

High temperature oxidation of hot-pressed aluminium nitride by water vapour

TSUGIO SATO, KIYOTAKA HARYU, TADASHI ENDO, MASAHIKO SHIMADA
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai 980, Japan

Hot pressed AlN without additives was oxidized at 1100 to 1400°C in dry air, wet air and wet nitrogen gas atmospheres with 1.5 to 20 kPa of water vapour pressure. AlN was oxidized by both air and water vapour, and formed α -Al₂O₃ film on the surface above 1150°C. The oxidation kinetics in air were parabolic and were promoted by water vapour. On the other hand, the oxidation kinetics in wet nitrogen were linear below 1250°C and parabolic above 1350°C. The oxidation rate in wet nitrogen was much greater than that in wet air. The rate of oxidation increased with increasing temperature until 1350°C, and then decreased. The parabolic rate constant decreased with increasing temperature and increased linearly with increasing water vapour pressure. The linear rate constant at 1150 to 1250°C increased with increasing the temperature with the apparent activation energy of 250 kJ mol⁻¹. The relation between the linear rate constant and water vapour pressure was of the Langmuir type.

1. Introduction

Because of its excellent physical properties such as high thermal conductivity, high electrical resistivity, low thermal expansion and high resistance to thermal shock, applications of AlN have focused on electronic substrates, heat radiation fins and refractory materials. To evaluate the suitability of AlN as a high temperature structural material, many studies have been devoted to the oxidation behaviour of AlN in air [1-6]. However, the results reported varied greatly, i.e., the oxidation temperature of AlN in air varied from 700 [3] to 1200°C [2]. Several factors such as grain size, porosity, impurity content and humidity may affect the oxidation behaviour of AlN. Long and Foster [1] reported that AlN test bars exposed to dry and wet air was stable below 700°C, but slightly attacked at 1000°C. The degree of oxidation was greater in wet air than that in dry air. However, the details of the role of water vapour on the oxidation of AlN have not yet been clarified. In the present study, a series of tests was carried out to evaluate the oxidation resistance of AlN ceramics in humidity atmospheres using hot pressed AlN without additives.

2. Experimental procedures

The diagram of experimental apparatus used was shown in previous paper [7]. AlN ceramics with a bulk density of 3.25 g cm⁻³ fabricated by hot-pressing without additives was cut into rectangular coupons, 2 × 10 × 10 mm, and weighed. The specimens were placed in a horizontal tubular electric furnace regulated at the desired temperature. Controlled humidity air or nitrogen gas was injected into the furnace at the rate of 20 ml min⁻¹. After maintaining the desired temperature and time, the specimen was withdrawn from the furnace and quickly cooled to room temperature, and then weighed. Crystalline phase and

microstructures on the surface of the samples oxidized were examined by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The partial water vapour pressure was adjusted to 1.5, 5, 10 and 20 kPa by bubbling air and nitrogen gas through the saturated aqueous solution of Ca(NO₃)₂·4H₂O at 25°C and distilled water at 33, 46 and 60°C, respectively.

3. Results and discussion

The chemical free energy changes for a possible oxidation reaction of AlN by O₂ and water vapour calculated using thermodynamical data from JANAF Thermochemical Tables [8] are shown in Fig. 1, where the partial pressures of the products, NO, NO₂ and NH₃ were 10⁻⁷ MPa and those of O₂, water vapour and N₂ were 0.1 MPa. Several reactions are thermodynamically possible, but the oxidation of AlN to Al₂O₃ and N₂ seems to be the most probable reaction in both O₂ and water vapour atmospheres.

XRD profiles of the as-prepared specimen reacted in wet N₂ of 20 kPa of water vapour pressure at 1100 and 1300°C for 100 h are shown in Fig. 2. As expected, the diffraction peaks corresponding to α -Al₂O₃ were detected in the oxidized specimens. The peak height increased with increasing temperature.

