Comments on "Kinetics of densification during hot-pressing of aluminium nitride"

Aluminium nitride (AlN) is of interest as a high-strength, corrosion resistant and refractory structural ceramic. Like many other non-oxide ceramics, however, powders of AlN do not sinter without additives [1] even though they can be hot-pressed to densities in excess of 96% of theoretical. LeCompte *et al.* [2] have recently reported the results of a study of the densification behaviour of AlN during hot pressing. They find two regimes, above and below 24 MPa, for which the stress exponents are approximately 10 and 1, respectively. In the high-pressure region, dislocation creep is assumed to be the densification mechanism, while the grain-size dependence at low pressures is indicative of a grain-boundary diffusion-controlled process. Furthermore, at low pressures, a threshold stress is apparent which the authors suggest may be controlled by second-phase particles located at grain boundaries, as described by Ashby [3]. In particular, a $V^{1/2}$ dependence of the threshold stress is observed where V is the volume fraction of the second phase. This is consistent with the Ashby model. However, the authors were not able to establish the validity of this approach because their work did not include direct structural examinations. We have observed the microstructures of hot-pressed AlN powders in the course of our studies of the consolidation of AlN by dynamic compaction [4] and have indeed observed a dispersion of discrete particles in the grain boundaries. Our observations are described below.

Table I gives the chemical analyses of two AlN powders used in our experiments.* These powders are typical of the commercial product and were synthesized by carbon reduction of alumina powder in the presence of nitrogen. The "insoluble residues" are presumably Al_2O_3 remaining from this processing. Scanning electron microscopy (SEM) of the as-received powder (Fig. 1) shows micron-sized agglomerates of ~0.1 μm grains. Our powders thus appear to be comparable to those used by LeCompte *et al.* [2].

A sample of powder 1 was hot-pressed in a graphite die at 27 MPa and 1700° C for 1 h. The resulting specimen had a density in excess of 99% theoretical ($3.26\,g\,cm^{-3}$). SEM of a fracture surface (Fig. 2) reveals a uniform equi-axed microstructure, with evidence of both inter- and transgranular fracture among 0.5–1.0 μm grains. This material was subsequently examined in the transmission electron microscope. Discs, 3 mm diameter were cut, ground and polished, and then ion-milled to produce regions of electron transparency. These were coated with ~ 10 nm of evaporated carbon to prevent surface charging and were examined in a Phillips 400 instrument augmented to carry out microanalysis by X-ray energy dispersive spectroscopy (XEDS) [5].

TEM shows that the equi-axed microstructure of hot pressed AlN also contains a dispersion of spherical particles of approximately 0.05 μm diameter located primarily at the grain boundaries

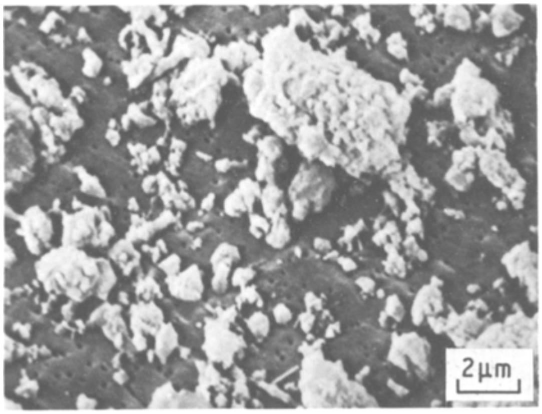

Figure 1 SE micrograph of powder 1. The underlying material is a support for the dispersed powder.

Figure 2 SE micrograph of a fracture surface of AlN hot-pressed at 27 MPa, 1700° C for 1 h.

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*Obtained from Material Research Corporation, Orangeberg, New York, USA.

