RESEARCH REPORT

Preparation of aluminum hydroxide, nordstrandite

Taichi SATO*

In order to prepare pure nordstrandite of aluminum hydroxide, gelatinous aluminum hydroxides prepared from aqueous solutions of chloride or nitrate of aluminum on the addition of alkali such as aqueous solutions of sodium or ammonium hydroxides are aged under different conditions for a given period at a selected temperature: the precipitates are aged in the mother liquors; the precipitates are washed by water and then aged in ammonia liquors or aqueous solutions of ethylenediamine. As the result, it is found that generally nordstrandite is not formed by the ageing in the mother liquor except for the addition of ethylenediamine as an alkaline solution; nordstrandite is formed as a mixture of bayerite and/or hydrargillite by the ageing in ammonia liquor, and pure nordstrandite is formed by ageing in aqueous solutions of ethylenediamine.

Keywords: aluminum hydroxide, nordstrandite, ethylenediamine, hydrargillite, bayerite

(Received April 1, 1988)

1. Introduction

For a general classification of the various modifications of aluminum hydroxides, they are divided into two groups of crystalline and gelatinous aluminum hydroxides (1): the most welldefined crystalline forms of three trihydroxides, $\text{Al}(\text{OH})_3$, gibbsite (also called as hydrargillite), bayerite and nordstrandite and of two modifications of aluminum oxyhydroxides, AlOOH , of boehmite and diaspore; gelatinous hydroxides consist of predominantly X-ray indifferent (amorphous) aluminum hydroxide and gelatinous boehmite (pseudoboehmite). For nordstrandite, however, the literatures on its preparation are limited in comparison with those for other aluminum hydroxides. According to Van Nordstrand et al. (2) reported at first this form, this trihydroxide is obtained when the gel prepared from aluminum chloride or nitrate solutions with ammonium hydroxide is aged in the mother liquor at a pH of 7.5 to 9. Also Hauschild has showed that nordstrandite is prepared purely by reacting aluminum, aluminum hydroxide gel or hydrolyzable aluminum compounds with aqueous solutions of alkyl-

lenediamines, in particular ethylene diamine (3). In contrast, nordstrandite has been discovered to occur naturally in some places (4), and accordingly the structure of nordstrandite has been proposed using the crystal obtained naturally (5, 6). On the one hand, the patents describing the manufacture of nordstrandite have been issued (7, 8). Nevertheless, there are some indistinct points on the formation of nordstrandite. Recently the present author has reported that amorphous aluminum hydroxide, pseudoboehmite, bayerite, hydrargillite and nordstrandite are formed by the hydration of amorphous alumina (9). Therefore this paper extends the work to obtain further information on the preparation of nordstrandite in comparison with the results for the preparation of gelatinous aluminum hydroxides (10–13).

2. Experimental

The following procedures were carried out to prepare nordstrandite: gelatinous aluminum hydroxides, precipitated from aqueous solutions of chloride or nitrate of aluminum in 0.25 mol dm^{-3} on the addition of aqueous solutions of sodium hydroxide in 1

* Faculty of Engineering, Shizuoka University (Hamamatsu-shi, Shizuoka and at present Alcan International, Kingston Laboratories (Kingston, Ontario, Canada).

mol dm⁻³ or ammonium hydroxide in 28% slowly at the rate of 5 or 50 cm³ min⁻¹ or rapidly at various pH values of 7, 9, 11 and 12 by agitating at 25°C (room temperature), were aged in the mother liquors for a given period at a selected temperature; gelatinous aluminum hydroxide, precipitated from aqueous aluminum chloride solution in 0.25 mol dm⁻³ on the addition of ammonia liquor in 28% at the rate of 5 cm³ min⁻¹ at pH 8, 9 and 10 at 25°C, were washed by water and then aged in aqueous ammonium hydroxide solution at pH 11.2–11.6; amorphous aluminum hydroxides, precipitated from aqueous solutions of chloride or nitrate of aluminum in 0.25 mol dm⁻³ on the addition of aqueous solutions of sodium hydroxide in 1 mol dm⁻³ or ammonium hydroxide in 28% at the rate of 5 cm³ min⁻¹ at pH 8 at 25°C, were washed by water and then aged in aqueous solutions of ethylenediamine.

