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Raw material effect on AlN powder synthesis from Al_2O_3 carbothermal reduction

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The effect of starting Al_2O_3 raw materials on the synthesis of AlN powder by Al_2O_3 carbothermal reduction was investigated. The reactivity of γ–Al_2O_3 among other materials, is excellent, at 1500° C. The skeleton of raw powders remains in the AlN particle shape. The thermal conductivity for hot-pressed AlN was severely affected by the oxygen content in AlN powder.

1. Introduction

Aluminium nitride (AlN) has attracted much attention as a high-thermal-conductivity ceramic substrate. Its thermal conductivity is affected by the purity of the raw powder. Oxygen has an especially marked effect on thermal conductivity [1, 2]. The development of high-purity powder is very important to the improvement of properties. Several methods have been proposed for synthesizing AlN powders, including direct nitridation of aluminium, reduction of Al_2O_3 [3, 4], fluoride decomposition [5], and striking a d–c arc between high-purity aluminium electrodes in nitrogen gas [6]. However, little information is available on the synthesis of aluminium.

Here we describe AlN formation from aluminium oxide compounds by a carbothermal reduction method. The most popular compound is α–Al_2O_3, but there are many other hydrated compounds like, η, θ and γ [6, 7]. These are intermediate compounds and are unstable at high temperature (1000° C), where these convert into unhydrated form of α–Al_2O_3. The carbothermal reaction of Al_2O_3 is given by $Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$. However, no information has been given as to the effect of these modifications on the above reaction.

2. Experimental procedures

Eight kinds of raw starting powder were obtained from different powder sources. The powder properties are shown in Table I. The average particle size, which is less than submicrometre order, is a measure derived from specific surface area by the Brunauer–Emmett–Teller (BET) method. Extremely large particle sizes were obtained by Fisher–Sub–Sieve Sizer (FSSS). These powders were mixed with amorphous carbon powder. The carbon content was slightly in excess ($C/Al_2O_3 = 4$ in weight ratio), compared to the theoretically calculated amount ($C/Al_2O_3 = 0.35$). Intimate mixtures were heated in an open furnace at 1500 and 1550° C for 5 h in flowing nitrogen gas. After the reaction, the mixtures were heated at 700° C for 3 h in air to remove residual unreacted carbon.

The synthesized powders thus obtained were evaluated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and oxygen analysis (impulse furnace infrared absorption method). Thermal conductivity was measured by a laser flash method for hot-pressed materials, which were obtained by hot pressing as-received powders in a carbon mould at 1800° C for 1 h in an N_2 atmosphere under 300 kg cm^{-2} pressure.

3. Results and discussion

3.1. Reactivity

The properties of the synthesized powders are given in Table II. AlN and Al_2O_3 were major phases detected in all runs. The total oxygen content in powders represents a reactivity measure for raw powders: lower oxygen contents mean higher reactivity. At 1500° C, marked differences were observed in reactivity; Al_2O_3 resulted in AlN powder with the lowest oxygen content, which was almost independent from the particle size of the raw powder. In the case of $Al(OH)_3$, this dependence of particle size on reactivity was observed to some extent, where differences in oxygen contents were relatively small in comparison with the differences in particle size. Both α–Al_2O_3 and $Al(OH)_3$ showed relatively high reactivity. On the other hand, η, θ and α–Al_2O_3 resulted in high-oxygen-content powders, even though their particle sizes were small.

