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Hydrolysis behavior of aluminum nitride in various solutions

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The AlN powder was immersed in deionized water, HCl aq, NaOH aq and H_3PO_4 aq to investigate their hydrolysis behavior at 283 to 373 K. The pH of the solutions were not varied at the initial stage in the case of deionized water, and they increased abruptly after the incubation time with evolution of NH_3. Time until the evolution of NH_3 decreased with increasing temperature. The hydrolysis at the higher temperature was different from at the lower. Below 351 K a crystalline bayerite was produced on the surface of AlN particle, while a crystalline boehmite was produced at higher than 351 K. The AlN powder was hydrolyzed more efficiently in HCl aq and NaOH aq compared with in the deionized water. While, H_3PO_4 aq restrained hydrolysis of AlN powder. © *2000 Kluwer Academic Publishers*

1. Introduction

Environmental problems are expected to become more serious in the 21 of century, and establishment of a recycling system will be required to save energy and materials. Only 3% of the electrical energy needed to make aluminum from bauxite is necessary to make secondary aluminum from aluminum scraps. Aluminum and its alloys are thus typical recyclable materials, and so the establishment of an aluminum recycling system is quite urgent. There are several problems, however, among which is the treatment of aluminum dross. Aluminum dross is a kind of scum formed on the surface of molten aluminum; it contains the compounds Al_2O_3, AlN, MgN, KCl, MgO, Fe_3O_4, Al_2S_3, Al_4C_3, and others in addition to aluminum. Approximately 50% of the aluminum dross is now used as a fluxing agent for steelmaking and the rest is treated as industrial waste. The compounds AlN, MgN, Al_4C_3, and Al_2S_3, however, react with water, that is, rain, and then harmful gases such as NH_3, CH_4, and H_2S evolve. Moreover these reactions are exothermic in most cases, so that they can be ignited in addition to having an unpleasant smell. The hydrolysis of aluminum nitride (AlN) in these reactions is currently the major problem. Because the reaction between molten aluminum and atmospheric nitrogen has negative Gibbs energy below 2836 K [1], AlN is present in most aluminum dross. Since the dross is now disposed of after pre-treatment in water, 90% of AlN must be hydrolyzed to neutralize its harmful effect. Thus it is a problem of how to efficiently react AlN with water. AlN is a useful electronic substrate and refractory material because of its excellent electronic and physical properties of high thermal conductivity and high electrical resistivity, and good mechanical properties at high temperature. The effect of moisture on the surface properties and dielectric properties have been reported. Young *et al.* reported the corrosion behavior of AlN substrate in various acidic and basic solutions [2]. Conditions of effective protection of AlN powder against moisture were evaluated by statistical analysis by Hotza *et al.* [3]. Srivastava *et al.* reported that dielectric constant of AlN increased after exposure to acid (HCl and HNO_3) vapours [4]. Bowen *et al.* reported that initial reaction product of AlN in water was found to be a porous amorphous AlOOH and then changed to a crystalline $Al(OH)_3$ [5]. The improvement of water resistance of AlN has been investigated in the electronic field. However, there are few studies on how the hydrolysis can be completed quickly.

In this work, the hydrolysis behavior of AlN was investigated when it was immersed in aqueous solutions of various pH. The reaction mechanism of AlN with the solutions is discussed.

2. Experimental

Commercial AlN powder* and AlN in bulk which was sintered from the powder were used. The specifications

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* Tokuyama Soda Co. Ltd., Japan.

TABLE I Chemical composition of AlN powder (ppm)

AlN	Ca	Mg	Si	Cr	Fe	Ni	Zn
Bal.	20	10	120	40	10	20	20

of the AlN powders is as follows: average particles size 0.5 μm; density 1630 kg/m^3; specific surface area 4–6 m^2/g. The chemical composition of the powder is shown in Table I.

The AlN powder and bulk were immersed in deionized water (pH 6.0–6.4), NaOH aq (pH 10), HCl aq (pH 2.2) and H_3PO_4 aq (pH 2.5) at various temperatures from 283 to 373 K. Specimens of 1 g were dipped in 200 mL solutions. The pH values of the solutions with increasing immersion time were measured. The powders were taken out of the solutions by filtering solutions through a membrane after the tests. The filtered powders were identified by X-ray diffraction (XRD) analysis. The specimens were observed by scanning electron microscopy (SEM) before and after the immersion tests. In addition, ammonium ion concentration of the solutions was measured by a commercial water analysis examination. The measurable range was 0.5 to 10 ppm of NH_4^+.