The precipitated aluminum hydroxide were centrifugarized, washed with distilled water as free as possible from alkali and anions, and then dried with acetone. The material so obtained were examined by thermogravimetry and differential thermal analysis (TG and DTA), X-ray diffraction study and infrared spectrophotometry. The TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus (Agne Research Center) using platinum-platinum/rhodium thermocouples and a Shinku Riko Model TGD-1500 RH-P differential thermobalance equipped with an infrared heater. For the measurement of differential thermoelectromotive force, α -alumina was used as a reference material. Specimens weighing 100–200 mg were heated at a rate of 5°C min⁻¹ under atmospheric pressure. The infrared spectra were obtained by a Nujol or Fluorube mull method on Japan Spectroscopic Co. Ltd. Model IRA-1 grating infrared spectrophotometer for measurement at 4000–650 cm⁻¹, and Model IR-F for measurement at 700–200 cm⁻¹, using a capillary film between thallium halide or polyethylene plates. X-ray powder diffraction diagrams were made with a Rigaku Denki Co. Ltd. Geigerflex recording X-ray diffractometer with filtered copper radiation (generator operating at 30 kV and 15 mA, divergence slits 1° × 1°, scanning speed 2 and/or 1/4° min⁻¹, chart speed 1 cm min⁻¹,

time constant 2S, scale factor 16, multiplier constant 1.0).

The concentration of aluminum in aqueous solutions was determined by titration with EDTA using xylenol orange as indicator (14).

3. Results and discussion

3.1 Ageing of precipitate in mother liquor

The aqueous solutions of sodium or ammonium hydroxide were added to the aqueous solutions of chloride or nitrate of aluminum at various pH values, and then the resulting precipitates were aged in the mother liquors for 1 h and 1, 7, 25 and 50 days at 30 and 50°C. The crystallographic composition of their precipitates examined by X-ray diffraction study is illustrated in Table 1.

This result corresponds fundamentally to those for the preparation and crystallisation of gelatinous aluminum hydroxide reported already (10, 11): the freshly precipitated gelatinous aluminum hydroxide exists in an amorphous type independently of the pH value and goes to pseudoboehmite by ageing in the mother liquor. By further ageing, however, hydrargillite is produced in contact with aqueous solution at low pH, and bayerite at higher pH. In Table 1 it is found that the formation of nordstrandite is observed as a mixture of bayerite in a few precipitates. When the gelatinous precipitates, prepared from aqueous aluminum nitrate solution on the addition of ammonia liquor in 28% at pH 9, was aged for 1 h and 7 days, X-ray diffraction diagrams showed that pseudoboehmite is produced by ageing for 1 h, and bayerite is formed in addition to pseudoboehmite by ageing for 7 days. By ageing for 25 days, however, the peaks of nordstrandite appear in addition to the pattern of bayerite and the band of pseudoboehmite which slightly still remain, and for 50 h the pattern of pseudoboehmite disappears and simultaneously the intensities of the bands due to bayerite and nordstrandite become more intense (Fig. 1). The formation of nordstrandite is also observed by the ageing for 25 and 50 days in the precipitates, prepared from aqueous aluminum chloride solution on the addition of sodium hydroxide solution at pH 11. In this case, the intensities of the peaks due to bayerite becomes weaker with in-

Table 1 Ageing of the precipitates^{a)}, prepared from aqueous solutions of chloride or nitrate of aluminum on the addition of aqueous solutions of sodium or ammonium hydroxides at various pH values, in the mother liquors

