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Effect of oxygen on sintering of AlN

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The effect of the oxygen impurity on the densification behaviour of AlN was investigated. AlN powders containing different amounts of oxygen were synthesized from alumina and hot-pressed. The way in which oxygen accelerates densification is remarkable. Contrary to what is expected from the densification equation, the sintering rate decreases during the holding time at temperatures above 1900° C. This discrepancy is caused by the liberation of oxygen during the hot-pressing. The compression test, conducted on the hot-pressed specimens, shows that oxygen impurity also improves the mechanical strength of sintered AlN. The sintered specimens with more than 2.5 wt % of oxygen have compressive fracture stresses above 150 kg mm^{-2}, which are adequate for a refractory material.

1. Introduction

Aluminium nitride has been regarded as a useful nitride ceramic because of its excellent mechanical properties at high temperature and inertness to corrosion by molten metals. AlN is a good thermal conducting and electrical insulating material, and therefore it is desirable to obtain a highly pure dense sintered body. However, AlN products sufficiently dense, pure and strong for commercial uses have not been obtained.

Raw powder materials of AlN refractory are usually synthesized by two methods. The first, which has been widely adopted, is a direct nitridation of aluminium powder by heating in an atmosphere of nitrogen. The azotized grains are pulverized and the operation repeated in order to complete nitridation. The other is a decomposition of an aluminium compound in an azotic atmosphere, with the most commonly used compound being alumina together with graphite. With AlN powders produced by these methods it is difficult to eliminate the impurities introduced from the raw materials, the process of reaction and grinding. Oxygen is the common impurity and arises from the surface of the aluminium powder, the pulverizing process and the handling process of fine powder in humid air. The trouble caused by the impurity oxygen on the thermal conductivity of AlN are reported by Slack [1]. The oxygen impurity may have an effect on the sintering behaviour of AlN, because of its influence on surface properties of the powder.

Since AlN reacts with oxygen, the very pure AlN just after synthesis tends to take oxygen during pulverizing and handling in the air. On the other hand, oxygen in AlN is vaporized as Al_2O when heated to more than 1600° C in Ar or N_2 [2, 3], therefore AlN can be purified, as far as oxygen is concerned, by heat treatment at high temperature.

Although AlN synthsized or heat treated at high temperature is inactive with circumferential gases [2], it grows into large particles during such treatment. Fresh surfaces exposed by pulverizing the stabilized and large grown particles of the AlN are still reactive to moisture. The amount of oxygen in AlN ball-milled with an organic solvent (e.g. ligroin) and dried in the air after heat treatment at 2000° C is shown in Fig. 1. It is seen that the amount of oxygen depends on surface area of powder.

Polycrystalline AlN has been prepared by several methods such as sintering of pressed powder [2, 4], reaction-sintering of the system Al-AlN powder [5] and hot-pressing [6]. Although AlN is difficult to sinter without any flux,

Komeya *et al.* found that it becomes easy to sinter when very fine powder is used [4, 7], but they did not report the level of oxygen impurity in the powders.

In the present work, the hot-pressing technique was applied with the intention of making dense specimens without any impurities. The sintering behaviour and strength of sintered samples having various oxygen contents were observed.

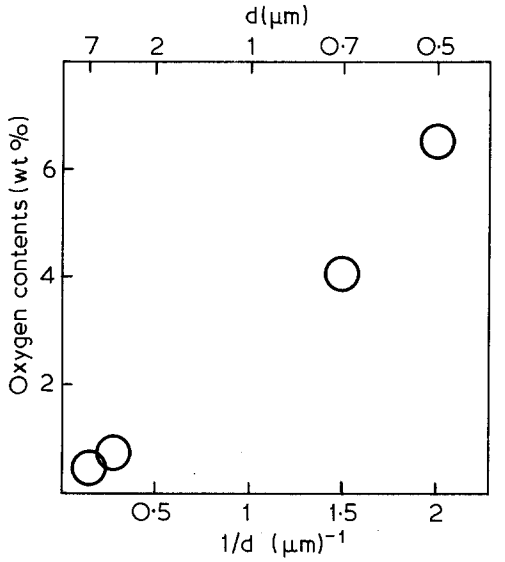


Figure 1 Mean grain size versus oxygen content of AlN after ball milling.