3. Results

3.1. Behavior of hydrolysis

Fig. 1 shows the time-dependent pH as a function of the duration of the hydrolysis process for an AlN-deionized water suspension. The pH was not varied at the initial stage and subsequently increased with an ammonia smell. The incubation time, denoted as the critical time (t_c), decreased with increasing solution temperature. The pH reached the maximum value of approximately 10 below 299 K of solution temperature and of 11 over 318 K, and then gradually decreased passing through the peak. The reason the maximum pH values below and at 299 K were less than those over 318 K is as follows. It has been reported that aluminum oxide or a hydroxide thin shell was formed on the surface of the AlN core at room temperature [5–7]. The shell thus acted as a hydrophobic coating, and prevented further reaction of the AlN with water. At higher temperature the water might penetrate smoothly and quickly inside the AlN particle. Thus the maximum pH at 318 K and above is higher than that below 299 K. The decrease in pH after reaching the maximum was caused by the dissolution of CO_2 gas in the solution. This behavior was confirmed by a blank test in which deionized water stood in an air atmosphere at room temperature.

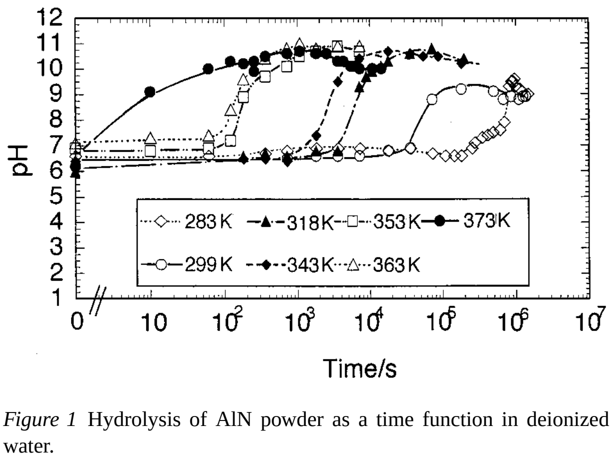

Figure 1 Hydrolysis of AlN powder as a time function in deionized water.

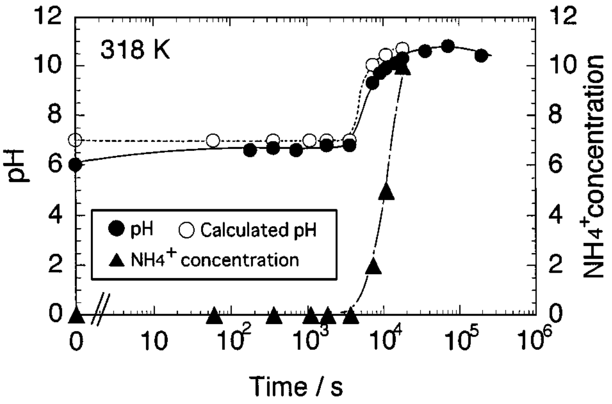

Figure 2 Concentration of NH_4^+ against immersion time (318 K).

A commercial water analysis examination of ammonium ion (NH_4^+) was performed to identify the AlN hydrolysis. Since the ammonia smell was identified as described above, NH_4^+ ion must be dissolved into the solution according to the following equation.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$
$$(NH_3 + H^+ \leftrightarrow NH_4^+)$$

The concentration of NH_4^+ against the immersion time at 318 K is shown in Fig. 2, where the calculated pH value from the NH_4^+ concentration is also shown. The change in NH_4^+ concentration corresponded to that in pH. No reaction except the AlN hydrolysis occur since the measured pH also corresponded to the calculated pH from the NH_4^+ concentration.