The time dependences of the weight gain for AlN oxidized in dry air, wet air and wet N₂ atmospheres at 1250°C are shown in Fig. 3, where the partial vapour pressure in wet air and wet N₂ were 10 kPa and dry air was controlled by passing air through a bottle packed P₂O₅ powder. The oxidation behaviours of AlN in air and wet nitrogen were quite different. The weight gain increased linearly with the reaction time in wet N₂. On the other hand, the oxidation in air was expressed by the usual parabolic equation of the weight gain against time

$$W^2 = kt + C$$

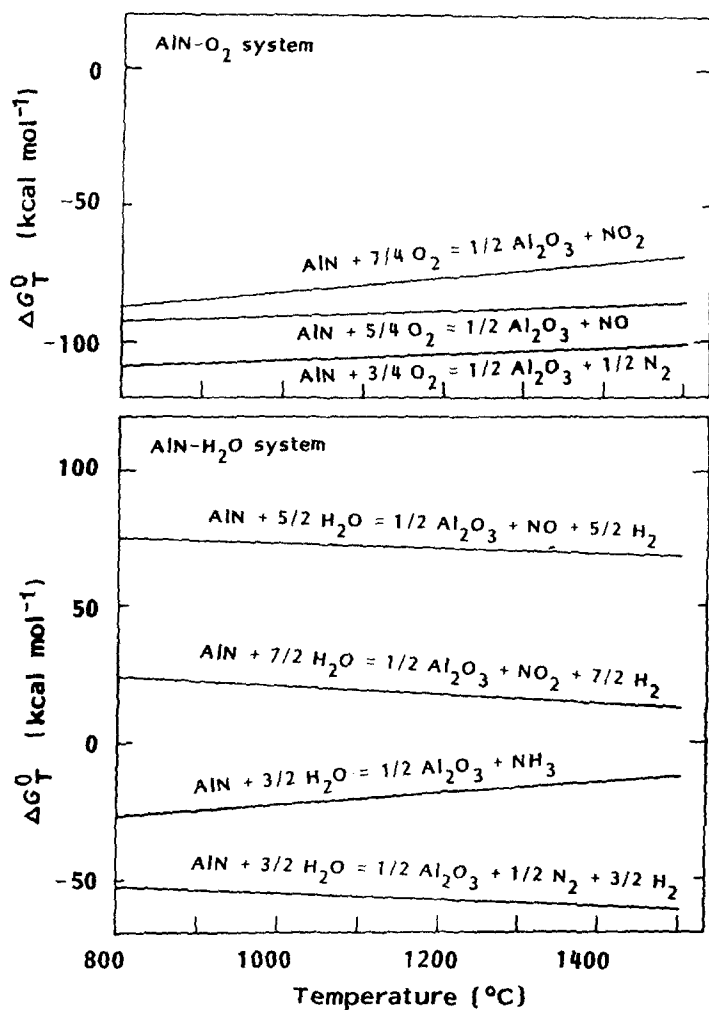


Figure 1 Chemical free energy changes of possible oxidation reaction for AlN by oxygen and water vapour.