TABLE I Raw starting powder properties

		Average grain size (μm)	Impurity (wt %)		
			Fe_2O_3	SiO_2	Na_2O
η–Al_2O_3	A	0.78	0.040	0.045	0.003
θ–Al_2O_3	B	0.51	0.040	0.045	0.003
α–Al_2O_3	C	$\simeq$ 1.0	0.040	0.045	0.003
$Al(OH)_3$	D	$\simeq$ 4	0.007	0.008	0.25
$Al(OH)_3$	E	$\simeq$ 0.4	0.007	0.010	0.25
$Al(OH)_3$	F	$\simeq$ 15	0.0017	0.0062	0.13
γ–Al_2O_3	G	0.005	< 0.0005	< 0.003	< 0.002
γ–Al_2O_3	H	< 0.005	< 0.0005	< 0.003	< 0.002
C		0.02	0.0015	< 0.0001	< 0.0001

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TABLE II Synthesized AlN powder properties

		1500° C			1550° C		
		Oxygen content (wt %)	Phase		Oxygen content (wt %)	Phase	
			AlN	Al_2O_3		AlN	Al_2O_3
Al_2O_3	A	39.0	++	++++	37.6	++	+++
	B	26.4	+++	+++	2.02	++++	(+)
	C	24.7	+++	+++	1.86	+++++	(+)
$Al(OH)_3$	D	2.78	+++++	(+)	1.06	+++++	-
	E	1.94	+++++	-	1.26	+++++	-
	F	5.09	+++++	(+)	1.60	+++++	-
γ-Al_2O_3	G	1.53	+++++	-	1.79	+++++	-
	H	1.58	+++++	-	1.49	+++++	-

X-ray peak intensity: +++++ > ++++ > +++ > ++ > (+) > −.

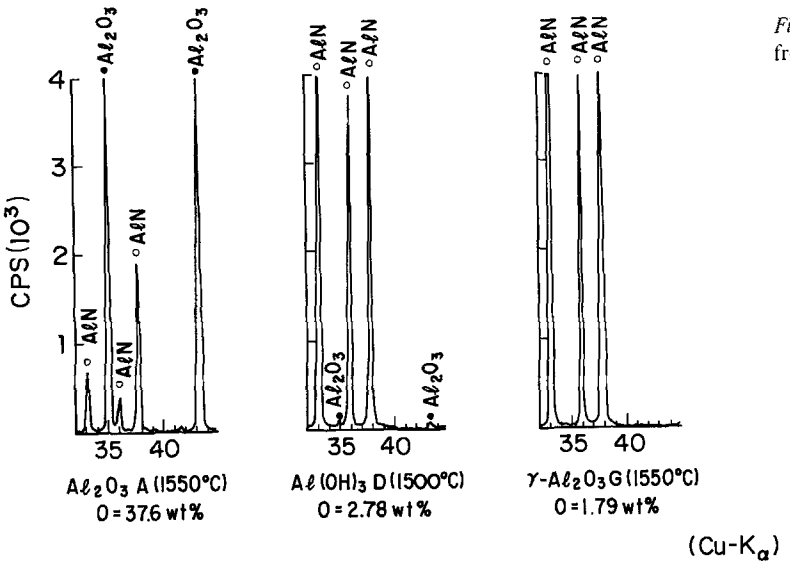

Figure 1 Typical XRD patterns of AlN synthesized from various Al_2O_3 sources.