Fig. 3 shows SEM micrographs of as received AlN powder and after the immersion tests at 299 K and 373 K. All immersed powder was extracted after the pH reached a saturation value. The surface of as received AlN powders was smooth and their morphology is approximately spherical (Fig. 3a). The powder after the immersion test at 299 K had an angular morphology (Fig. 3b). The particle size increased because of being secondary particles and the morphology was angular; these powders had a rough surface. The surface morphology of the immersed AlN powder at 373 K (Fig. 3c) was irregular and was quite different from Fig. 3b. The hydrolysis behavior of AlN at lower temperature is most likely different from at higher temperature. So $\ln(1/t_c)$ was plotted against the reciprocal of the absolute temperature ($1/T$), that is, an Arrhenius plot, as shown in Fig. 4. Slope of the straight line changes at approximately 350 K. Namely, the hydrolysis mode below 350 K is different from that over 350 K.

All powders were identified by X-ray diffraction analysis as shown in Fig. 5. A little AlN which had not reacted with water remained in each immersed powder. Crystalline bayerite, $Al(OH)_3$, was identified after the immersion test at 318 K. While crystalline boehmite,

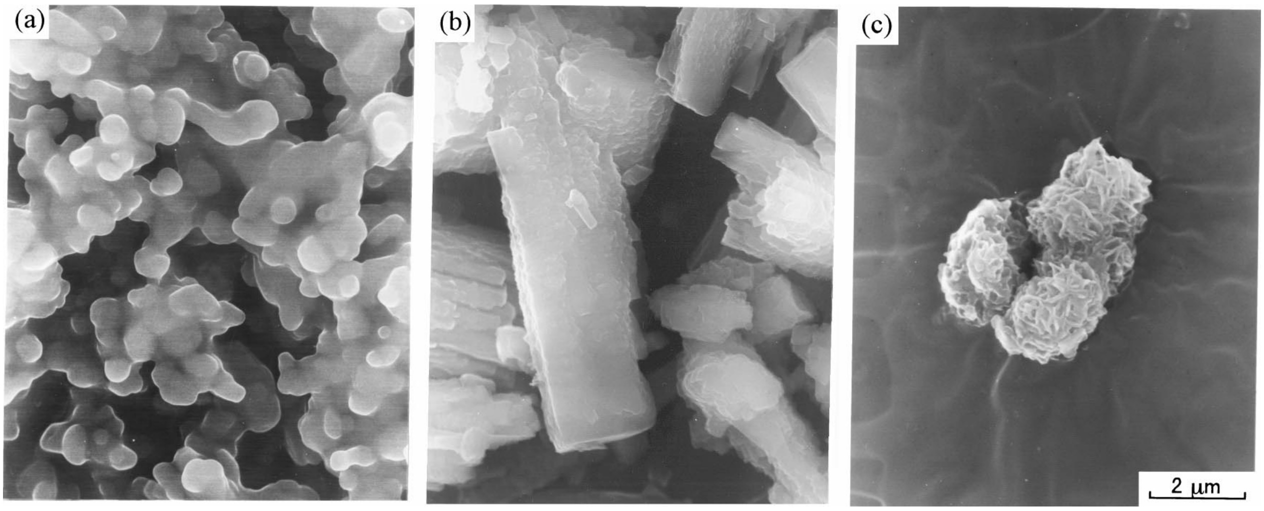

Figure 3 Microstructures of as received and immersed AlN powders. (a) As received (b) After immersion at 299 K (c) After immersion at 373 K.

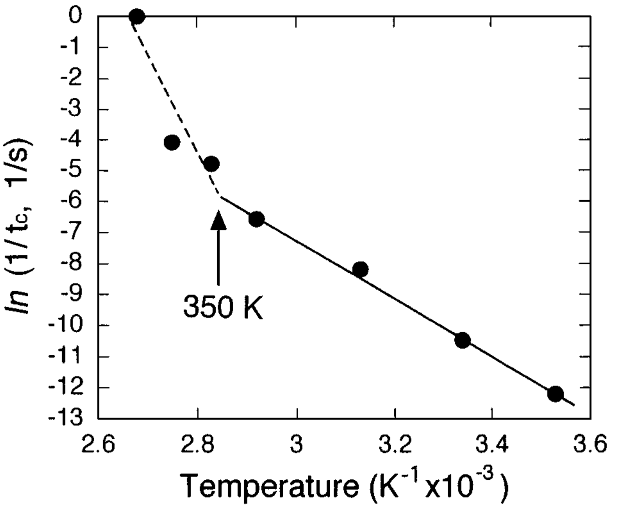

Figure 4 Arrhenius plot of AlN powder hydrolysis.