Specimen No.	Precipitation			Ageing			Crystallographic composition ^{c)}
	Al-salt ^{b)}	Added alkali ^{c)}	Rate of addition of alkali ^{d)} , cm ³ min ⁻¹	pH	Temp., °C	Time day	
1	AlCl ₃	NaOH	5	7	30	1/24	A
2	"	"	"	"	"	1	A
3	"	"	"	"	"	7	A
4	"	"	"	"	"	25	A
5	"	"	"	"	"	50	A
6	"	NH ₄ OH	"	"	"	1	A
7	"	"	"	"	"	25	A, Bo
8	"	"	"	"	"	50	A, H
9	Al(NO ₃) ₃	NaOH	"	"	"	1/24	A
10	"	"	"	"	"	1	A
11	"	"	"	"	"	7	A, Bo
12	"	"	"	"	"	25	A, Bo
13	"	NH ₄ OH	"	"	"	1	A, Bo
14	"	"	"	"	"	25	A, H
15	"	"	"	"	"	50	A, H
16	AlCl ₃	NaOH	"	9	"	1/24	A, Bo
17	"	"	"	"	"	1	Bo
18	"	"	"	"	"	7	Bo
19	"	"	"	"	"	25	Bo
20	"	"	"	"	"	50	Bo, H
21	"	NH ₄ OH	"	"	"	1/24	A
22	"	"	"	"	"	1	Bo, A
23	"	"	"	"	"	7	Bo, A
24	"	"	"	"	"	25	Bo, H
25	"	"	"	"	"	50	Bo, H
26	Al(NO ₃) ₃	NaOH	"	"	"	1/24	A
27	"	"	"	"	"	1	Bo, A
28	"	"	"	"	"	7	Bo, A
29	"	"	"	"	"	25	Bo
30	"	"	"	"	"	50	Bo, B
31	"	NH ₄ OH	"	"	"	1/24	Bo
32	"	"	"	"	"	1	Bo
33	"	"	"	"	"	7	Bo, B
34	"	"	"	"	"	25	B, N, Bo
35	"	"	"	"	"	50	B, N
36	AlCl ₃	NaOH	"	11	"	1/24	Bo, B
37	"	"	"	"	"	1	B, Bo
38	"	"	"	"	"	7	B
39	"	"	"	"	"	25	B, N
40	"	"	"	"	"	50	B, N
41	"	NH ₄ OH	"	"	"	1/24	Bo, B
42	"	"	"	"	"	1	B
43	"	"	"	"	"	25	B
44	"	"	"	"	"	50	B

Table 1 (Continuation)

Specimen No.	Precipitation			Ageing			Crystallographic composition ^{c)}
	Al-salt ^{b)}	Added alkali ^{c)}	Rate of addition of alkali ^{d)} , cm ³ min ⁻¹	pH	Temp., °C	Time day	
45	Al(NO ₃) ₃	NaOH	5	11	30	1/24	Bo, B
46	"	"	"	"	"	1	B
47	"	"	"	"	"	25	B
48	"	"	"	"	"	50	B, H
49	"	NH ₄ OH	"	"	"	1/24	Bo, B
50	"	"	"	"	"	1	B
51	"	"	"	"	"	7	B
52	"	"	"	"	"	25	B
53	"	"	"	"	"	50	B
54	AlCl ₃	NaOH	50	12	"	1/24	B
55	"	"	"	"	"	1	B, H
56	"	"	"	"	"	7	B, H
57	"	"	"	"	"	25	B, H
58	"	"	"	"	"	50	B, H
59	"	NH ₄ OH	"	9	50	1/24	A
60	"	"	"	"	"	1	A, Bo
61	"	"	"	"	"	7	A, Bo
62	"	"	"	"	"	25	A, Bo
63	"	"	R	7	"	1/24	A, Bo
64	"	"	"	"	"	1	Bo
65	"	"	"	"	"	7	Bo, B

a) The precipitates were prepared at 25°C.

b) The concentrations of aluminum salts in aqueous solutions are in 0.25 mol dm⁻³.

c) The added alkaline solutions are sodium hydroxide solution in 1 mol dm⁻³ and ammonia liquor in 28%.

d) R means that alkali is rapidly added into aqueous solution of aluminum salt.

e) A, Bo, B, H and N represent amorphous aluminum hydroxide, psendoboechmite, bayerite, hydrargillite and nordstrandite, respectively.

creasing those of nordstrandite. Accordingly it seems that the preparation of pure nordstrandite is slightly difficult when the precipitates prepared from aqueous solutions of chloride or nitrate of aluminum on the addition of aqueous solutions of sodium or ammonium hydroxides, are aged in the mother liquors.