2. Experimental procedure

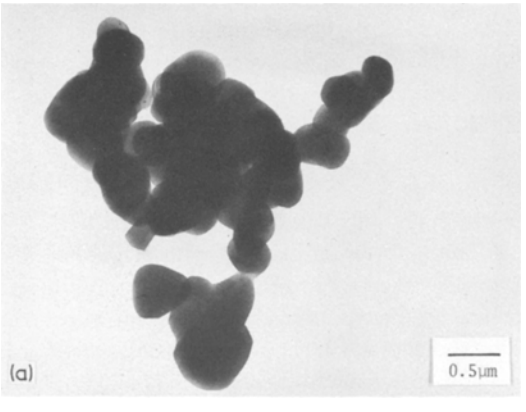
2.1. AlN powders

AlN powders were synthsized by reduction and nitridation of alumina [8]. Two kinds of powder were used, having been synthesized at 1720 and 2000° C and having different amounts of oxygen. Electron micrographs of synthesized AlN particles are shown in Fig. 2 and the results of emission spectrochemical analysis, oxygen contents and mean grain sizes are presented in Table I. The impurity concentration, determined by neutron activation analysis, was acceptably low except for oxygen.

2.2. Hot-pressing

AlN powders were hot-pressed in a graphite die susceptor in a high frequency induction furnace with an atmosphere of nitrogen. 420 mg of powder was hot-pressed into an 8 mm diameter disc at temperatures from 1600 to 2100° C and at applied pressures of from 15 to 450 kg cm^{-2}.

Most experiments were carried out under isothermal conditions. The powders were initially compressed at 300 kg cm^{-2} at room temperature and then heated at a fixed pressure at a rate of about 5° C sec^{-1} up to scheduled temperatures after holding 10 min at 1000° C to get thermal equilibrium. The relative density of the hot-



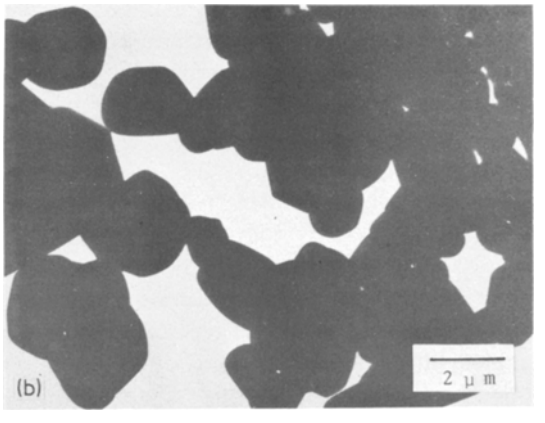


Figure 2 Electron micrographs of AlN powders synthesized from alumina (a) at 1720° C and (b) at 2000° C.

TABLE I Emmission spectrochemical analysis, oxygen contents and mean grain size of AlN powders

Nitridation Temperature (° C)	Ca	Mg	Cr	Mn	Cu	Fe	Si	Amount of oxygen (wt %)	Mean grain size (μm)
1720	+	+	tr	tr	tr	++	++	7.22	0.4
2000	tr	tr	–	–	tr	tr	+	1.63	2.5

++ represent weak about 100–200 ppm, + very weak, tr faint trace and – not detected.

pressing was calculated from the shrinkage of the compact obtained from the LVDT, and the final density was measured by displacement in ethanol.

2.3. Measurement of fracture stress of compression

The test pieces were cut from the centre of the discs fabricated by hot-pressing. Those specimens, 2 mm × 2 mm × 2 mm, were ground to produce smooth parallel surfaces. The fracture stresses of compression were measured using an Instron Universal Testing Instrument TM-SM. The compressive stress was loaded at a rate of 0.0125 cm min^{-1} parallel and perpendicular to the directions of hot-pressing until the specimen was broken.

