu Cement, Synthesis of aluminum orthophosphate
Y. Hariya Lab., Hokkaido University, Stability relations of kaersutite
M. Morita Lab., Toshiba Corp., Morphological study on silica scale
J. Ikeuchi, *et al.*, Government Industrial Res. Inst. Tohoku, Corrosion behavior of various materials exposed to geothermal fluids
Somiya – Yoshimura Lab., Tokyo Institute of Technology
Hydrothermal Synthesis of fine powders:
ZrO_2, Cubic ZrO_2, HfO_2, CeO_2, $LaFeO_3$, etc.
Hydrothermal decomposition of ilmenite
Phase diagram Nd_2O_3-P_2O_5-H_2O, ZrO_2-CeO_2
Reaction Products CaO-nAl_2O_3-H_2O
Non-oxide ceramic powders in high pressure high temperature ammonia
Hydrothermal reaction sintering

These papers mentioned above were presented at the International Symposium on Hydrothermal Reactions.

6. Between 1983–2000

i) M. Koizumi Lab., Osaka University: His laboratory studied zeolite continuously.

ii) S. Hirano, S. Naka, *et al.* [39a], Nagoya University, reported preparation of carbon by pressure pyrolysis of p-terphenyl in pressure of critical water. The effect pyrolysis pressure and supercritical water on the formation and morphology of formed carbon were studied by the pressure carbonization of p-terphenyl in the presence of supercritical water up to 1500 Kg/cm^2 and 700°C.

They used in the case of p-terphenyl : water = 1: 5 (mol ratio), 1000 Kg/cm^2, 560°C, 2 h, methane : ethane = 7:1, in the case of 2 h 15 min methane 75 mol%, ethane 20 mol% CO_2 5 mol%, in the case of 2 h 45 min. methane 85 mol%, ethane 13 mol%, CO_2 2 mol%. After 3h, carbonization finished.

iii) S. Hirano [39b] has studied growth of calcite single crystal for a long time. Hydrothermal conditions were at 500°C and 200°C under 100°C MPa for 3 days. Solutions were 3m NaCl, 2m KCl, 3m KOH, 3m NaOH, 3m KOH, 3m $NaNO_3$, 2m KNO_3, 1.5m $Ca(NO_3)_2$, and 3m NH_4NO_3.

iv) M. Daimon, K. Asaga, K. H. Lee, *et al.* [40], reported the hydrothermal synthesis of PZT[$Pb(Zr_{0.52}Ti_{0.48})O_3$] under hydrothermal conditions. Using $Pb(NO_3)_2$, $ZrOCl_2$ and $TiCl_4$ in KOH solution below 200°C. Formation of PZT was very fast in 10M KOH solution. PZT was detected by X-ray 200°C for 30 min., 150°C for lh, 100°C for 5h and 70°C for 4 days. They used Teflon bottle.

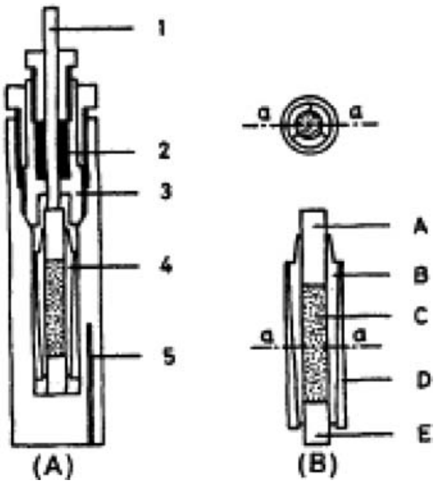


Figure 6 Apparatus for hydrothermal hotpresing. (A) Autoclave, showing (1) piston, (2) gland packing, (3) cone, (4) hot-pressing die, and (5) thermocouple well. (B) Hot-pressing die (cross section at a-a is shown at top), including (A) upper rod, (B) ring, (C) inner case, (D) wet starting powder, (E) outer case, and (F) lower rod.