AlOOH, was produced after the immersion at 373 K. In the immersion test at 351 K, both phases, $Al(OH)_3$ and AlOOH, were identified. Therefore, the following two reactions can be considered below and over approximately 351 K:

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3 \qquad (T < 351\,K) \tag{2}$$

$$AlN + 2H_2O \rightarrow AlOOH + NH_3 \qquad (T > 351\,K) \tag{3}$$

Bowen *et al.* reported that the reaction taking place in deionized water at 298 K is [5]

$$AlN + 2H_2O \rightarrow (AlOOH)_{amorphous} + NH_3 \tag{4}$$

As the NH_3 was ionized in water, the pH was raised according to Equation 1. The amorphous AlOOH (boehmite) changed to a more stable phase, i.e. crystalline $Al(OH)_3$ (bayerite) at room temperature by the following equation:

$$(AlOOH)_{amorphous} + H_2O \rightarrow Al(OH)_{3\,crystalline} \tag{5}$$

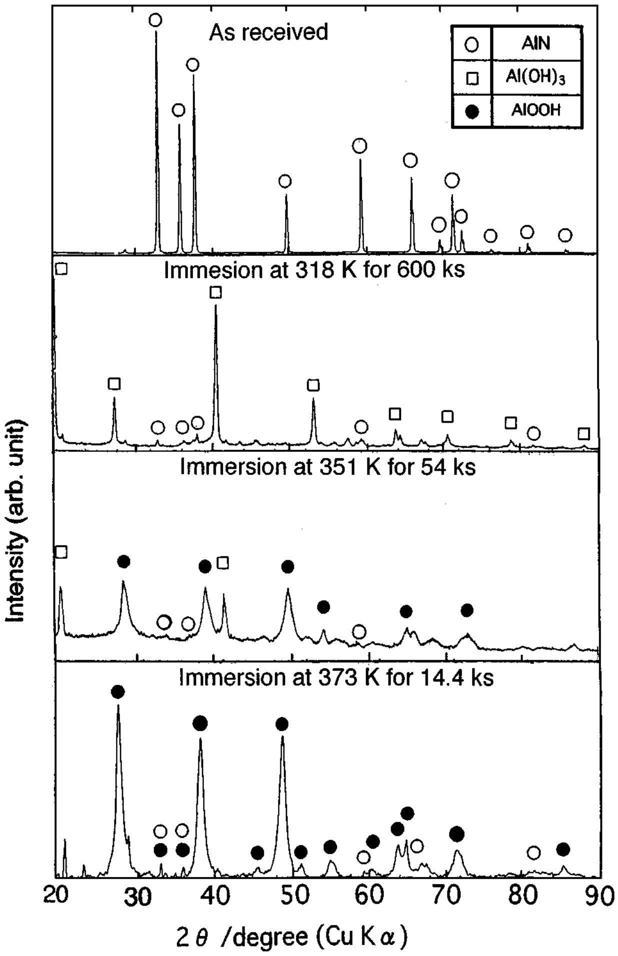

Figure 5 X-ray diffraction analyses of as received and immersed AlN powders.

It has been reported that the amorphous boehmite was produced after 28.8 ks immersion in water at room temperature, and then changed to a crystalline bayerite after 57.6 ks immersion [5]. In the present study, the amorphous boehmite was not identified since the immersion test was performed for over 100 ks. That is to say, the amorphous boehmite might have changed to a more stable phase of crystalline boehmite during the immersion.

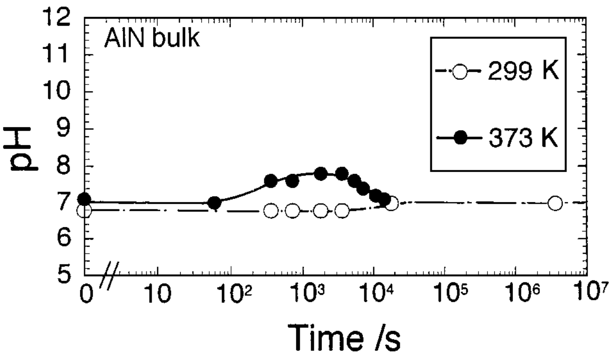

Figure 6 Hydrolysis of AlN bulk substrate as a time function.