3. Results

3.1. Densification rate during hot-pressing

As previously mentioned, the oxygen content of AlN decreases during the sintering process at a rate depending on temperature, atmospheric gas flow, and packing density of the AlN powder. Decrements of oxygen content after hot-pressing and sintering of the pressed powder are presented in Table II. This purification has an effect on the densification behaviour, as would be expected from the data shown in Fig. 3.

According to the densification rate equation for the final stage of hot-pressing [9], there is a linear relation between $\ln(1-\rho)$ and t at constant temperature, disregarding the effect of the surface energy, where ρ and t are the relative density of the compact and the holding time, respectively. In the case of AlN, the relative density was increased as shown in Fig. 4a of the higher oxygen content powder, and in Fig. 4b of the lower oxygen content. On the plot of $\ln(1-\rho)$ against time, as t increases $\ln(1-\rho)$ decreases linearly, except the samples of higher oxygen content at the temperature above 1900° C.

TABLE II The oxygen content before and after hot pressing of AlN

Oxygen in powder AlN (wt %)	Oxygen after hot pressing (at 1780° C, 60 min.) (wt %)	Oxygen after pressing and sintering (1800° C, 2 hr) (wt %)
0.57	0.32	
0.78	0.41	0.20
0.90	0.44	0.36
1.63	0.94	
4.42	4.20	0.57
6.68	4.49	0.76
7.22	2.86	

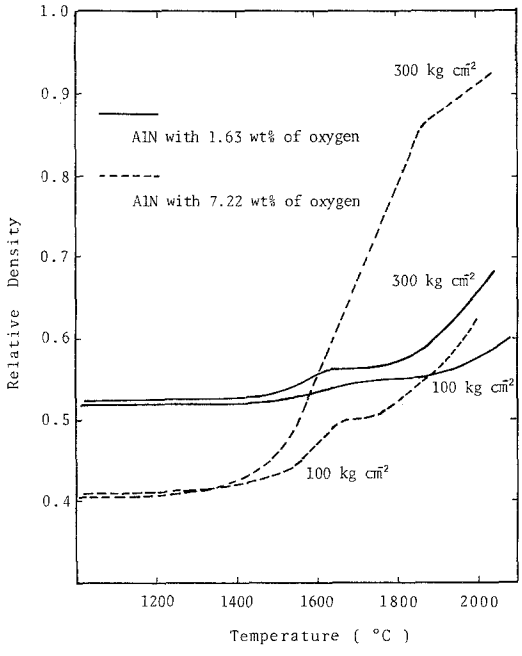


Figure 3 Effects of pressure and oxygen impurity on the densification of AlN powders. Compacts were preloaded and held at 300 and 100 kg cm^{-2}, and heated at a rate of 5° C min^{-1}.

3.2. Microstructure

The fractured surfaces of the specimens hot-pressed for 120 min at each temperature and pressure were examined by SEM. A selection is shown in Fig. 5. The difference between the degree of densification of the high and low oxygen containing powders is distinguishable. The mean grain sizes after 120 min were measured from these photographs. The grain size was independent of the pressing pressure but depended upon temperature as follows:

Oxygen in powder (wt %)	Mean grain diameter (μm)				
	powder	1600° C	1800° C	2000° C	2100° C
7.22	0.4	0.9	1.2	2.7	–
1.63	2.5	–	2.4	3.2	5.2

Little grain growth in the purer AlN occurred up to 2000° C, but grain growth is evident even at lower temperatures in the oxygen-doped AlN. The latter grew to about half the size of the former at the sintering temperature.