3.2 Ageing of gelatinous aluminum hydroxide in ammonia liquor

After the gelatinous aluminum hydroxides, prepared from aqueous aluminum chloride solution on the addition of ammonium hydroxide solution in 28% at pH 8–10, were separated from mother liquors, those precipitates were washed by water and aged in fresh ammonia liquor at pH values of 11.2–11.6 for 15, 25 and 35 days at 30 and 40°C. As the

results shown in Table 2, the formation of nordstrandite is observed as the mixture of bayerite and/or hydrargillite in all the resulting materials. Especially the formation of hydrargillite depends on the pH value to prepare initial precipitate: when the precipitates prepared at pH 9 are aged in ammonia liquor at 30°C, the resulting materials consist of a mixture of nordstrandite and bayerite only, although hydrargillite coexists in them as the temperature of ageing rises (Fig. 2). From these results it is deduced that the preparation of pure nordstrandite is not completed even by ageing of the washed precipitate in ammonia liquor.

3.3 Ageing of gelatinous aluminum hydroxide in aqueous solution of ethylenediamine

Fig. 1 X-ray diffraction diagrams of the precipitates prepared from aqueous aluminum nitrate solution on the addition of ammonium liquor at pH 9 and aged in the mother liquor for a given period (numbers on curves refer to specimen Nos. seen in Table 1).

When the gelatinous aluminum hydroxides, prepared from aqueous solutions of chloride or nitrate of aluminum on the addition of aqueous solutions of sodium or ammonium hydroxides at pH 8, were aged for 1 h and 1, 7, 30 and 60 days at 40 or 60°C in aqueous solutions of ethylenediamine in 2, 5, 8, 10, 30 and 70% which indicate the pH values of 10.8, 11.2, 11.4, 11.6, 12.5 and 13.8, respectively, in ethylenediamine solution in 100% the resulting materials gave the crystallographic compositions shown in **Table 3**.

This suggests that by the ageing of amorphous aluminum hydroxide for 7 days at 40°C nordstrandite is formed in aqueous solutions of ethylenediamine below 30%, and pseudoboehmite in aqueous solutions of ethylenediamine in above 70%, corresponding to the fact that pseudoboehmite is largely precipitated in the range of pH between 7 and 10 (10). In aqueous solutions of ethylenediamine in above 70%, however, nordstrandite is formed by the ageing for a longer time over 30 days at a higher temperature of 60°C. In Table 3, pseudoboehmite exists as a mixture of nordstrandite in the resulting materials by the ageing for 1 h, but disappears by the ageing for a day, except the ageing of the

