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Protection of AlN powder against hydrolysis using aluminum dihydrogen phosphate

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Abstract

The hydrolysis of AlN powder in a dilute aqueous suspension was studied by following the pH vs. time in different media. The results show that phosphoric acid is effective in protecting AlN powder at room temperature, whereas at elevated temperatures hydrolysis takes place. When silicic acid or aluminum dihydrogen phosphate were present in the slurry no hydrolysis was observed even at 70°C. Further experiments indicate that by soaking in aluminum dihydrogen phosphate, water-resistant AlN powder can be prepared which will not react with water even after drying and/or redispersion. The protected AlN powder is hydrophilic, which facilitates aqueous powder processing. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aluminium nitride; Powders: chemical preparation; Substrates; Suspensions

1. Introduction

Aluminum nitride (AlN) has a unique set of material properties which are useful in many electronic, structural and refractory applications. Due to its high thermal conductivity, high electrical resistivity, low dielectric constant, low thermal expansion coefficient, high strength and high-temperature stability, aluminum nitride is very attractive as a substrate material for power circuits and as a packaging material for integrated circuits.[1] One of the major problems in the fabrication of AlN ceramics is the well-known reactivity of AlN powder with water. To avoid hydrolysis, non-aqueous powder processing is required or, alternatively, water resistant AlN powder should be used.[2] Most of the commercially available water-resistant AlN powders are coated with one of the carboxylic acids. These acids are hydrophobic (water repellent) and so powders cannot be dispersed in water without the addition of a hydrophilic surfactant. This in turn, requires the addition of an antifoaming agent to reduce the surface tension, which causes extensive foaming of the slurry.[3]

In the current study we report on the protection of AlN powder by the addition of anions, which form hydrophilic, water-resistant, complexes on the AlN powder surface in order to enable aqueous powder processing of AlN powder. The work is based on the results of our earlier investigation which revealed that in the presence of phosphoric or silicic acid the reactivity of AlN powder can be suppressed or even prevented, presumably due to the formation of impermeable, water-insoluble complexes on the particles' surface which prevent the access of water to the AlN core.[4]

2. Experimental

The AlN powder used throughout the experimental work was an AlN Grade B powder (H.C. Starck, Berlin) with a nominal particle size of 1.2 μm, oxygen content of 2.2% and a specific surface area of 3.2 m^2/g. Since during AlN decomposition in water ammonia is formed, the hydrolysis reactions can easily be followed by monitoring the pH of the slurry with time and/or temperature. For the hydrolysis tests, suspensions consisting of various amounts of AlN powder in solutions of phosphoric acid, silicic acid and aluminum dihydrogenphosphate [commercially available solution of $Al(H_2PO_4)_3$, TKI Hrastnik, Slovenia] were prepared. These slurries were then stirred for 1–24 h at room temperature and at 70°C, while the pH was continuously monitored. After the hydrolysis

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test slurries were filtered and washed to remove excess water. Cakes were dried at 80°C for 1 h and stored in airtight plastic containers for subsequent analysis. X-ray analysis was used to identify the crystalline phases after the hydrolysis test. Oxigen content was determined with ELTRA ON 900 Oxygen determinator (Eltra, Germany). Unreacted powders were redispersed in water to check the possibility of permanent AlN powder protection by adsorbed anions.

3. Results and discussion

For hydrolysis tests low solids loading was selected in order to assure a sufficient concentration of dissolved silica and phosphate anions to form at least a monolayer of silicates or phosphates on the AlN powder surface. The concentration of SiO_2 in the solution of silicic acid was determined by ICP–AES and was 126 mg SiO_2/l, corresponding to 2 mg SiO_2/m^2 AlN. This is above the calculated value of 0.7 mg SiO_2/m^2 AlN needed to cover the AlN surface. This calculation was made taking into account that one silicic acid molecule covers about 0.16 nm^2 of the particle's surface.[5] At pH = 3 the concentration of phosphate anions relative to the AlN powder surface was 1.1 mg $H_2PO_4^-/m^2$ AlN for the phosphoric acid and $Al(H_2PO_4)_3$ solutions. This concentration should also be high enough to form a continuous monolayer on the powder surface. The phosphate molecule is larger than the silicate[5,6] molecule and, therefore, the calculated concentration to form a monolayer should be even lower than 0.7 mg/m^2. The pH-time profiles for diluted (2 wt.%) AlN suspensions at room temperature are presented in Fig. 1. There was no significant change in the pH of the slurries during the 24-h period, indicating that the hydrolysis reactions did not occur. This was later confirmed by the measurement of oxygen content and the SEM morphology observation. The oxygen contents were found to be 2.4, 2.9 and 3.1 wt.% for the as-received AlN powder, the powder soaked in a solution of silicic acid and the powder soaked in a solution of $Al(H_2PO_4)_3$, respectively. After 24 h of soaking, the oxygen concentration is slightly higher than that of the as-received powder, but still far below the 48,9 wt.% in hydrolysed AlN as measured by Bowen et al.[7] in the powder after soaking for 24 h in water. The morphology of the protected powder does not differ from the as-received powder (Fig. 2a and