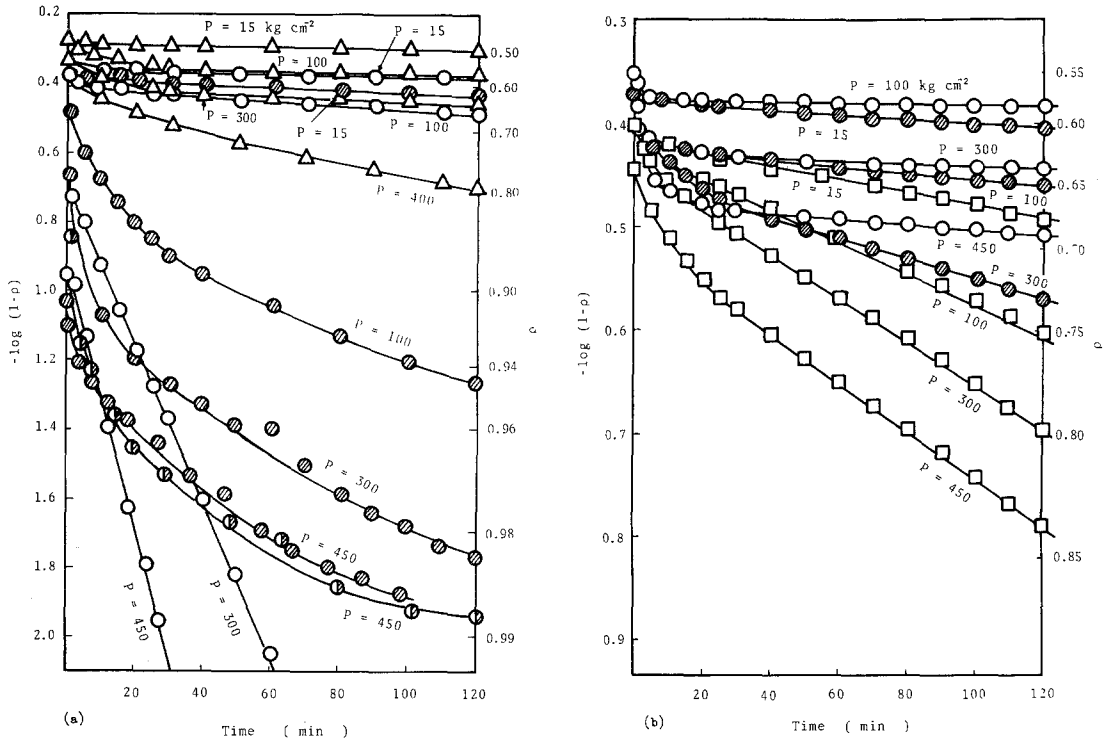


Figure 4 $\log(1-\rho)$ versus time for hot-pressing AlN at various pressures and at temperatures of 2100° C [-□-], 2000° C [-⊕-], 1900° C [-⊕-], 1800° C [-○-] and 1600° C [-△-]. (a) AlN with 7.22 wt % oxygen (b) AlN with 1.63 wt % oxygen.

3.3. Fracture stress of compression

The fracture stress of compression and hot-pressing conditions are given in Fig. 6. Specimens broken at stresses less than about 40 kg mm^{-2} show intergranular fracture. Most of the sintered AlN containing more oxygen show predominantly transgranular fracture, except at low pressure and at low temperature. Some of them have the compressive fracture stress of more than 100 kg mm^{-2}. Those specimens are far stronger than graphite and alumina, (90%), which were measured as 15–30 and 65 kg mm^{-2}, respectively. In this series, it was difficult to obtain strength of more than 50 kg mm^{-2} for the hot-pressed purer AlN.

4. Discussion

4.1. Densification rate

AlN powder containing higher oxygen was densified as shown in Fig. 4a. The densification rate equation presented by Sakai and Iwata was as follows [9]:

$$-\ln(1-\rho) = \frac{9}{2}\frac{40D\Omega}{kTd^2}(p_2-p_1)\,t - \ln(1-\rho_0). \quad (1)$$

where D is the self diffusion coefficient, Ω the volume of rate-determining ion, k Botzmann's constant, T the absolute temperature, d the average grain diameter, p_2-p_1 the difference between applied pressure and the gas pressure in the pores and ρ_0 the initial density of the powder compact. It indicates the linear relations between $\ln(1-\rho)$ and t. At the temperatures higher than 1900° C, however, the densification rate decreased gradually during the holding period, due to the liberation of impurity oxygen during the hot-pressing. Decreasing oxygen content in AlN occurred above 1800° C and became vigorous with increasing temperature [2]. Though the rate of oxygen loss in hot-pressing was much slower than in sintering the pressed powder, it was more intense above 1900° C. As shown in Fig. 4a, densification at 2000° C under load of 300 kg cm^{-2} was initially faster than that at 1800° C under the same load but subsequently the reverse was true, so that powder hot-pressed at 2000° C could not reach the final density of that at 1800° C. The effect of oxygen loss in purer AlN was not clear, but it was probably due to the small initial amount of oxygen in it.

