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Colloidal Dispersion of Alumina–Carbon Homogeneous Mixtures for Carbothermal Synthesis of AlN

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Abstract

Synthesis of AlN by carbothermal reduction requires the preparation of an intimate alumina–carbon mixture to assure the complete alumina nitridation. In laboratory-scale tests mixtures are usually homogenized using organic liquids. However, an aqueous media seems to be the most useful method for large-scale carbothermal production of AlN. In the present work a method to prepare aqueous suspensions of alumina–carbon mixtures is studied. The stability and rheological behaviour of the different suspensions prepared have been examined by means of viscosity measurements.

Die Herstellung von AlN durch thermische Reduktion erfordert eine intensive Mischung von Kohlenstoff und Al_2O_3 um eine vollständige Nitridierung des Al_2O_3 zu gewährleisten. Im Labormaßstab werden die Mischungen gewöhnlich mit organischen Flüssigkeiten homogenisiert. Für eine großtechnische Herstellung des AlN erscheint jedoch ein wässriges Medium als am besten geeignet. In dieser Arbeit wurde ein Verfahren zur Herstellung wässriger Suspensionen von C–Al_2O_3 Mischungen untersucht. Die Stabilität und das rheologische Verhalten der verschiedenen Suspensionen wurde durch Viskositätsmessungen bestimmt.

La synthèse de l'AlN par réduction carbothermique nécessite, afin d'assurer la nitruration complète de l'alumine, la préparation d'un mélange intime alumine–carbone. Dans les essais à l'échelle du laboratoire, les mélanges sont habituellement homogénéisés par utilisation de liquides organiques. Cependant, un milieu aqueux semble être la méthode la plus appropriée à la production carbothermique d'AlN à grande échelle. On a étudié une méthode de préparation de suspensions aqueuses de mélanges alumine–carbone. On a examiné la stabilité et le comportement rhéologique des différentes suspensions préparées à l'aide de mesures de la viscosité.

1 Introduction

Some different processes have been developed to synthesize aluminium nitride powders, such as direct nitridation of the metal, carbonitridation of alumina, chemical vapour deposition from aluminium chloride and ammonia, aluminium nitridation by using electric-arc plasma, etc.[1,2] Among them the carbothermal reduction of alumina has been considered as the most suitable method for large-scale production of high purity AlN powders.

The carbothermal reduction of alumina implies a treatment of an intimate mixture of alumina and a source of carbon (graphite, carbon black, active carbon) in a nitrogen atmosphere at temperatures ranging from 1400 to 1600°C.

The carbothermal reaction strongly depends on the homogeneity of the Al_2O_3–C mixture. A complete conversion of Al_2O_3 into AlN is needed to obtain high purity AlN powders for uses in microelectronic substrates fabrication, where a high thermal conductivity is required. It is well known that thermal conductivity of AlN depends on the oxygen content, as a consequence the presence of unreacted alumina in the final powder yields to a high oxygen content that will affect deleteriously the thermal conductivity of the sintered compact.

In the carbothermal reduction processes organic liquids are commonly used to homogenize the starting powders with the carbon source. Homogenization in an aqueous media presents some

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difficulties due to the hydrophobic character of the carbon and the surface characteristics of the reactive carbon sources (e.g. carbon black) that makes difficult the preparation of a well-dispersed slurry. Nevertheless, homogenization in aqueous media could be the most advantageous method for large-scale production of nitride powders by carbothermal reduction. The use of organic liquids is more expensive and needs recycling systems for liquid recovering that implies additional production costs. In addition, it involves environmental and health problems which can be avoided by using water.

The aim of this work is the preparation of homogeneous and nitridable mixtures of alumina–carbon in aqueous media. For this purpose a study of the rheological behaviour of aqueous suspensions of carbon and alumina–carbon was performed. Low viscosity and high stability were considered as the parameters that assure the appropriate homogeneity of the mixtures.

2 Experimental

Alumina Alcoa CT3000SG (average particle size $d = 0{\cdot}5\ \mu m$, specific surface area $S_s = 8\ m^2/g$, main impurity 0·1 wt% MgO) and carbon black N220 ($S_s = 106\ m^2/g$, main impurity 0·4 wt% S) were used as starting materials.