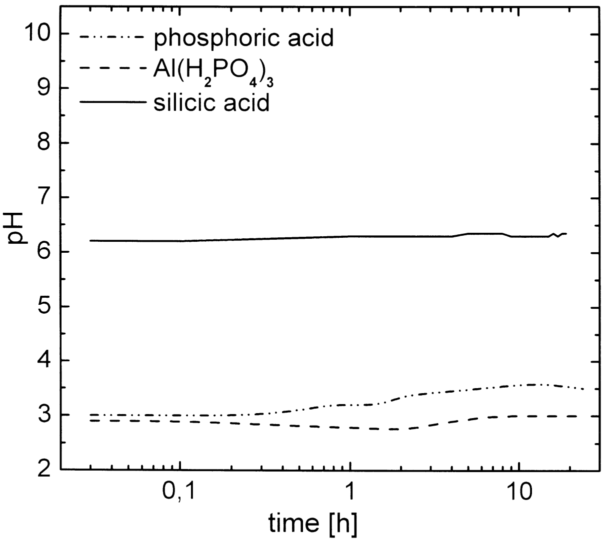

Fig. 1. pH-time profile for diluted suspensions of AlN in phosphoric acid, $Al(H_2PO_4)_3$ and silicic acid solutions at room temperature.

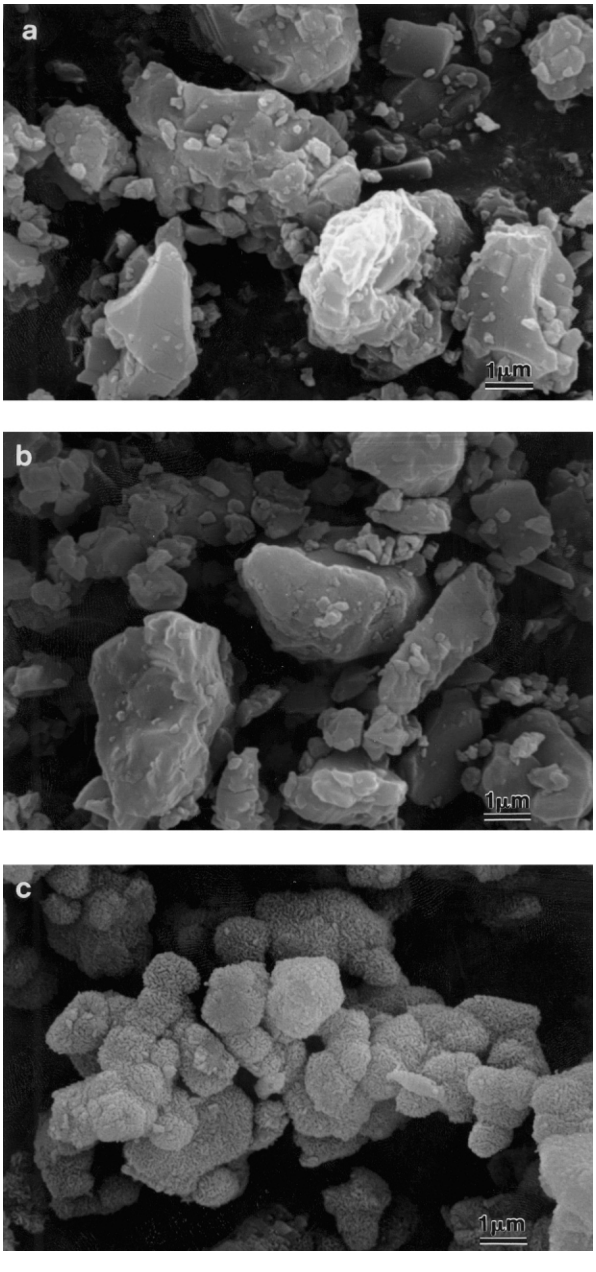

Fig. 2. SEM pictures of AlN powders: a — as received powder, b — redispersed powder [soaked in solution of $Al(H_2PO_4)_3$] after hydrolysis test, c — unprotected powder after hydrolysis test.

b), whereas the morphology of the hydrolysed AlN powder soaked in distilled water changes significantly (Fig. 2c). After the hydrolysis tests the slurries were stored at room temperature and periodically checked for pH over the next 14 days. There was no significant pH change observed during this period confirming that at room temperature AlN powder is stable in these three media.