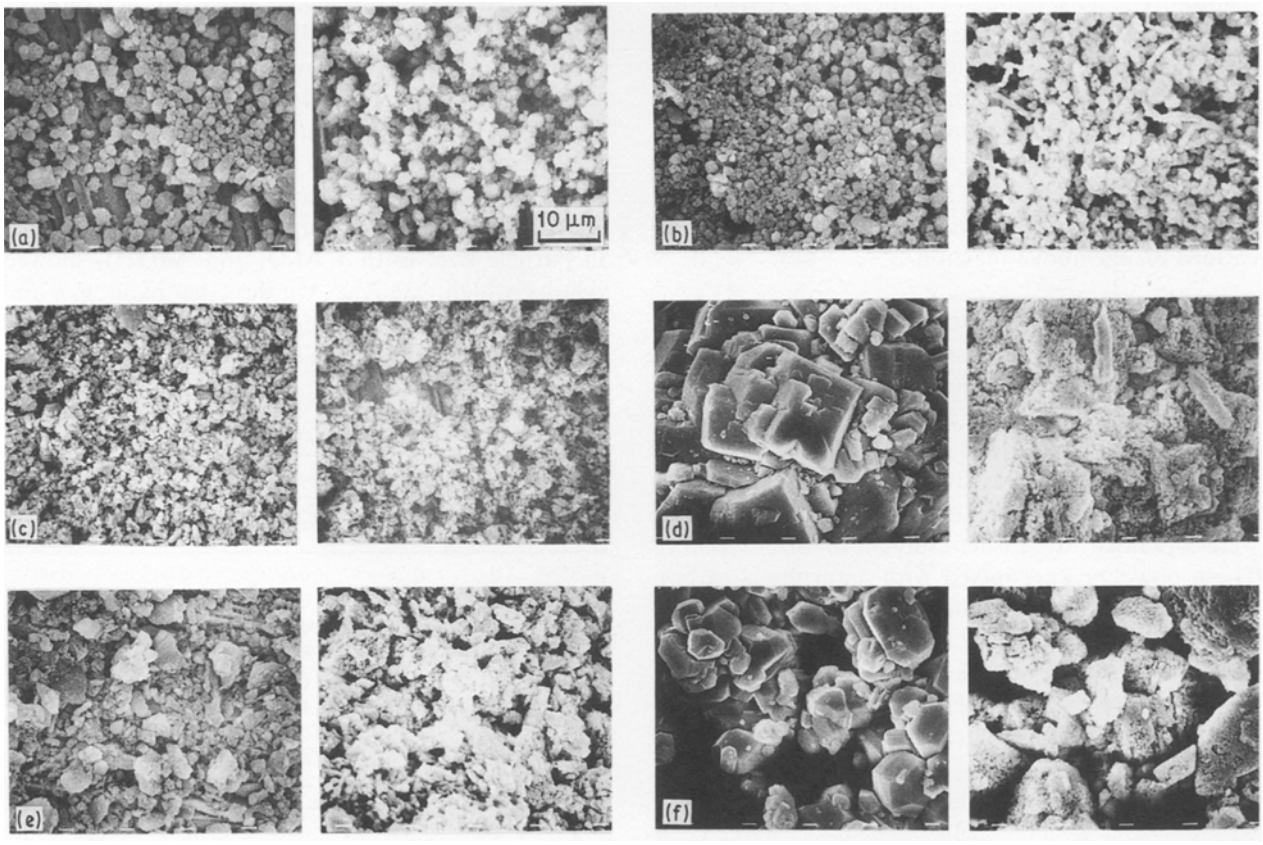

Figure 2 SEM micrographs, before (left) and after (right) nitridation (1550° C) for (a–c) α-Al_2O_3: (d–f) $Al(OH)_3$; (g, h) γ-Al_2O_3 raw powders.

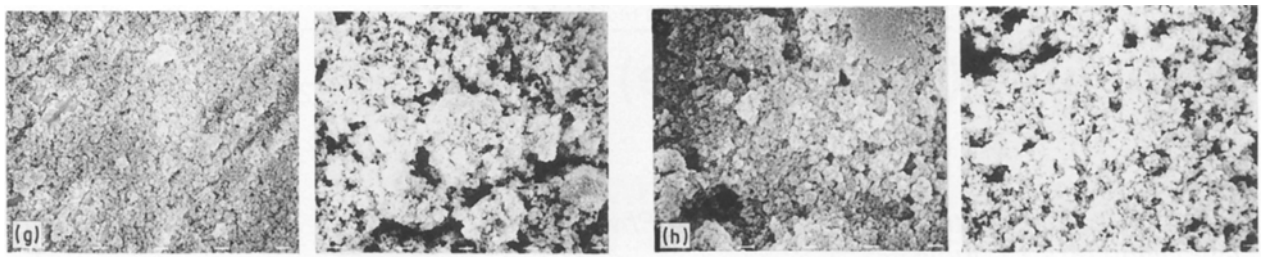

Figure 2 Continued.