Aqueous suspensions of alumina, carbon and mixtures of them were prepared, adding an alkali-free anionic polyelectrolyte as deflocculant agent. Solid concentration ranged from 10 to 20 wt% for carbon black, 50 to 80 wt% for alumina and 30 to 42·2 wt% for the mixtures Al_2O_3–C (Table 1). Deflocculation was achieved adding a concentration of 1 wt% of deflocculant agent in the alumina suspensions and a 20 wt% (in relation with the carbon black content) in the case of carbon and alumina–carbon mixtures.

The preparation of alumina slips have been reported elsewhere[3] and will not be discussed here.

Alumina–carbon slurries were obtained by mixing suspensions of each material prepared separately. Subsequently the mixture was homogenized in an alumina ball mill for 3 h. The alumina/carbon weight ratio was kept constant for all mixtures ($Al_2O_3/C = 2{\cdot}36$). This value corresponds to the stoichiometric amount fixed by reaction (1) plus a 20 wt% in excess:

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO \qquad (1)$$

The excess of carbon was added to assure the complete transformation of alumina into aluminium nitride. The final solid content in each suspension is reported in Table 1. The experimental procedure followed in preparing the mixtures is shown in Fig. 1.

Table 1. Suspensions prepared

	% *Solid*	% *Deflocculant*	% Al_2O_3	% *Carbon*
Carbon black				
C10	10	20		
C15	15	20		
C20	20	20		
Alumina				
A50	50	1		
A55	55	1		
A60	60	1		
A65	65	1		
A80	80	1		
Alumina–carbon				
A50C15	30·0		21·1	8·9
A55C15	30·7		21·5	9·1
A60C15	31·7		22·4	9·4
A50C20	35·0		24·6	10·4
A60C20	37·8		26·5	11·3
A65C20	39·0		27·4	11·6
A80C20	42·2		29·7	12·6

The rheological behaviour of the different suspensions was studied using a rotational viscosimeter (Haake Rotovisco RV20). Measurements were performed at a constant temperature of $25 \pm 0{\cdot}1°C$.

Selected slurries were cast on porous moulds in order to remove the liquid vehicle. The resulting cake was dried in an oven at 120°C and subsequently powdered and deagglomerated by dry milling in an alumina jar with alumina balls.

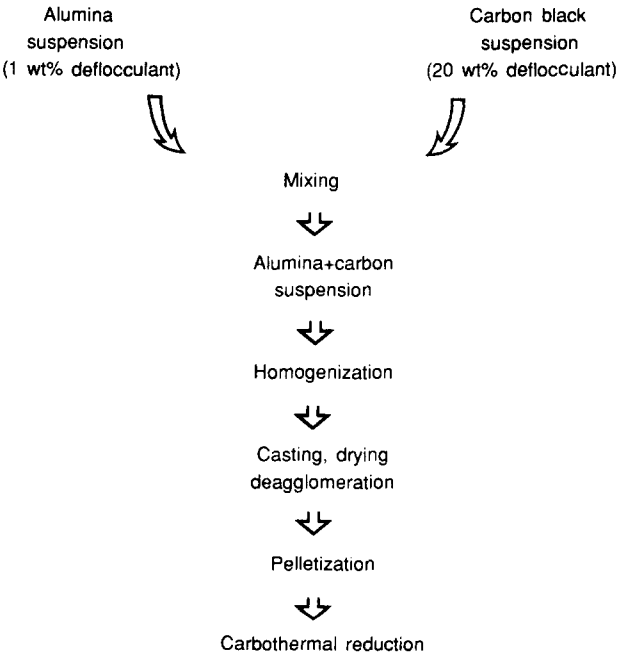

Fig. 1. Experimental procedure.

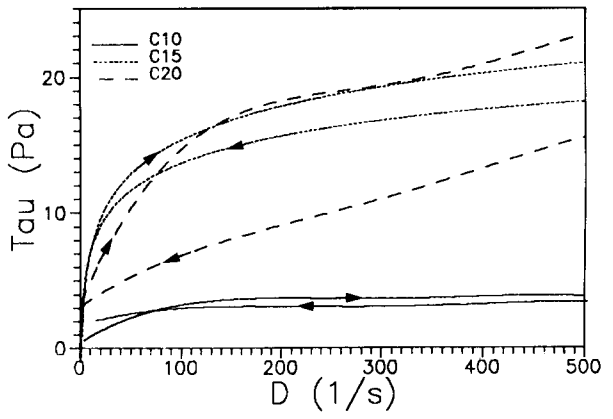

Fig. 2. Shear stress versus shear rate curves for carbon black suspensions with a 10, 15 and 20 wt% solid content. Deflocculant concentration: 20 wt%.