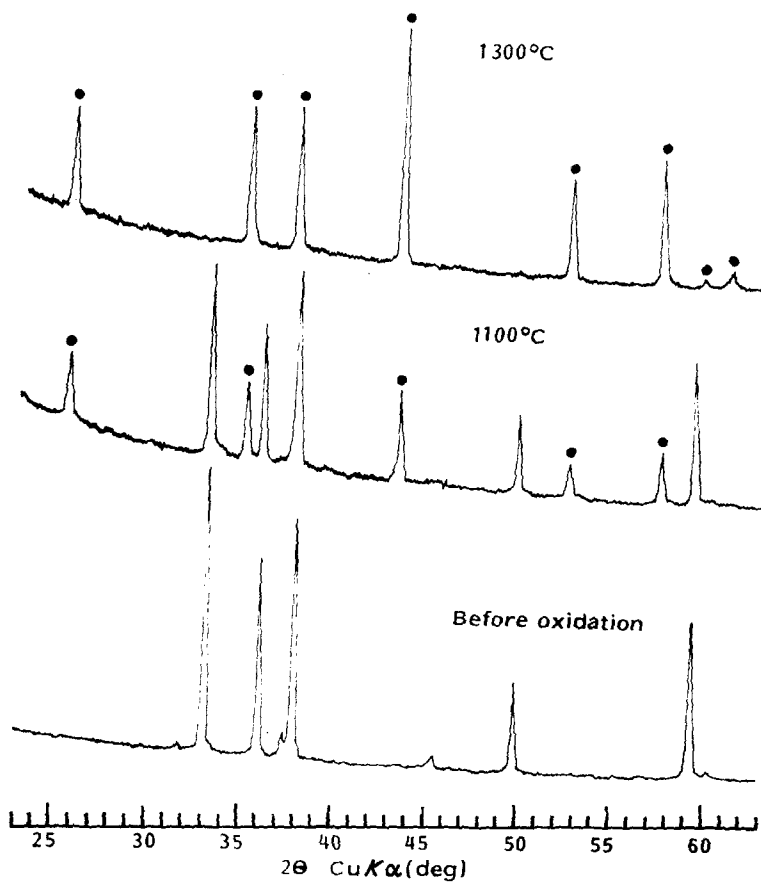


Figure 2 XRD profiles of AlN and the oxidation products by water vapour at 1100 and 1300°C for 100 h, $P_{\text{H}_2\text{O}} = 20 \text{ kPa}$. ●, $\alpha\text{-Al}_2\text{O}_3$.

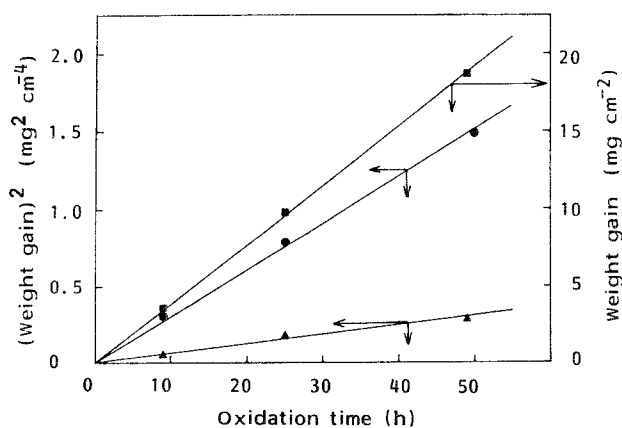


Figure 3 Time dependence of the weight gain of AlN samples oxidized in dry air, wet air and wet nitrogen atmospheres. ■, Wet N₂; ●, wet air; ▲, dry air.

where W is the sample weight gain, k is the parabolic constant, t is the time and C is a constant that adjusts for the small initial nonparabolic behaviours due to uncertainty of the time zero. The rate of oxidation in air was promoted by water vapour. It was notable that the rate of oxidation in wet N₂ was more than 10 times greater than that in wet air. These results indicated that the porous α -Al₂O₃ film was formed by the reaction between AlN and water vapour, and the free AlN surface exposing to the gas phase remained. Therefore, the rate of reaction was controlled by the chemical reaction on the surface and the kinetics approached linearity. On the other hand, in air, the dense α -Al₂O₃ film was formed. Since the normal gaseous diffusion could not easily occur, the kinetics became parabolic.

Time dependences of weight gain for AlN oxidized in wet N₂ at 20 kPa and various temperatures are shown in Fig. 4. It was seen that the oxidation proceeded above 1150°C, but no significant weight change was observed at 1100°C. The rate of oxidation increased with increasing temperature until 1350°C, but greatly decreased at 1400°C. The kinetics were linear below 1250°C and parabolic above 1350°C.