Table 2 Ageing of gelatinous aluminum hydroxides^{a)} in ammonia liquors

Specimen No.	Precipitation pH	Ageing			Crystallographic composition, B / N / H ^{c)}
		pH ^{b)}	Temp., °C	Time, day	
66	8	11.2	30	15	100/ 55/38
67	"	"	"	25	100/ 62/42
68	"	"	"	35	100/ 69/ 0
69	"	11.4	"	15	100/ 58/ 0
70	"	"	"	25	100/ 56/37
71	"	"	"	35	100/ 62/ 0
72	"	11.6	"	15	100/ 73/47
73	"	"	"	25	100/ 72/56
74	"	"	"	35	100/ 56/38
75	9	11.2	"	15	92/100/ 0
76	"	"	"	25	90/100/ 0
77	"	"	"	35	84/100/ 0
78	"	11.4	"	15	67/100/ 0
79	"	"	"	25	58/100/ 0
80	"	"	"	35	77/100/ 0
81	"	11.6	"	15	60/100/ 0
82	"	"	"	25	75/100/ 0
83	"	"	"	35	61/100/ 0
84	10	11.2	"	15	100/ 90/ 0
85	"	"	"	25	100/ 89/ 0
86	"	"	"	35	100/ 92/ 0
87	"	11.4	"	15	100/ 94/ 0
88	"	"	"	25	100/ 90/ 0
89	"	"	"	35	100/ 96/ 0
90	"	11.6	"	15	100/ 98/ 0
91	"	"	"	25	100/ 93/ 0
92	"	"	"	35	100/ 96/ 0
93	"	11.2	40	15	100/ 75/47
94	"	"	"	25	100/ 73/59
95	"	"	"	35	100/ 72/49
96	"	11.4	"	15	100/ 70/45
97	"	"	"	25	100/ 75/48
98	"	"	"	35	100/ 80/37
99	"	11.6	"	15	100/ 84/60
100	"	"	"	25	100/ 81/57
101	"	"	"	35	100/ 92/61

a) Gelatinous aluminum hydroxides were prepared from aqueous aluminum chloride solution in 0.25 mol dm⁻³ on the addition of ammonia liquor in 28% at the rate of 5 cm³ min⁻¹ at pH 8–10 at 25°C and washed by water.

b) Ageing in fresh ammonia liquor in 28%.

c) The ratios of the intensities of X-ray diffraction peaks at 4.72, 4.79 and 4.82 Å due to bayerite, nordstrandite and hydrogillite, respectively.

Fig. 2 X-ray diffraction diagrams of gelatinous aluminum hydroxides aged in ammonia liquor at pH 11.2 for 35 days (numbers on curves refer to specimen Nos. seen in Table 2; numerals in parentheses represent the pH values to prepare initial precipitates and ageing temperatures, °C, respectively).

precipitates, prepared from aqueous solutions of chloride or nitrate of aluminum on the addition of aqueous sodium hydroxide solution in aqueous solution of ethylenediamine in 70%. Especially, for the ageing of the precipitate prepared from aluminum chloride solution pseudoboehmite still remains by the ageing for 7 days, and disappears by the ageing for 30 days. It is thus considered that amorphous aluminum hydroxide goes to pseudoboehmite by the ageing in aqueous solutions of ethylenediamine and to nordstrandite by further ageing.

For the materials, precipitated from aluminum chloride solution on the addition of sodium hydroxide solution and aged in 8% ethylenediamine solution at 40°C, some representative X-ray diffraction diagrams, infrared spectra and curves of thermal

analysis are shown in Figs. 3–5. Furthermore the X-ray diffraction data of nordstrandite prepared in this work are given in Table 4 in comparison with them reported in the literature (5a). In Fig. 3, the X-ray diffraction diagram of the material aged for 1 day exhibits the pattern of nordstrandite, and the intensities of the bands become more intense by the ageing for 30 days. The infrared spectrum of nordstrandite (Fig. 4) which is clarified in the material prepared by

Fig. 3 X-ray diffraction diagrams of gelatinous aluminum hydroxides aged in aqueous solution of ethylenediamine in 8% (numbers on curves refer to specimen Nos. seen in Table 3).

Fig. 4 Infrared spectra of gelatinous aluminum hydroxides aged in aqueous solution of ethylenediamine in 8% (numbers on curves refer to specimen Nos. seen in Table 3).