The immersion test of AlN bulk materials was carried out to investigate the effect of surface area of AlN on the hydrolysis and the result of pH change is shown in Fig. 6. The total surface area of AlN powder (1 g) is approximately 5 m^2, while that of the AlN bulk substrate (1 g) is 2.7×10^{-4} m^2. No marked pH increase was noticed even after 100 ks at 299 K. At 373 K the pH value slightly increased to 8. The maximum pH value was also low in comparison with that of AlN powder at 373 K. Fig. 7 shows surface microstructures of AlN bulk substrate after the immersion tests, and Fig. 8 shows the XRD analysis of AlN bulk substrate after these tests. Although by the XRD analysis no compound was identified except AlN after the immersion test, the surface morphology after the immersion at 373 K was irregular and was similar to that of the immersed powder at 373 K (see Fig. 3c). Therefore, it is believed that the hydrolysis behavior was the same. The same reaction would occur at 299 K after a longer immersion time although almost no change was identified. Since the reaction would occur on the extreme thin surface layer, only a minimal amount of bayerite or boehmite was present unidentifiable by XRD analysis. The hydrolysis reaction of AlN progressed quickly for AlN powder which had larger surface area because there was greater contact area.

3.2. Effect of solutions

The AlN powders were immersed in acidic and basic solutions, HCl aq, H_3PO_4 aq and NaOH aq, and the results of pH change are shown in Fig. 9. The pH values increased to approximately 11 in the case of HCl aq and NaOH aq. In the deionized water the pH value increased up to 9, while it was unchanged in H_3PO_4 aq solution. After the immersion test, $Al(OH)_3$ was mainly identified in the cases of NaOH aq and HCl aq, while for the deionized water a slight amount of AlN changed to $Al(OH)_3$ at 299 K. Young *et al*. reported that in the AlN substrate plate immersion test in NaOH aq., the following reactions (6)–(8) occurred [2]:

$$\begin{aligned} &2AlN + 2NaOH + 8H_2O \\ &\quad \rightarrow Na_2Al_2O_4 \cdot 6H_2O + 2NH_3 \qquad (6) \\ &Na_2Al_2O_4 \cdot 6H_2O \\ &\quad \rightarrow 2NaOH + 2Al(OH)_3 + 2H_2O \qquad (7) \end{aligned}$$