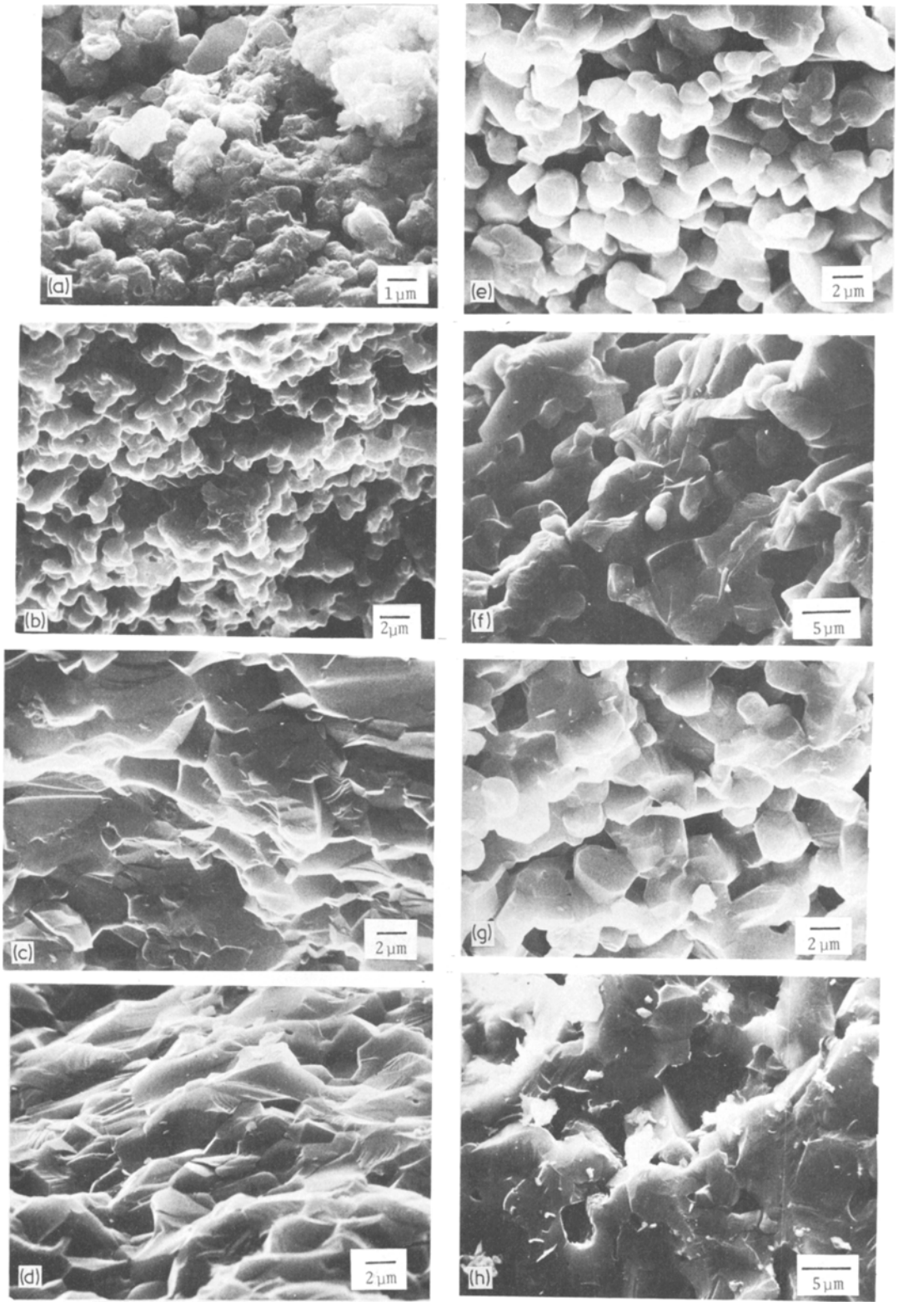


Figure 5 Scanning electron micrographs of the fracture surface of AlN. AlN with 7.22 wt% oxygen hot pressed at 1600° C and 300 kg cm^{-2} (a), at 1800° C and 100 kg cm^{-2} (b), at 1800° C and 300 kg cm^{-2} (c), at 2000° C, 100 kg cm^{-2} (d), AlN with 1.63 wt% of oxygen hot-pressed at 1800° C and 300 kg cm^{-2} (e), at 2000° C and 300 kg cm^{-2} (f), at 2000° C, 400 kg cm^{-2} (g), at 2100° C and 400 kg cm^{-2} (h).