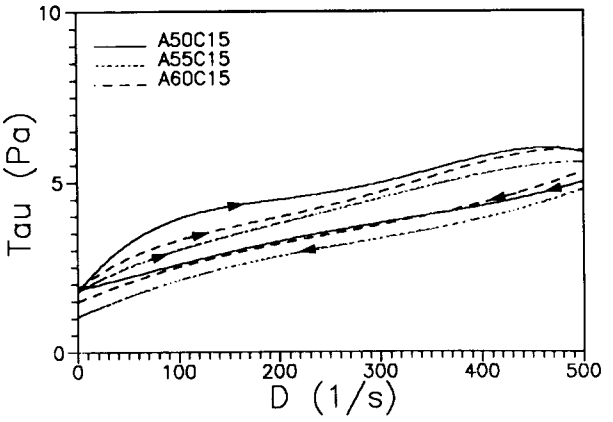

Fig. 4. Shear stress versus shear rate curves for aqueous suspensions of alumina–carbon black mixtures prepared from carbon slurries C15.

Spherical pellets were prepared from these powdered mixtures and subsequently subjected to carbothermal reduction at temperatures ranging from 1500 to 1600°C under a nitrogen flow of 0·3 litre/min. Pellet size ranged from 0·5 to 3 mm in diameter. The advance of the carbothermal reaction was followed by means of quantitative XRD analysis.

3 Results and Discussion

3.1 Carbon black suspensions

The preparation of stable and homogeneous carbon black suspensions requires a relatively high concentration of organic deflocculant due to its high specific surface area and submicronic particle size. Figure 2 shows the shear stress versus shear rate curves for carbon black suspensions with 10, 15 and 20 wt% solid content. A 20 wt% of deflocculant (in relation with the carbon content) was used in all cases. Lower deflocculant content strongly increases the viscosity of the suspension and the time-dependent behaviour. A pseudoplastic behaviour is observed in all cases and the thixotropic cycle increases as the solid content increases.

The apparent viscosity of those suspensions versus solid content, at a shear rate of $500\,s^{-1}$, is plotted in Fig. 3. As can be observed, relatively high viscosity values were found for the suspensions with a 15 wt% and a 20 wt% carbon black content (C15 and C20). The preparation of carbon suspensions with higher solid concentrations (>20 wt%) requires the use of higher deflocculant additions.

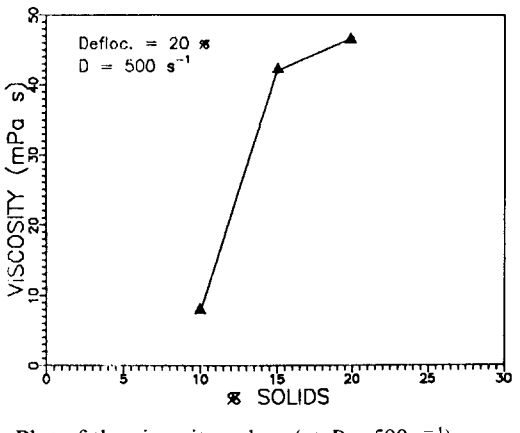

Fig. 3. Plot of the viscosity values (at $D = 500\,s^{-1}$) versus solid content for carbon black suspensions.

3.2 Alumina–carbon black suspensions

Figures 4 and 5 show the shear stress versus shear rate curves for the suspensions of Al_2O_3–C mixtures prepared from carbon black suspensions C15 and C20 respectively. A pseudoplastic behaviour and a thixotropic cycle is also observed in all cases and increase for higher carbon black content (C15 versus C20 series) and total solid content.