v) N. Yamasaki, K. Yanagisawa, *et al.* [41], Kochi University reported radioactive waste treatments by hydrothermal hot pressing in 1985. High level of radioactive waste solidified into silica rich materials containing 70 wt%. quartz and 30 wt% of amorphous aluminosilicate by this process. The apparatus is shown in Fig. 6. High mechanical strength and low leachability were important properties. The addition of 10 wt% of $Al(OH)_3$ to the

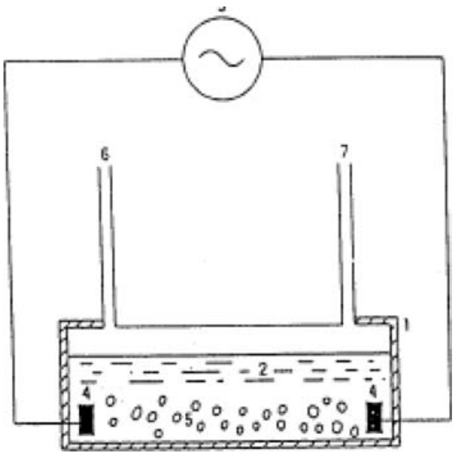


Figure 7 Schematic Illustration of Iwatani Process
1. Reaction vessel
2. Water
3. Spark generator
4. Electcrodes
5. Metal Pellots
6. Metal and water supply
7. Discharge of powder and gas

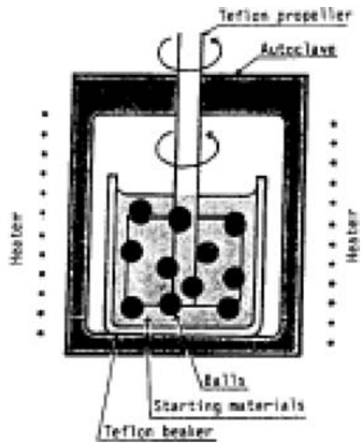


Figure 8 Experimental apparatus.

starting powder reduced the leachability by immobilizing Na into aluminosilicates.

The 21.8 wt% of waste, 68.2 wt% of the matrix and 10 wt% of $Al(OH)_3$ were mixed with NaOH solution. And then the materials were treated hydrothermally at 350°C,66 Mpa from outside of the autoclave for 6h. This is one good approach for radioactive wastes.

vi) S. Somiya, M. Yoshimura, *et al.* [42], Tokyo Institute of Technology prepared Ba-ferrite by the hydrothermal-mechanochemical method. The apparatus is shown in Fig. 8. $Ba(OH)_2$ and $FeCl_3$ were used as starting materials. Ba^{2+}/Fe^{3+} was 1.8, OH- concentration was kept 3 mol/L at 200°C under 2 MPa. Number of stainless balls was from 200°C to 700°C of 5 mm in diameter. Rotation rate was 0 to 107 rpm and cocking time was 0 to 24 h. They made Ba-ferrite under hydrothermal conditions.

vii) M. Yoshimura, N. Ishizawa Lab. [43], Tokyo Institute of Technology, prepared $BaTiO_3$ films by hydrothermal electrochemical method. Titanium plate 0.1 mm thick was ued as working electrode (anode). Reactions were performed in electrolytes such as $Ba(NO_3)_2$ aq. or $BaCl_2$ aq and H_2O. The electrolyte was 200 ml and working electrode was 2.1 cm^2. As a counter-electrode (cathode), a platinum plate was 9 mm × 30 mm × 0.15 mm. Distance between the working electrode and the platinum counter-electrode was 3 mm. Current density was 10 and 100 mA cm^{-2}. One of the results is shown in Fig. 9. They made the powders, thin films, etc. (Fig. 10).

viii) M. Yoshimura [44] developed his study field from hydrothermal to soft chemical process. Whenever you look at MRS Bull., vol. 25, No. 9, September 2000, you are able to understand Soft Processing.