The equlibrium reactions, which are likely to occur at the AlN powder surface during soaking in silicic acid and phosphate solutions, are presented in Fig. 3a and b, respectively. Using routine DRIFT measurements, however, the presence of Al–O–Si bonds on the powder soaked in silicic acid could not be unambiguously confirmed. The same problem also occurs with detection of phosphates on the AlN powder surface.[8] This is because the characteristic wavelengths for these bonds are in the region of the very strong Al–N stretching frequencies centered at ~700 cm^{-1} and are also partly hidden beneath the Al–O–Al stretching.[9] More thorough investigation and spectra evaluation should be performed to determine the surface composition. In addition, ESCA analysis should be used to determine the surface silicate and phosphate concentrations at the treated AlN powder surfaces.

For the hydrolysis tests at elevated temperatures the solutions were heated to 70°C before 2 wt.% of AlN powder was added. Results are presented on Fig. 4. After dispersion in hot phosphoric acid solution the pH of the diluted AlN slurry started to rise immediately and reached an equilibrium pH value of 8.1 after approximately 1 h. In contrast, during the 24-h period, no change in pH could be detected in the hot silicic acid and hot $Al(H_2PO_4)_3$ solutions. Based on these results it appears that complexes formed by chemisorption of dissolved SiO_2 are stable at room temperature as well as at elevated temperatures. The same holds for phosphate complexes formed by the chemisorption of phosphate anions on the AlN powder surface in the $Al(H_2PO_4)_3$ solution. Phosphate complexes formed on the AlN powder surface in diluted phosphoric acid, in contrast, are stable at room temperature, whereas at 70°C hydrolysis takes place. Alumosilicates, which most probably form on the AlN powder surface in the silicic acid solution, are insoluble at room temperature as well as at elevated temperatures. Aluminium phosphates, which are likely to be formed on the AlN powder surface in dilute phosphoric acid, are also insoluble at room temperature, whereas at higher temperatures their solubility in an acidic environment becomes substantial.[10] This can explain the re-established reactivity of AlN powder in hot phosphoric acid solution. The mechanisms of silicate and phosphate layer formation is presented on Fig. 3. The reasons for the resistance of AlN powder in hot $Al(H_3PO_4)_3$ solution are not yet clear. Since the concentration of phosphate anions in the phosphoric acid and $Al(H_3PO_4)_3$ solutions was nearly the same, the role of cations in the formation of phosphate complexes is being considered. It is worth mentioning, that

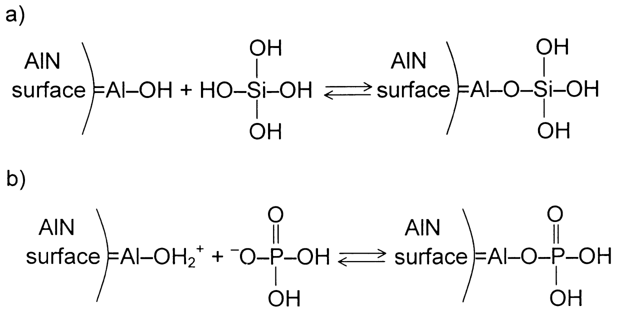

Fig. 3. Reaction scheme for chem-adsorption of (a) silicic acid and (b) phosphate anions onto the AlN powder surface.