The apparent viscosity values (at $D = 500\,s^{-1}$) versus total solid content of these suspensions are

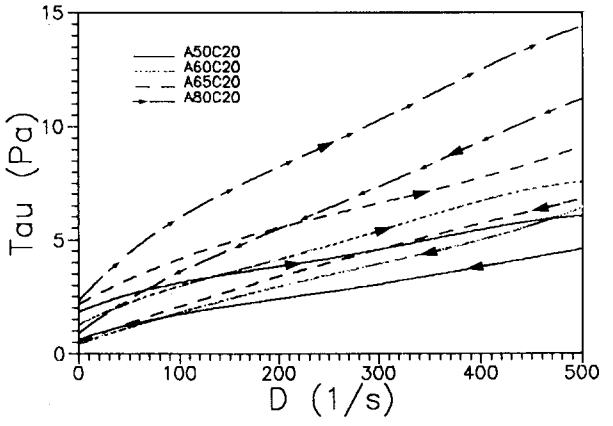

Fig. 5. Shear stress versus shear rate curves for aqueous suspensions of alumina–carbon black mixtures prepared from carbon slurries C20.

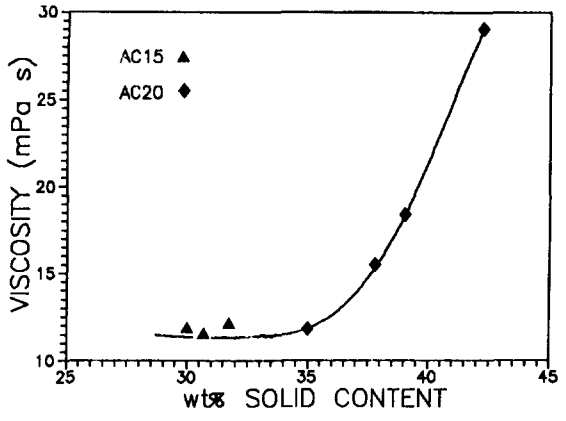

Fig. 6. Apparent viscosity values versus total solid content for aqueous suspensions of alumina–carbon black mixtures.

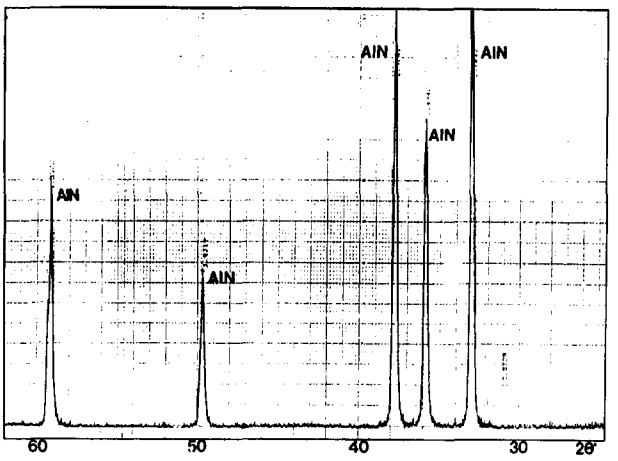

Fig. 7. XRD pattern of synthesized AlN powder.

plotted in Fig. 6. As can be observed, the carbon black governs the rheological behaviour of the alumina–carbon slurries. The total solid content varies over a short range, as does the carbon content. However, the viscosity values increase significantly from a carbon black concentration of 10·4 wt%, corresponding to a total solid content of 35 wt% (A50C20).

In the present work viscosity values of 40 mPa s have been considered as the limit to assure the stability and homogeneity of the Al_2O_3–C mixtures. As a consequence these suspensions must be prepared with a total solid content lower than 40 wt%. Higher solid concentrations yield a viscous slurry in which the homogeneity is difficult to control.

3.3 Carbothermal reduction

Carbothermal treatments were performed at temperatures ranging from 1500 to 1600°C under a nitrogen flow of 0·3 litre/min. The excess of carbon was removed from the reaction product by burning at 700°C in air and the final powder was analysed by quantitative XRD. A treatment at 1560°C for 10 h gives rise to the complete transformation of alumina into aluminium nitride. The XRD pattern of AlN powder is shown in Fig. 7. The oxygen content of this powder, determined by neutron activation analysis, was 1·7 wt%.

4 Conclusions

Homogeneous and stable suspensions of alumina–carbon mixtures have been prepared in aqueous media by using an anionic polyelectrolyte as deflocculant agent. Low viscosity values have been obtained for Al_2O_3–C suspensions with a solid content lower than 40 wt%. These conditions assure the appropriate homogeneity for carbothermal reduction synthesis of aluminium nitride powders.

References

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