ix) N. Sakagami Lab. [45], Tohoku University and Akita National College and Technology, have studied hydrothermal growth of ZnO for a long time. One of the experimental conditions are as follows:

Growth temperature 370–400°C

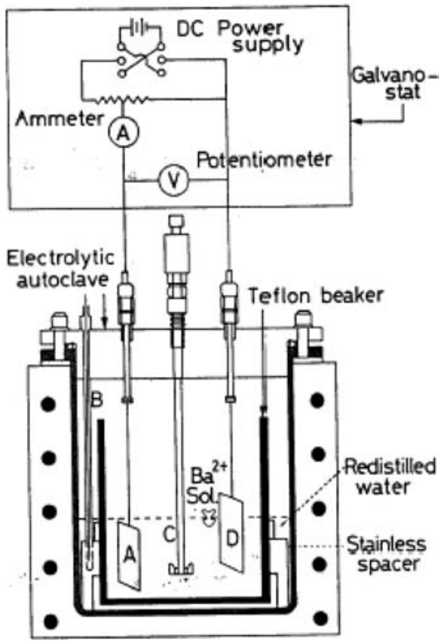


Figure 9 Schematic illustration of the electrochemical cell and circuit arrangements for the hydrothermal electrochemical method. (A) Pt plate, cathode, (B) Thermocouple, (C) Stirrer, (D) Ti plate, anode.

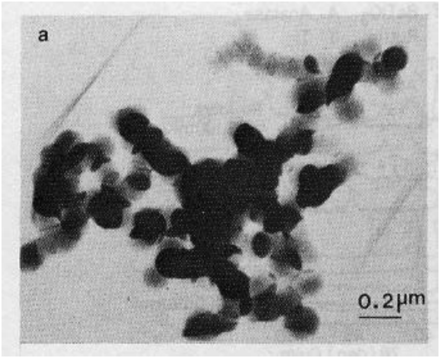


Figure 10 TEM micrograph of the $BaTiO_3$ powders obtained after hydrothermal oxidation of titanium plate in 0.5N $Ba(NO_3)_2$ solution at 200°C.

Temperature difference 10°C

Pressure 700–1200 atm Solvent (H_2O) 3M KOH + 1M LiOH Filling fraction 80% Nutrient ZnO powder (sintered) Crucible Pt (0.4 mm thick)

Growth duration 10–20 days

Grown crystal was about 10 mm in length after 2 weeks from 2 mm of seed crystal.

x) K. Ioku [46], Ioku grarudated from Tokyo Institute of Technology, and now Tohoku University through Kochi University and Yamaguchi University. He is interested in appatite and hydroxyapatite. One of his results is as follows: Ultrafine hydroxyapatite powder prepared 100–200°C under saturated water vapor for 10 h. An autoclave was Teflon beaker of 1 dm^3. Between the autoclave and the Teflon beaker, the space was filled up with NH_4OH for pH = 10. Hydrothermal synthesis of hydroxyapatite was operated at 200°C under 2 Mpa for 10 h about 25 mm × 90 mm in size. Medium aspects ratio was 3.2.

xi) S. Matsumoto [47], Sakai Chemical Ind. Co., Ltd., reported industrial production of iron oxide for magnetic tape.

$$Fe^{3+}\text{salt} + 3\ OH- \rightarrow Fe(OH)_3$$

As for crystal control agents, polycarboxylic acid or sulfonic acid were used. Then pH of solution was 10–12 by alkali. Colloid put into the autoclave under 130–200°C for 30–180 min. The product was acicular α-Fe_2O_3.

xii) Y. Shibasaki [48], Government Industrial Institute Nagoya, Japan, was running short of good kaolin materials to make ceramics bodies. This is one reasons why Y. Shibasaki [48], studied artificial clay (Figs. 11, 12). He has studied artificial clay since 1988 as one of national research projects. Starting materials were silica gel, diatomite, $AlCl_3$, Al $(NO_3)_3$, etc., and 170–350°C for 1 to a long days in the Teflon vassel (below 350°C) or stainless steel bombs (over 200°C). One of the results is shown in Fig. 12. Presently, he makes artificial clay below 300°C, 100 atm. Grain size was less than 0.2 μm and it was good for dispersion.