Table 3 Ageing of gelatinous aluminum hydroxides^{a)} in aqueous solutions of ethylenediamine

Specimen No.	Precipitation		Ageing			Crystallographic composition
	Al-salt	Added Alkali	Concn. of en ^{b)} , % (v/v)	Temp., °C	Time, day	
102	AlCl ₃	NaOH	8	40	1/24	N, Bo
103	"	"	"	"	1	N
104	"	"	"	"	30	N
105	"	"	"	"	60	N
106	"	NH ₄ OH	"	"	1/24	Bo, H
107	"	"	"	"	1	N
108	"	"	"	"	7	N
109	"	"	"	"	30	N
110	"	"	"	"	60	N
111	Al(NO ₃) ₃	NaOH	"	"	1/24	Bo, N
112	"	"	"	"	1	N
113	"	"	"	"	30	N
114	"	"	"	"	60	N
115	"	NH ₄ OH	"	"	1/24	Bo, N
116	"	"	"	"	1	N
117	"	"	"	"	7	N
118	"	"	"	"	30	N
119	"	"	"	"	60	N
120	AlCl ₃	NaOH	70	60	1/24	Bo, N
121	"	"	"	"	1	N, Bo
122	"	"	"	"	7	N, Bo
123	"	"	"	"	30	N
124	"	"	"	"	60	N
125	"	NH ₄ OH	"	"	1/24	Bo, N
126	"	"	"	"	1	N
127	"	"	"	"	7	N
128	"	"	"	"	30	N
129	Al(NO ₃) ₃	NaOH	"	"	1/24	Bo, N
130	"	"	"	"	1	N, Bo
131	"	"	"	"	7	N
132	"	"	"	"	30	N
133	"	"	"	"	60	N
134	"	NH ₄ OH	"	"	1	N
135	"	"	"	"	7	N
136	"	"	"	"	30	N
137	"	"	"	"	60	N
138	AlCl ₃	"	100	"	1/24	Bo, N
139	"	"	"	"	60	N
140	"	NaOH	2	40	7	N
141	"	"	5	"	7	N
142	"	"	10	"	7	N
143	"	"	"	60	7	N
144	"	"	30	40	7	N
145	"	"	70	"	7	Bo
146	"	"	100	"	7	Bo

a) Gelatinous aluminum hydroxides were prepared from aqueous solutions of chloride or nitrate of aluminum in 0.25 mol dm⁻³ on the addition of sodium hydroxide solution in 1 mol dm⁻³ and ammonia liquor in 28% at rate of 5 cm³ min⁻¹ at pH 8 at 25°C and washed by water.

b) ethylenediamine.

Fig. 5 TG and DTA curves of gelatinous aluminum hydroxides aged in aqueous solution of ethylenediamine in 8% (numbers on curves refer to specimen Nos. seen in Table 3). (a) TG curves, (b) DTA curves.

ageing for 30 days shows the OH stretching band at $3700\text{--}330\text{ cm}^{-1}$ [3610, 3540 (shoulder), 3510 (shoulder), 3490, 3420 and 3360 cm^{-1}] the OH bending band at $1100\text{--}900\text{ cm}^{-1}$ [1065, 1040, 1020, 980 and 925 cm^{-1}], the broad band centred around 840 and 730 cm^{-1} due to the vibration of the Al–OH group and the Al–O stretching frequency at $475\text{--}325\text{ cm}^{-1}$ [472, 460, 430, 410, 395, 375, 360, 350 and

Table 4 X-ray diffraction data (intensity and interplanar spacings) for nordstrandite

This work		Literature ^{a)}	
d, Å	I/I ₀	d, Å	I/I ₀
4.793	100	4.791	100
4.328	18.9	4.318	28
4.209	16.1	4.207	26
4.167	13.5	4.158	21
3.895	7.9	3.888	13
3.617	6.5	3.604	11
3.426	4.1	3.430	7
2.480	8.1	2.482	13
2.454	5.8	2.453	7
2.391	18.2	2.393	29
2.269	17.8	2.265	33
2.015	14.6	2.017	27
1.901	16.2	1.901	22
1.785	7.2	1.783	13
1.597	3.0	1.597	5
1.547	2.5	1.541	5
1.517	3.1	1.516	7
1.478	3.4	1.479	7
1.439	7.7	1.441	14
1.430	2.6	1.430	5

a) Ref. 5a as a triclinic.