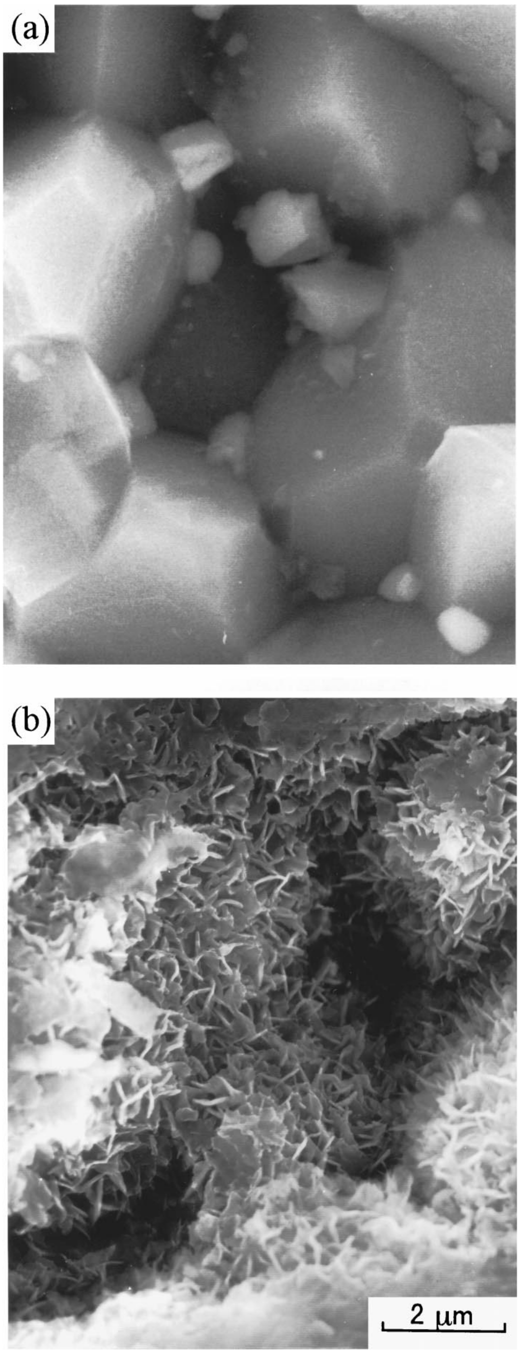

Figure 7 Microstructures of as received and immersed AlN bulk. (a) As received (b) After immersion at 373 K.

From reactions (6) and (7), the overall reaction is

$$AlN + 4H_2O \xrightarrow[(NaOH)]{} Al(OH)_3 + NH_4OH \qquad (8)$$

That is to say, NaOH acts as a catalytic agent to accelerate the AlN hydrolysis. While although Young [2] also reported that only several atomic layers of AlN substrate surface are etched off in acid solutions, in the present study the hydrolysis of AlN powder was accelerated more than in the deionized water. Because aluminum was dissolved in acidic and basic solutions as Al^{3+} and AlO_2^-, respectively on the basis of potential-pH equilibrium diagram [8]. Therefore, the hydrolysis of AlN powder was promoted in NaOH aq and HCl aq.

On the other hand, in the case of H_3PO_4 aq, phosphate may have been produced on the AlN surface and acts the

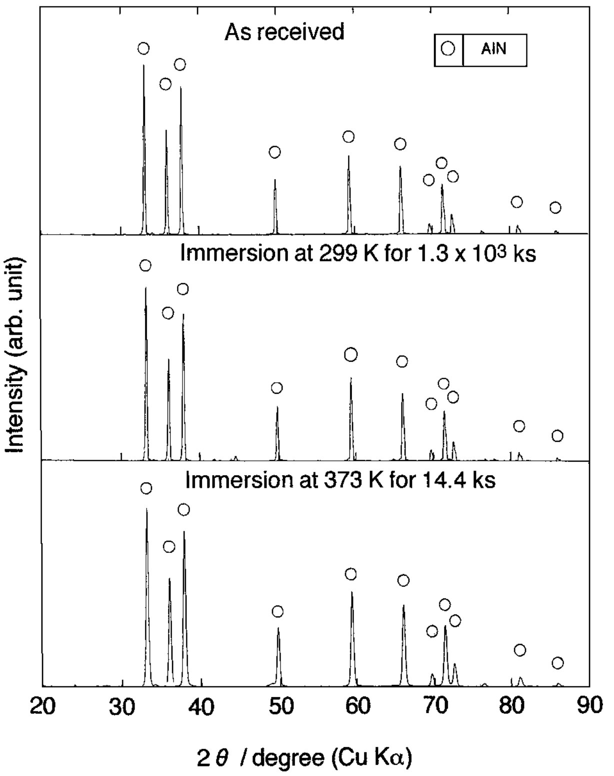

Figure 8 X-ray diffraction analyses of AlN bulk substrate.

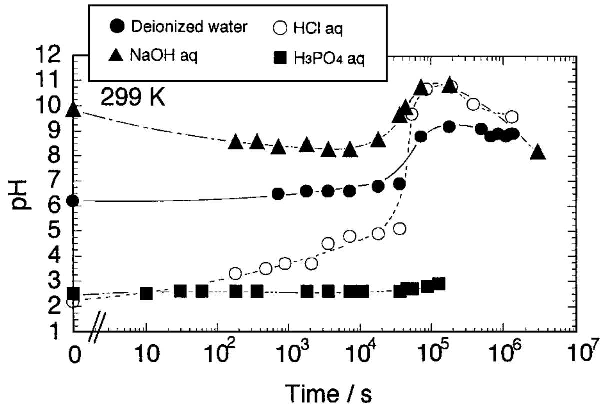

Figure 9 Effect of solutions on AlN hydrolysis at 299 K.

coating layer, so that almost no hydrolysis took place. This might be the same reason that the TOYALNITE that AlN powder was treated in phosphoric acid showed good protection ability [9].