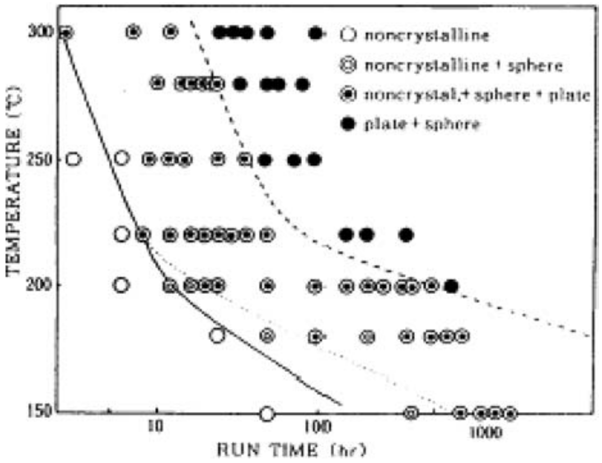


Figure 11 Results of experiment, relations among reaction time, temperature and reaction products.

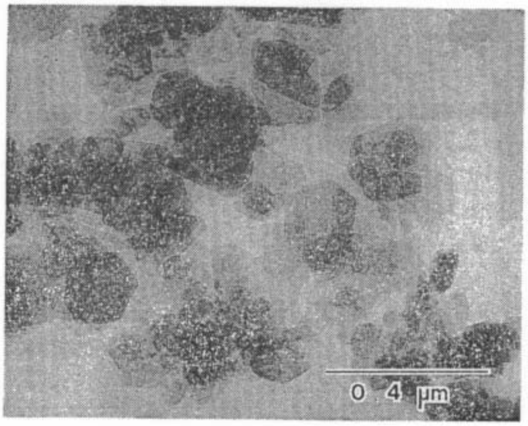


Figure 12 SEM of artificial kaolin.

TABLE VI Powder Properties for Typical Hydrothermal $BaTiO_3$ Products [52]

Rade name	BT–01	BT–03	BT–05
Average particle size	0.1 μm	0.3 μm	0.5 μm
Specific surface area	13 m^2/g	4.0 m^2/g	2.0 m^2/g
SrO (wt%)	0.05 >	0.05 >	0.05 >
CaO (wt%)	0.005 >	0.005 >	0.005 >
Na_2O (wt%)	0.005 >	0.005 >	0.005 >
SiO_2 (wt%)	0.01 >	0.01 >	0.01 >
Al_2O_3 (wt%)	0.005 >	0.005 >	0.005 >
Fe_2O_3 (wt%)	0.005 >	0.005 >	0.005 >

TABLE VIIA Powder Properties for Barium Titanates by Various Methods [52]

Production method	Hydrothermal	Solid phase	Oxalate	Co-precipitate
Producer	A(Sakai)	B	C	D
Grade name	BT–04A	–	–	–
Ba/Ti ratio	1.000	1.001	0.995	0.997
S.S.A. (m^2/g)	2.3	2.8	2.8	2.2
Impurities (%)				
SrO	0.010	0.003	0.004	0.008
CaO	0.001	0.006	0.001	0.002
Na_2O	0.001	0.002	0.002	0.001
SiO_2	0.001	0.016	0.007	0.006
Al_2O_3	0.001	0.010	0.002	0.001
Fe_2O_3	0.001	0.001	0.001	0.006