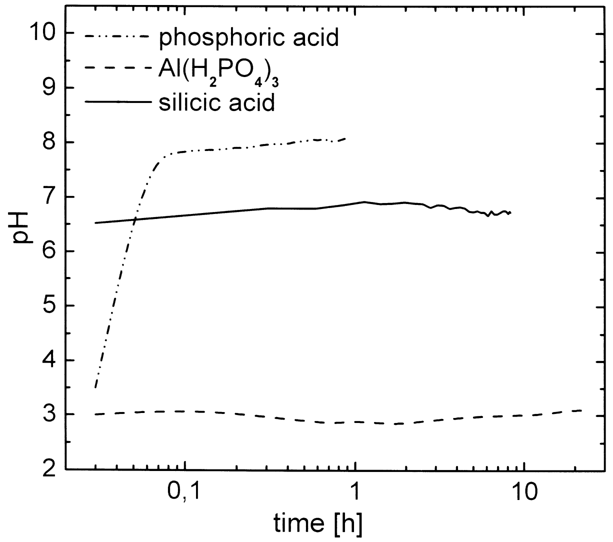

Fig. 4. pH-time profile for diluted suspensions of AlN in phosphoric acid, $Al(H_2PO_4)_3$ and silicic acid solutions at 70°C.

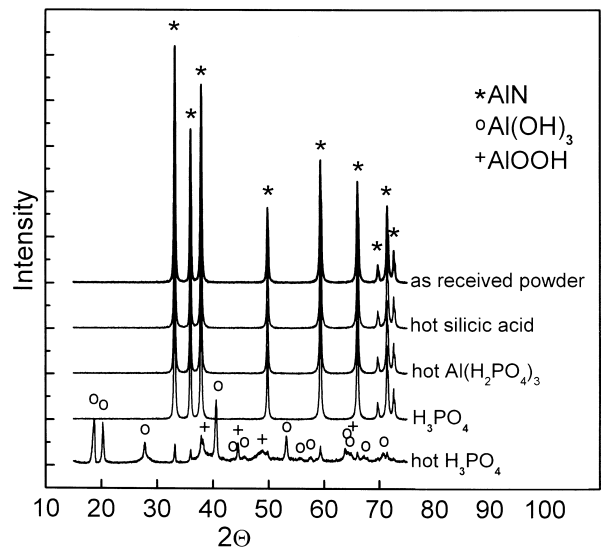

Fig. 5. XRD patterns of AlN powders after a hydrolysis test in different media.

commercially available water resistant Toyalnite AlN powder (Japan Fine Ceramics Ctr, Mutsuno, Atsuta-ku, Nagoya, Japan) is protected against hydrolysis by the small amount of phosphate adsorbed on the powder surface.[8]

The results of the hydrolysis tests at room temperature and 70°C were also confirmed by XRD analysis. As shown in Fig. 5, the XRD pattern of those samples where no pH change was detected revealed only the presence of AlN, whereas in the XRD pattern of AlN powder after the hydrolysis test in the hot phosphoric acid solution pronounced peaks of aluminum hydroxides are also present.

Powder which was soaked for 24 h in phosphoric acid, silicic acid and $Al(H_2PO_4)_3$ solution at room temperature and in silicic acid and $Al(H_2PO_4)_3$ at 70°C was filtered, washed and redispersed in distilled water. Here again, 2 wt.% solids loading was selected for the slurries subjected to the hydrolysis test. Except for the powder soaked in hot $Al(H_3PO_4)_3$ solution, all redispersed powders reacted with water, though at a rate considerably lower than that of the as-received powder (Fig. 6). When soaked powder is filtered, washed and dried, these complexes are partially washed away. In addition, after redispersion in distilled water the equlibrium reactions shown in Fig. 3 are moved to the left and part of the complexes forming the protective surface layer has to be dissolved to reach the equilibrium concentration in the slurry. If for either of the above reasons the protective surface layer is not continuous, the AlN will not be water resistant. This seems to be the case for powders soaked in cold and hot silicic and phosphoric acid and in cold $Al(H_2PO_4)_3$. Soaking in hot $Al(H_3PO_4)_3$ solution, in contrast, offers the possibility of permanent AlN powder protection. Since reactions at the AlN powder surface in $Al(H_3PO_4)_3$ solutions at room and elevated temperatures are not known yet, they need to be more thoroughly investigated. The effectiveness of AlN powder protection after soaking in hot $Al(H_3PO_4)_3$ was later confirmed by redispersing this powder in deionised water at a higher solids loading (30 vol.%) for a longer period of time. During 10 days the pH remained constant and subsequent XRD analysis of this powder revealed only the presence of AlN in the sample. The morphology was very similar to that shown in Fig. 2b, but the oxygen content increased from starting 2.4 to 5.2 wt.%.