4. Discussion

4.1. Thermodynamics

The molecular formulas of bayerite and boehmite corresponding to the rational formula of $Al(OH)_3$ and AlOOH, are $Al_2O_3 \cdot 3H_2O$ and $Al_2O_3 \cdot H_2O$, respectively. Equations 6 and 7 are rewritten as follows:

$$2AlN(s) + 6H_2O(l) \rightarrow Al_2O_3 \cdot 3H_2O(s) + 2NH_3(g) \quad (9)$$

$$2AlN(s) + 4H_2O(l) \rightarrow Al_2O_3 \cdot H_2O(s) + 2NH_3(g) \quad (10)$$

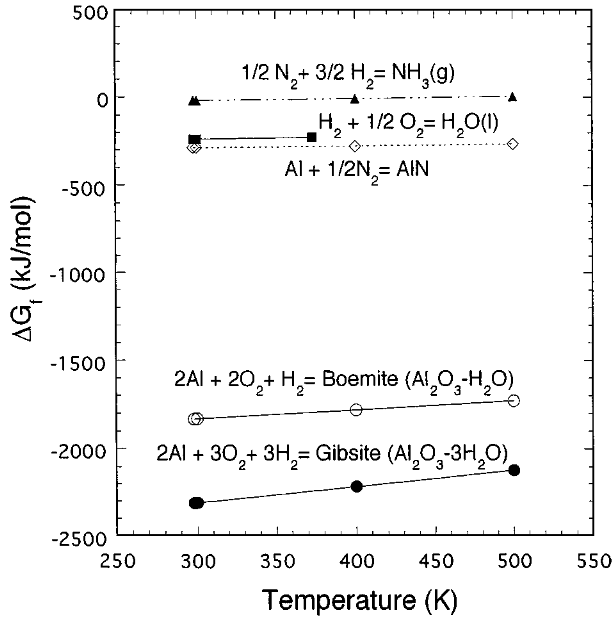

Figure 10 Gibbs standard formation energy.

No thermodynamics data of bayerite could be found, so the data on gibbsite ($Al_2O_3 \cdot 3H_2O$) which is thought to be almost the same was used in the following calculation. The standard formation Gibbs energy (ΔG_f) of bayerite and boehmite is shown in Fig. 10 [10]. Both ΔG_f are negative in the range of 283 to 373 K. The Gibbs energy changes of Equations 9 and 10 are calculated using next equations,

$$\Delta G_{(9)} = \Delta G_f(Al_2O_3 \cdot 3H_2O) + 2RT \ln(p_{NH_3}) - 2\Delta G_f(AlN) - 6\Delta G_f(H_2O) \quad (11)$$

$$\Delta G_{(10)} = \Delta G_f(Al_2O_3 \cdot H_2O) + 2RT \ln(p_{NH_3}) - 2\Delta G_f(AlN) - 4\Delta G_f(H_2O) \quad (12)$$

where p_{NH_3} is NH_3 partial pressure. Substituting each value into Equations 11 and 12, we obtain the next conditions when the ΔG are negative, that is, both the reactions will be able to occur.

$$p_{NH_3}(\text{in Equation (9)}) < 3.0 \times 10^{27}[\text{Pa}] \quad (T = 298\,\text{K})$$

$$p_{NH_3}(\text{in Equation (9)}) < 1.6 \times 10^{23}[\text{Pa}] \quad (T = 373\,\text{K})$$

$$p_{NH_3}(\text{in Equation (10)}) < 1.2 \times 10^{26}[\text{Pa}] \quad (T = 298\,\text{K})$$

$$p_{NH_3}(\text{in Equation (10)}) < 2.9 \times 10^{23}[\text{Pa}] \quad (T = 373\,\text{K})$$

These critical values are extremely larger than the atmospheric pressure (1 atm $\approx 1.0 \times 10^5$ Pa). Therefore, both reactions of Equations 9 and 10 could have occurred at the temperature of the present study.