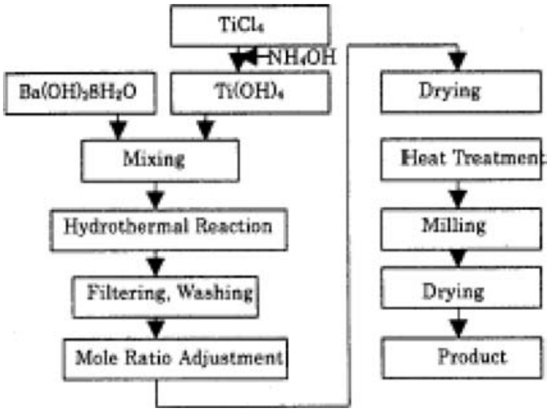


Figure 13 Flow sheet of Hydrothermal Synthesis for Barium Titanate.

xiii) The research results from laboratories of Somiya, Tokyo Institute of Technology; Taki, Yamanashi University; Hirano, Nagoya University; Yamasaki, Kochi University; etc., were published in 1989 as a book of "Hydrothermal Reactions for Materials Science and Engineering" from Elsevier [49]. I do not want to explain

TABLE VIIB Dielectric Properties for Barium Titanate Ceramics [52]

Production method	Hydrothermal	Solid phase	Oxalate	Co-precipitate
Producer	A(Sakai)	B	C	D
Grade name	BT–04A	–	–	–
Green density (g/cm^3)	3.62	3.57	3.43	3.5
Fired At 1300°C				
Sintered density (g/cm^3)	5.95	5.95	5.93	5.67
T.C.C. (%)($-55\sim+125$°C)	$-2.6\sim+13.2$	$-9.7\sim+24.5$	$-2.1\sim+9.9$	$-6.7\sim+19.5$
Dielectric constant at 20°C	3060	2980	2770	2970
Dielectric loss at 20°C (%)	0.61	0.96	0.99	0.99

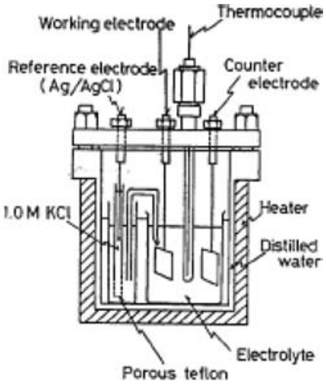


Figure 14 An apparatus for electrochemical synthesis of oxide films at elevated temperature under high pressure.

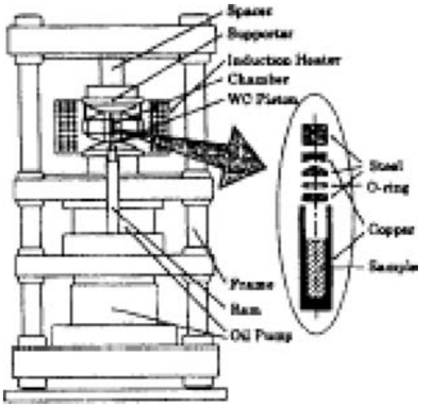


Figure 16 Very high pressure equipment and hydrothermal cell.

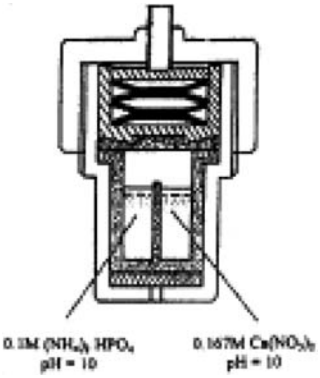


Figure 15 Multi-chamber autoclave for preparation of hydroxyapatite.

my results again in detail. I, however, mentioned very fine powders produced by hydrothermal methods for ceramic application. After "the First Symposium on Hydrothermal Reactions" in 1982 and publication of "Hydrothermal Reactions for Materials Science and Engineering," Japan has become one of the active countries around the world for hydrothermal research.

xiv) T. Moriyoshi (Tokushima University), N. Yamasaki (Kochi University), etc. [50], have organized the following international conferences in Takamatsu, Japan.