At 1550° C, both $Al(OH)_3$ and α–Al_2O_3 were almost completely converted into AlN. However, η–Al_2O_3 still remained as Al_2O_3 in a large amount. θ and α–Al_2O_3 also showed slightly small traces of Al_2O_3.

From these experimental results, it may be seen that the difference in reactivity is, probably related to the conversion rate to Al_2O_3 during heating. The detailed conversion mechanism is not clear but, for the first approximation, reactivity is of the order of γ-Al_2O_3 > $Al(OH)_3 \gg Al_2O_3$ (α, θ, η).

Typical XRD patterns are shown in Fig. 1. The amount of residual Al_2O_3 is shown for typical raw powders. Figure 2 shows SEM micrographs, before and after nitridation. The AlN grain shape was strongly correlated to the raw powder particle shape. Thus, raw powder skeleton remains in synthesized powders.

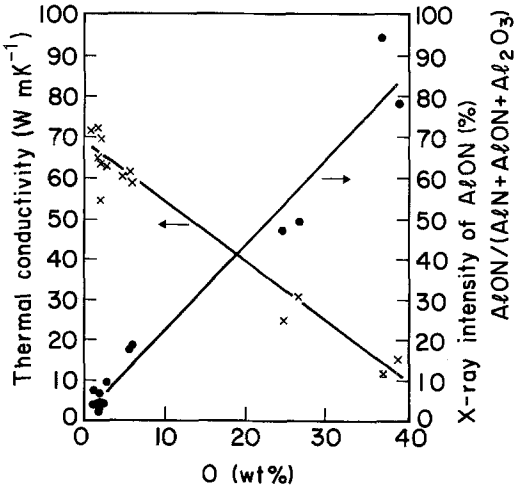

Figure 3 Hot-pressed AlN thermal conductivity and 'Alon' formation as a function of oxygen content in synthesized AlN powder (hot pressed at 1800° C for 1 h in N_2 under 300 kg cm^{-2}).

3.2. Thermal conductivity

The thermal conductivities for hot-pressed specimens were evaluated (Fig. 3). It was found that the thermal conductivity increased almost linearly with oxygen content decrease, and vice versa with the 'Alon' (Spinel phase [6, 7]) content. 'Alon' is a compound formed by a reaction between residual Al_2O_3 and AlN. However, during hot pressing, not only is 'Alon' formed, but also oxygen dissolution into AlN occurs. In this case, cation vacancy formation [8] is thought to be due to the following reaction, $AlN + xAl_2O_3 \rightarrow Al_{1-x}N_{1-3x}O_{3x}$. Accordingly, phonon scattering might be enhanced by the mass defects caused by such aluminium vacancies, resulting in the low thermal conductivity for AlN.

4. Conclusions

Among various Al_2O_3 sources, γ–Al_2O_3 reactivity with carbon at high temperatures was the highest. The skeleton of raw powder remained in the synthesized AlN powder shape. The thermal conductivity of the hot-pressed material has a strong correlation with the oxygen contents in AlN powders.

References

1. G. A. SLACK, *J. Phys. Chem. Solids* **34** (1973) 321.
2. T. SAKAI and M. IWATA, *J. Mater. Sci.* **12** (1977) 1659.
3. T. SAKAI, M. KURIYANA, T. INUKAI and T. KIJIMA, *Yogyo-Kyokai-Shi* **86**, 4 (1978) 30.
4. N. KURAMOTO, *Ceramics* **22** (1987) 29.
5. I. C. HUSEBY, *J. Amer. Ceram. Soc.* **66** (1983) 217.
6. G. LONG and L. M. FOSTER, *ibid.* **42** (1959) 53.
7. G. YAMAGUCHI and H. YANAGIDA, *J. Chem. Soc. Jpn* **32** (1959) 1264.
8. I. ADAMS, T. R. AUCOIN and G. A. WOLF, *J. Elec. Chem. Soc.* **109** (1962) 1050.

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