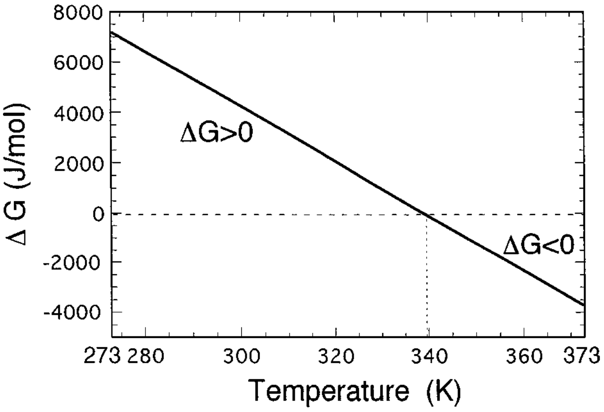

Figure 11 Gibbs energy change from gibbsite to boehmite.

Next, the following reaction should be considered:

$$Al_2O_3{\cdot}3H_2O(s) \rightarrow Al_2O_3{\cdot}H_2O(s) + 2H_2O(l) \quad (13)$$

The Gibbs energy change of Equation 13 is,

$$\Delta G_{(13)} = \Delta G_f(Al_2O_3{\cdot}H_2O) + 2\Delta G_f(H_2O) - \Delta G_f(Al_2O_3{\cdot}3H_2O) \quad (14)$$

Equation 14 is plotted against the temperature in Fig. 11. The $\Delta G_{(13)}$ changes from positive to negative at 338 K. As described in Section 3.1, the boehmite was formed at over 350 K. The results well corresponded to the thermodynamic analysis. Therefore, the hydrolysis mechanism of AlN is as follows. Below 351 K hydrolysis progresses according to Equation 9, while over 351 K it progresses according to a two-step reaction: the reaction not of Equation 3 but Equation 9 occurred first followed by the reaction of Equation 13. However, amorphous boehmite would have been formed before the formation of bayerite [5], although the phase could not be identified in this work. At both lower and higher temperature, the reaction of Equation 5 would first occur, and subsequently the reactions of Equations 9 and 13.

5. Conclusions

AlN powder and bulk substrate were immersed in deionized water and in various acidic and basic solutions. The reaction behavior of AlN with water yielded the following results.

1) Higher temperature and larger surface area of AlN caused more efficient acceleration of the hydrolysis.

2) The hydrolysis behavior changed at 351 K. Below 351 K crystalline bayerite and NH_3 were produced, while crystalline boehmite and NH_3 were produced a above 351 K.

3) The hydrolysis of AlN powder was accelerated in NaOH aq and HCl aq in comparison with in deionized water. While, H_3PO_4 aq restrained hydrolysis of AlN powder.

References

1. G. A. SLACK and T. F. McNELLY, *J. Crystal Growth* **34** (1976) 263.
2. C. D. YOUNG and J. G. DUH, *J. Mater. Sci.* **30** (1995) 185.
3. D. HOTZA, O. SAHLING and P. GREIL, *ibid.* **30** (1995) 127.
4. K. K. SRIVASTAVA, M. ZULFEQUAR and A. KUMAR, *ibid.* **25** (1990) 2861.
5. P. BOWEN, J. G. HIGHFIELD, A. MOCELLIN and T. A. RING, *J. Am. Ceram. Soc.* **73** (1990) 724.
6. J. G. HIGHFIELD and P. BOWEN, *Anal. Chem.* **61** (1989) 2399.
7. A. ABID, R. BENSALEM and B. J. SEALY, *J. Mater. Sci.* **21** (1986) 1301.
8. M. POURBAIX, in “Atlas of Electrochemical Equilibria in Aqueous Solutions” (National Association of Corrosion Engineers, Houston, Texas, USA, 1974) p. 168.
9. H. GORTER, H. GERRETSEN and R. A. TERPSTRA, in Third Euro-Ceramics, edited by P. Durán and J. F. Fernández (Faenza Editrice Ibérica S. L., Spain, 1993) Vol. 1, p. 615.
10. I. BARIN, in “Thermochemical Data of Pure Substances (Part I and II)” VCH verlagsgesellschaft mbH, Weinheim, Germany, 1989) p. 42, 56, 57, 649, 942.

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