1. The First, December, 1994, 224 pages
2. The Second, December, 1996, 242 pages
3. Workshop on Solvothermal and Hydrothermal Reactions, January, 1996, 134 pages
4. Solvothermal and Hydrothermal Process, September, 1997, 74 pages

There were many papers by Japanese.

xv) K. Yanagisawa, N. Yamasaki [51], Kochi University organized the Sixth International Symposium on Hydrothermal Reactions and the Fourth International Conference on Solvothermal Reactions. It was a joint meeting, July, 2000, at Kochi, Japan. There were many papers by Japanese.

xvi) At this symposium, K. Abe, *et al.* [52] of Sakai Chemical Industry Co., Ltd., reported "Development and Industrialization of Hydrothermally Synthesized Barium Titanate for Ceramic Capacitors." Flow sheet of hydrothermal process is shown in Fig. 13. Ba/Ti = 1.3. The slurry was allowed to react in a Teflon coated autoclave at 200°C for 2 h. After cooling, the slurry was neutralized by the addition of acetic acid to neutralize excess $Ba(OH)_2$ to pH 7.0. After that, oxalic acid solution was added to the reactant under stirring to make barium oxalate precipitate to adjust Ba/Ti ratio to 1.00. All processes were carried out under CO_2-free conditions. Properties of hydrothermal $BaTiO_3$ powder are shown in Table 6, 7a, b.

xvii) Y. Matsumoto, *et al* [53] of Kumamoto University reported about manganese oxides. Its film was deposited on a Pt electrode by electrochemical oxidation of solution containing La^{3+}, Sr^{2+}, and Mn^{2+} ions in an autoclave at 150°C under pressure of 1.0 Mpa. The electrolytes were nitrates and chlorides of these metals in aqueous solutions.

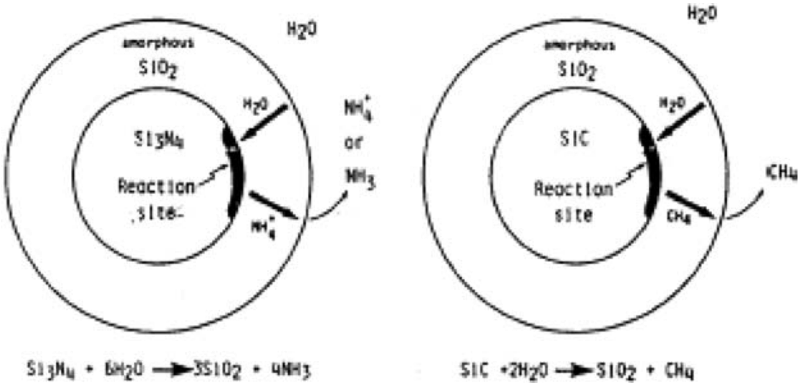


Figure 17 Reaction model of hydrothermal oxidation of Si_3N_4 and SiC powder.