Scanning electron micrographs of the fracture surface of the Al₂O₃ films formed on the surface at 1250, 1350 and 1400°C are shown in Fig. 5. The Al₂O₃ film at 1250°C was quite porous, consisting of a large number of pores of 20 to 100 nm diameter. The pore size decreased with increasing temperature, and only a few small pores were found in the Al₂O₃ film oxidized

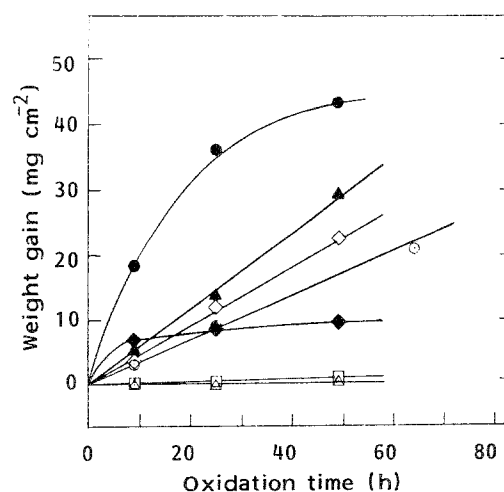


Figure 4 Time dependence of weight gain in wet nitrogen atmospheres at 20 kPa of water vapour pressure and various temperatures. ●, 1350; ▲, 1250; ◇, 1225; □, 1200; ◆, 1400; □, 1150; △, 1100°C.

at 1400°C. Since the α -Al₂O₃ formed on the surface was densified by increasing the oxidizing temperature, the denser surface film controlled the diffusion of water vapour from the surface to interior, thus the kinetics became parabolic above 1350°C. Since the pore size decreased with increasing temperature, the rate of oxidation also decreased with increasing temperature in the regions where the oxidation was proceeded by these parabolic kinetics.

The humidity dependence of the rate constant at 1250 and 1350°C, where the kinetics were linear and parabolic, is shown in Fig. 6. The parabolic rate constant, K' , at 1350°C increased linearly with increasing water vapour pressure. These results confirm that the oxidation rate is controlled by the diffusion of water vapour through the Al₂O₃ film. On the other hand, the plots of the linear kinetic rate constant, k , at 1250°C against water vapour pressure did not form a straight line. As shown in Fig. 7, the Langmuir plot of the rate constant $1/k$ against $1/P_{\text{H}_2\text{O}}$ was linear. These results indicated that the rate of the oxidation at 1250°C was controlled by the direct reaction between AlN and water vapour adsorbed on the surface.

Arrhenius plots of the linear kinetics rate constant at water vapour pressure of 10 and 20 kPa are shown in Fig. 8. The apparent activation energy was

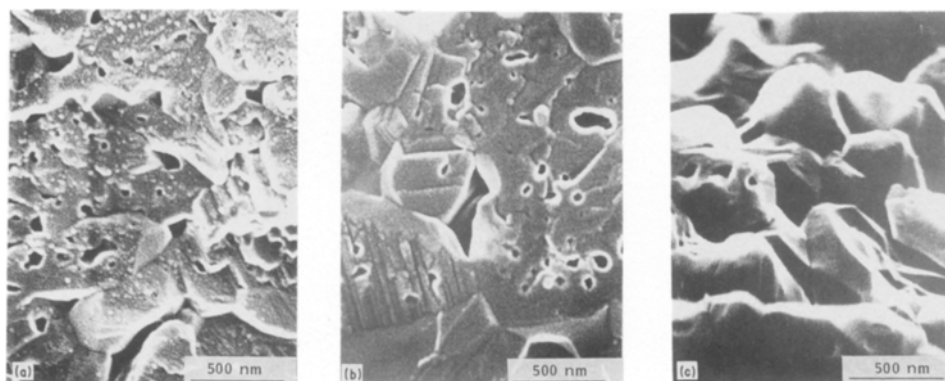


Figure 5 Scanning electron micrographs of the fracture surface of the Al₂O₃ film formed by the reaction between AlN and water vapour at 20 kPa and (a) 1250, (b) 1350 and (c) 1400°C for 49 h.