325 cm^{-1}]. The DTA curve of nordstrandite (Fig. 5) reveals an endothermic reaction at 280°C , corresponding to the change in the TG curve which gives a loss in weight of 36.2% at 1000°C . This result resembles that for type II of bayerite and/or hydrargillite (15), but it is presumed that the dehydration behaviour of nordstrandite is more analogous to that of bayerite-II than hydrargillite-II (16).

4. Conclusion

As mentioned above, it is apparent that when the precipitates, prepared from aqueous solutions of aluminum salts on the addition of alkaline solutions, are aged in the mother liquors or the washed gelatinous aluminum hydroxides in ammonia liquor, nordstrandite is formed only as a mixture of bayerite and/or hydrargillite. However, since pure nordstrandite is formed by the ageing of amorphous aluminum hydroxide in aqueous solution of ethylenediamine, it is expected that the formation of nordstrandite might be made by the ageing of the precipitate prepared

from aqueous solution of aluminum salt on the addition of ethylenediamine solution as an alkali. Accordingly the further examination has been carried out as follows: the precipitates, prepared from aqueous solution of aluminum chloride in 0.25 mol dm^{-3} on the addition of ethylenediamine solution in 50% at pH 7, 9 and 11.6 at 25°C , were aged in the mother liquor for a month at 30°C . As a result, it is found that the resulting materials are made of nordstrandite except a mixture of nordstrandite and pseudoboehmite for the precipitate at pH 7, although the material at pH 9 is more crystalline than that at pH 11.6. Hence it is presumed that pure nordstrandite is formed by the ageing of amorphous aluminum hydroxide in the presence of ethylenediamine under some selected condition.

Acknowledgements

The author wishes to thank Dr. K. Sato and Mr. K. Ishikawa with the assistance of experimental work and the Association for the Encouragement of Research in Light Metals (Keikinzoku Shogaku Kai) for a grant in connection with the present study.

References

- 1) T. Sato: *Thermochimica Acta*, **88** (1985), 69.
- 2) R. A. Van Nordstrand, W. P. Hettinger and C. D. Keith: *Nature* **177** (1956), 714.
- 3) U. Hauschild: *Z. anorg. allgem. Chem.* **324** (1963), 15.
- 4) J. R. D. Wall, E. B. Wolfenden, E. H. Beard and T. Deans: *Nature*, **196** (1962), 264; J. H. Hathaway and S. O. Schlanger: *Amer. Mineral*, **50** (1965) 1029; R. Schoen and C. E. Rokerson: *Amer. Mineral*, **55** (1970) 43.
- 5) a) H. Saalfeld and B. Mehrotra: *Naturwissenschaften*, **53** (1966), 128; b) H. Saalfeld and O. Jarchow: *Neues. Jahrb. Mineral Abh.*, **109** (1968), 185.
- 6) H. J. Bosmans: *Acta Crystallogr.*, **26** (1970), 649.
- 7) U. Hauschild: *Brit. Patent* 950, 165 (1964); *Ger. Patent* 1,182,643 (1964); *U. S. Patent* 3,222,130 (1965).
- 8) A. C. Kelly, L. R. Barsotti and R. B. Emerson: *U.S. Patent* 3,623,837 (1971).
- 9) T. Sato: *J. Jpn. Institute of Light Metals*, **37** (1987), 729.
- 10) T. Sato: *Z. anorg. allgem. Chem.*, **391** (1972), 69.
- 11) T. Sato: *J. Appl. Chem. Biotechnol.*, **24** (1974), 187.
- 12) T. Sato, S. Ikoma and F. Ozawa: *J. Chem. Techn. Biotechnol.*, **30** (1980), 225.
- 13) T. Sato, M. Suzuki and S. Ikoma: *J. Chem. Techn. Biotechnol.*, **31** (1981), 745.
- 14) J. Kinnunen and B. Wennerstrand: *Chemist-Analyst*, **46** (1957), 92.
- 15) T. Sato: *J. Appl. Chem.*, **9** (1959), 331.
- 16) T. Sato: *J. Thermal Anal.*, **32** (1987), 61.