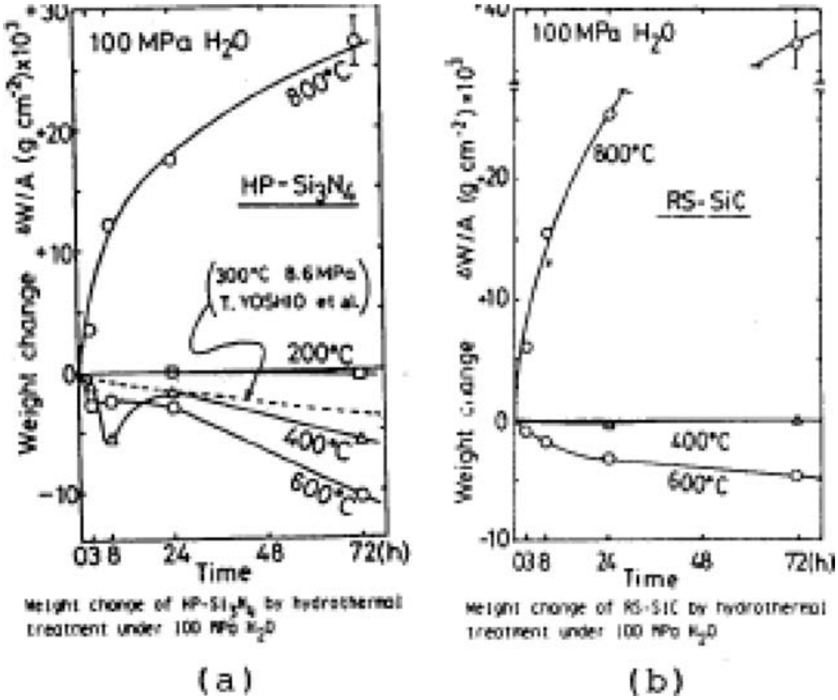


Figure 18 (a) Weight change of HP-Si_3N_4 by hydrothermal treatment under 100 MPa H_2O. (b) Weight change of RS-SiC by hydrothermal treatment under 100 MPa H_2O.

The deposited oxide films contained La^{3+}, Sr^{2+} and water molecules in the structure and had layers similar to hydrated manganese dioxdes such as $Mn_7O_{13}\cdot 5H_2O$ and $Na_4Mn_{14}O_{24}\cdot 9H_2O$. The apparatus is shown in Fig. 14.

7. From 2001—to date

N. Yamasaki moved from Kochi University to Tohoku University and also K. Ioku recently moved from Yamaguchi University to Tohoku University. Therefore, at present, Tohoku is one of the major centers for hydrothermal work.

At present time, Tohoku University and Kochi University are very active. Also Tokyo Institute of Technology is active continuously for hydrothermal and/or soft chemistry route. Many Japanese Universities and companies have been set up for hydrothermal works. I do not mention in detail because these are in too many places.

xviii) The 7th International Symposium on Hydrothermal Reactions [54] was held in December, 2003, in Changchun, China. There were 68 papers. Among 68 papers, 29 papers were by Japanese.

Tohoku University	13
Kochi University	7
Kumamoto University	2
Tokyo Inst. Technology	2
Shizuoka University	1
Chuo University	1
Yamaguchi University	1
Osaka University	1
From industries	2

xix) At this symposium, K. Yanagisawa [55] presented his paper, "Direct Hydrothermal Synthesis of Multi-Component Oxides by High Temperature Mixing Method." They used multi-chamber autoclave made of stainless steel with Teflon lining. Two methods, low temperature and high temperature mixing method for hydroxyapatite. One method was as follows: (1) the autoclave was rotated with 20 rpm at room temperataure to mix two solutions in the autoclave and then heated to 200°C. (2) the autoclave was heated to 200°C without rotation. After the temperature of the solutions reached to 200°C, the autoclave was rotated. Both case, temperature was at 200°C for 24 h. The autoclave is shown in Fig. 15.

xx) N. Yamasaki's laboratory [56] recently has studied on hydrothermal diamond. Hydrogenated diamond powder, iron powder, and 1, 1, 1-trichloroethane with 10 M NaOH at 300°C under 1 Gpa for 1–3 days. Then they confirmed formation of diamond hydrothermally.

Very fine diamond powder 1–2 μm was sintered by new bond formation among each diamond particles under hydrothermal conditions. Chlorinated hydrocarbon was 1, 1, 1-trichloroethane and alkaline solvent was 10 M NaOH. The piston cylinder type vessel was heated to 300°C under pressures of 0.5–2 Gpa for 2–72 h. The apparatus is shown in Fig. 16.

8. Hydrothermal corrosion [57]

Several papers appeared on hydrothermal corrosion, silicon carbide, silicon nitride, were studied. Tohoku University, Okayama University, industry, and our laboratory have done this subject.

The reactions were as follows:

$Si_3N_4 + 6H_2O = 2SiO_2 + 4NH_3$

$SiC + 2H_2O = SiO_2 + CH_4$

These are shown in Fig. 17 for powders and Fig. 18 for sintered bodies.

9. Summary

This is a summary paper of main hydrothermal works in Japan.

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