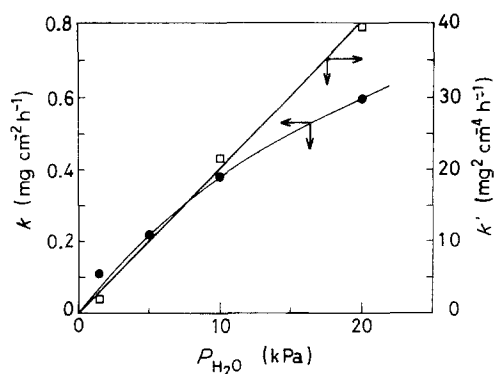


Figure 6 Relation between water vapour pressure and the linear rate constant at 1250°C and parabolic rate constant at 1350°C. ●, 1250°C; □, 1350°C.

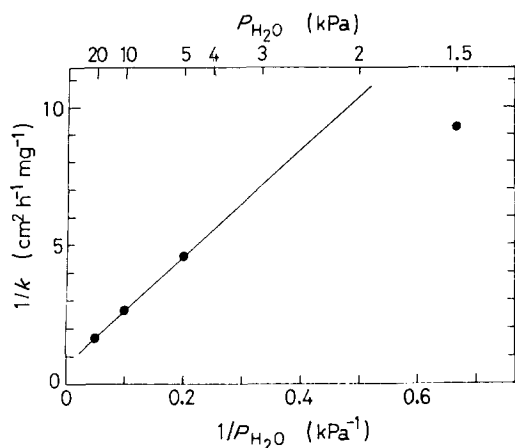


Figure 7 Langmuir plot of the linear rate constant and water vapour pressure.

250 kJ mol⁻¹, and no significant effect of water vapour pressure was observed.

4. Conclusions

According to the present experimental results, the following conclusions may be drawn.

1. The kinetics of the oxidation for AlN by air were parabolic, and were promoted by water vapour.
2. The rate of oxidation in AlN by water vapour was controlled by the surface chemical reaction between

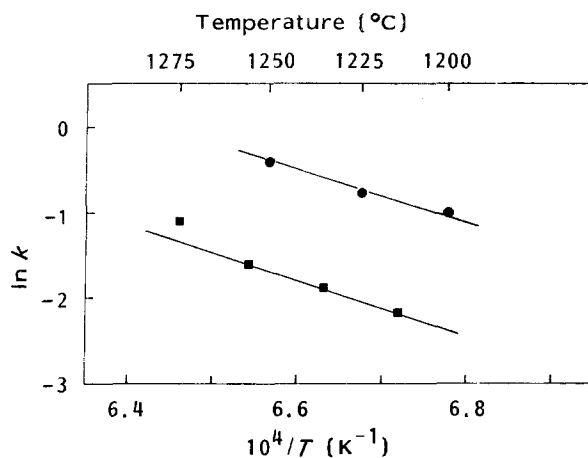


Figure 8 Arrhenius plots of the linear rate constants. $P_{\text{H}_2\text{O}} =$ ●, 20; ■, 10 kPa.

AlN and water vapour adsorbed below 1250°C, and by the diffusion of water vapour through Al₂O₃ film above 1350°C.

Acknowledgement

The authors are indebted to the management of Toshiba Co. for supplying the AlN samples used in the present study.

References

1. G. LONG and M. FOSTER, *J. Amer. Ceram. Soc.* **42** (1959) 53.
2. T. RENNER, *Z. Anorg. Allgem. Chem.* **298** (1952) 22.
3. K. M. TAYLOR and C. LENIE, *J. Electrochem. Soc.* **107** (1960) 308.
4. N. G. COLES, D. R. GLASSON and S. A. A. JAYAWEERA, *J. Appl. Chem.* **19** (1969) 178.
5. P. BOCH, J. C. GALNDUS, J. JARRIGE, J. P. LECOMPTE and J. MEXMAIN, *Ceramics Int.* **8** (1982) 34.
6. V. A. LAVRENKO and A. F. ALEXEEV, *ibid.* **9** (1983) 80.
7. T. SATO, S. OHTAKI, T. ENDO and M. SHIMADA, *J. Amer. Ceram. Soc.* **68** (1985) C320.
8. D. R. STULL and H. PROPHET (eds), JANAF Thermochemical Tables, 2nd edn NSRDS-NBS 37 (US Government Printing Office, Washington, DC, 1971).

Received 26 August
and accepted 9 October 1986