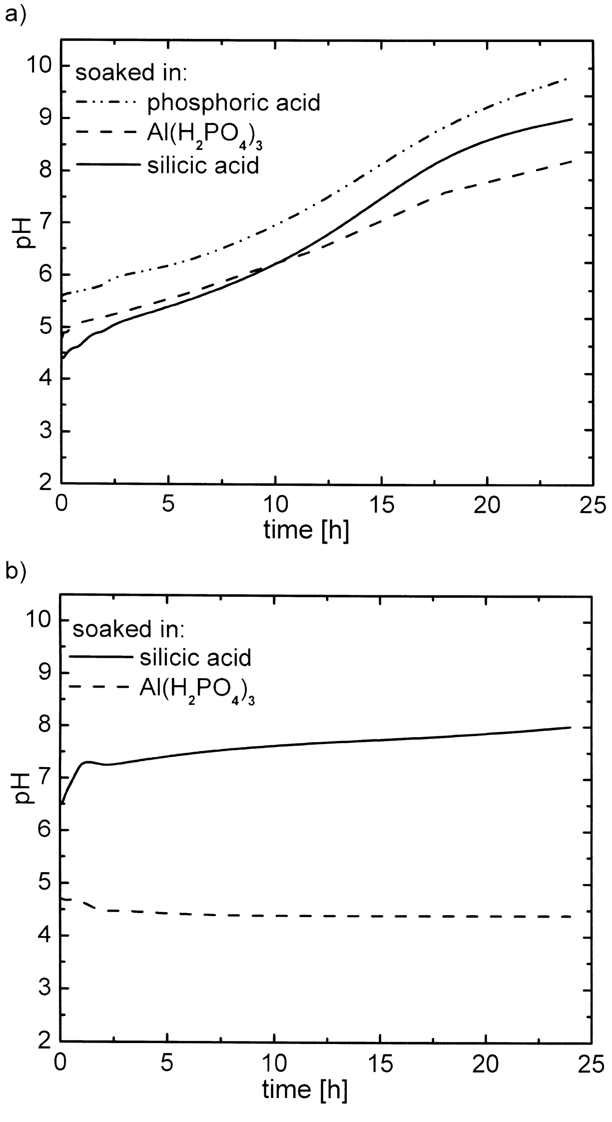

Fig. 6. Room-temperature pH-time profiles for diluted suspensions of redispersed AlN powder in distilled water: (a) AlN powder soaked at room temperature in phosphoric acid, silicic acid and $Al(H_3PO_4)_3$ solutions; (b) AlN powder soaked at 70°C in silicic acid and $Al(H_2PO_4)_3$ solutions.

4. Conclusions

In the presence of dissolved silica and phosphate anions aqueous processing of AlN powder is possible provided that the concentration is high enough to enable at least a monolayer of the complex to be formed on the particles' surface. After soaking in phosphoric or silicic acid solutions the reactivity of filtered, washed and redispersed AlN powder is reduced but not prevented. Soaking in a solution of aluminum dihydrogenphosphate at elevated temperatures offers the possibility of preparing water-resistant AlN powder.

References

1. Sheppard, L. M., Aluminum nitride: a versatile but challenging material. *Am. Ceram. Soc. Bull.*, 1990, **69**, 1801–1812.
2. Groat, E. A. and Mroz, J. Jr., Aqueous processing of AlN powders. *Ceramic Industry*, 1990, March, 34–38.
3. Reed, J. S., *Introduction to the Principles of Ceramic Processing*. John Wiley & Sons, New York, 1988.
4. Krnel, K. and Kosmač, T., Reactivity of AlN powder in dilute inorganic acids. *J. Am. Ceram. Soc.*, 2000, **83**, 1375–1378.
5. Hyde, B. G. and Anderson, S., *Inorganic Crystal Structures*. John Wiley & Sons, New York, 1989.
6. Lazarini, F. and Brenčič, J., *Splošna in Anorganska Kemija*. DZS, Ljubljana, 1992.

7. Bowen, P., Highfield, J. G., Mocellin, A and Ring, T. A., Degradation of aluminum nitride powder in an aqueous environment. *J. Am. Ceram. Soc.*, 1990, **7**, 724–728.
8. Mobley, W. M., *Colloidal properties, processing and characterization of aluminum nitride suspensions*. PhD thesis, Alfred University, Alfred, New York, 1996.
9. Neergaard, L. J., Nawaz, M. B., Tong, Y, Jones, M. and Cesarano III, J., Silicone-coated alumina powders by the emulsion technique. *J. Mater. Sci.*, 1996, **31**, 4779–4783.
10. *Handbook of Chemistry and Physics,* ed. R. C. Weast. 55th edn. CRC Press, Cleveland, 1974.