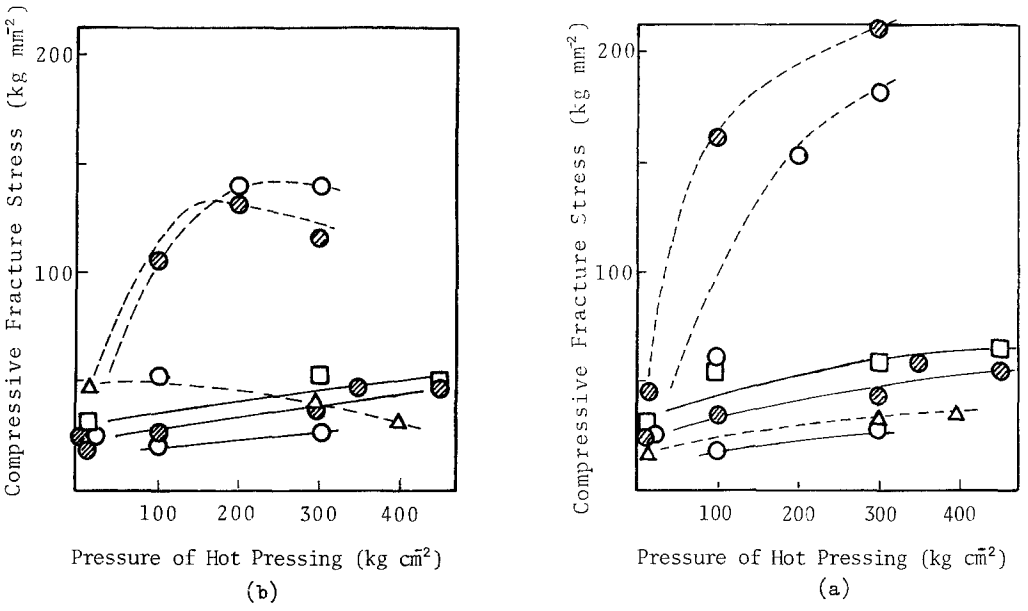


Figure 6 Compressive fracture stress of AlN after hot-pressing at various pressures and temperatures for 120 min. (a) Compressed parallel to the hot pressing direction (b) Compressed perpendicular to the hot pressing direction. ------- AlN raw material with 7.22 wt% oxygen; ——— AlN raw material with 1.63 wt% oxygen. Sintering temperature □ 2100° C, ● 2000° C, ○ 1800° C, △ 1600° C.

The self diffusion coefficient D is given from the Equation 1. The first term of the right side of the equation is given as the slope in Fig. 4. Applying mean grain sizes described in Section 3.2 as d, the self diffusion coefficient D was calculated from the densification data except for the case when $p_2 - p_1 = 15\,\mathrm{kg\,cm^{-2}}$. The log D values are plotted against reciprocal temperature in Fig. 7. The Arrhenius plots for the less pure AlN are higher by about one order of magnitude than that for purer one, and may have been caused by a higher concentration of cation vacancy in oxygen-doped AlN. The activation energy calculated from each curve is approximately same, 110 kcal mol^{-1}, in the temperature range up to 2000° C.

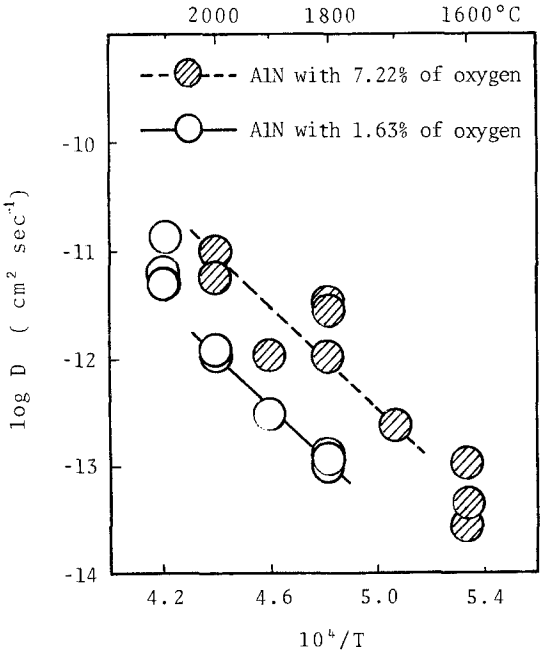


Figure 7 Temperature dependence of the diffusion coefficient for the densification process.

4.2. Mechanical strength

A compressive fracture stress of AlN having high oxygen content strongly depended on the temperature and the pressure of the hot-pressing. The specimens hot-pressed at 1600° C were brittle, were not strengthened by increase of pressure, and were broken intergranularly. The strength of the specimens hot-pressed above 1800° C depended on pressure remarkably, and strengths over 150 kg mm^{-2} could be obtained when pressures of more than 200 kg cm^{-2} were applied in this temperature range. These specimens fractured mostly transgranularly. The relation between strength and hot-pressing conditions is similar to that between relative density and hot-pressing conditions: when specimens were pressed at the pressure of higher than 300 kg cm^{-2}, little orientation was observed; as hot-pressing pressure increased, fracture stress of compression perpendi-

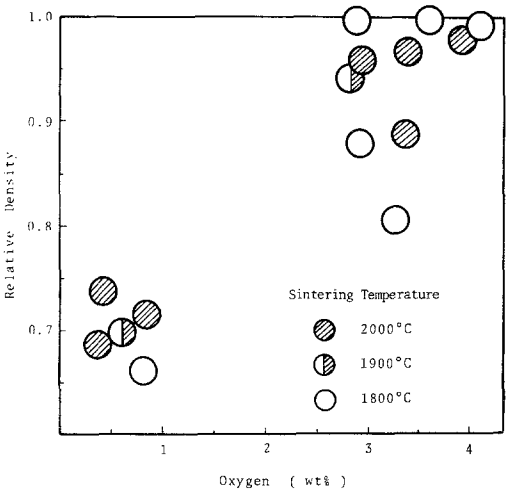


Figure 8 Relative density versus oxygen contents in AlN hot-pressed for 30 min under an applying pressure of 400 kg cm^{-2}.

cular to the hot-pressing direction decreased, but stress parallel to the direction increased. Under the hot-pressing pressure, a lateral layer structure occurred in the compact. Compressive fracture stress of the purer sample was weaker than that for high oxygen content.

In Fig. 8 the relative densities of AlN hot-pressed at 400 kg cm^{-2} for 30 min are plotted against the amount of oxygen after sintering at each temperature . Mean grain size of purer powder is larger than that of higher oxygen content. Considering the grain size effects, it seems to be difficult to get dense strong sintered body from the purer powder, however the powder having higher oxygen content can be made into dense and strong compacts.

5. Conclusion

AlN powders with different amounts of oxygen impurity were hot-pressed. Powder which contained less than 2 wt% oxygen was difficult to sinter. The self diffusion coefficient for powder with 1.63 wt% oxygen is one tenth of that with 7.22 wt% at the temperature about 1800° C.

Sintered AlN polycrystals containing 3 wt% or more oxygen have a density close to the theoretical value and a compressive fracture stress of more than 150 kg mm^{-2}. Thus it has adequate density and strength to be a practical refractory material. The elimination of oxygen during hot-pressing process at above 1900° C causes difficulty in densifying the powder.

In this work, the recommended hot-pressing condition for fine AlN is approximately 1800° C with an applied pressure of 200 to 300 kg cm^{-2}. It was difficult, however, to make dense sintered material having an oxygen content of less than 1 wt%.

Acknowledgments

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