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TABLE I Analysis of AlN powders

Powder	AlN	Content (wt %)								
		Free Al	C	Insoluble residues	Co	Cr	Fe	Ni	Si	Mg
1	93.0	2.0	0.06	4.2	0.1	0.06	0.06	0.06	0.01	0.1×10^{-4}
2	92.7	2.0	0.05	4.9	0.1	0.08	0.08	0.08	0.01	0.1×10^{-4}

(Fig. 3). XEDS analysis (Fig. 4) shows that Si is preferentially contained in the particles; little or no silicon was observed in the surrounding grains of AlN. A more complete characterization, including an analysis of N and O content, was not possible using XEDS since this technique cannot detect elements of low atomic number [5].* Furthermore, it proved impossible to obtain electron diffraction patterns from individual particles because they were too thick. Our efforts to identify the precipitate material are continuing.

The evolution of the second phase in hot-pressed AlN is of considerable interest. It is possible that the precipitates derive from an oxidation product which initially coats individual grains more uniformly. The role of silicon in such a precipitation process is uncertain since, from Table I, it may be seen that this is a minor constituent. It is worth noting, however, that a non-crystalline intergranular phase is observed in dynamically consolidated specimens of AlN and that it, too, contains silicon. Although further study is required to clarify the details of the second-phase formation, our observations should dispel the concerns of LeCompte *et al.* [2] regarding the development of a dispersion of grain-boundary particles during hot pressing. In this sense it appears that the model of Ashby provides at least a plausible explanation of the threshold stress observed for low pressure densification.

Note added in proof: Further analysis has shown the precipitates to contain Co, Cr, Fe and W. Some XEDS lines of W mask those of Si, complicating the interpretation of the spectra.

Acknowledgement

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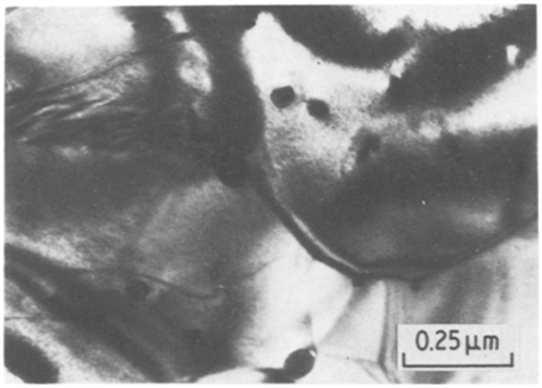

Figure 3 TE micrograph of hot-pressed AlN showing precipitates at grain boundaries.

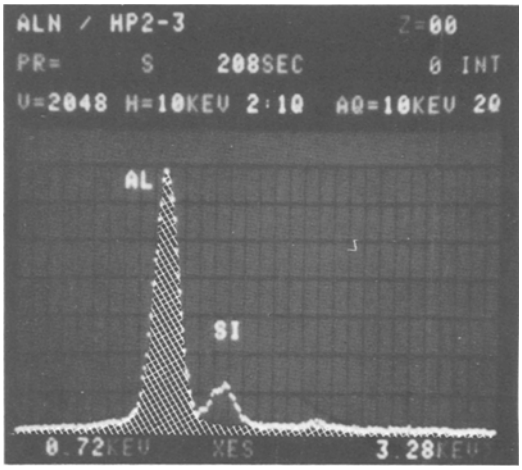

Figure 4 XEDS analysis of the precipitate (white dots) and the surrounding grains (hatched area).

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[*] Recent developments in electron loss spectroscopy (EELS) [5, 6] show that the combination of EELS and XEDS can be effective in analysing this type of multiphase ceramic material [6].

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The effect of the second-phase volume fraction on the grain size stability and flow stress during superplastic flow of binary alloys

Recently, Arieli [1] considered the effect of the second-phase volume fraction on the flow stress during superplastic flow of binary alloys and he showed, for five different superplastic binary alloy systems, that at constant temperature and strain rate the flow stress increases with the deviation of the second-phase volume fraction from that required for maximum grain-size stability. This deviation was characterized by a parameter $Z = (X'_\beta/X_\beta)$ where X'_β is the volume fraction determined from the phase diagram and X_β is the volume fraction of the second-phase required to stabilize the matrix grain size according to an analysis by Hellman and Hillert [2]:

$$X_\beta = \frac{4}{9\beta'}\frac{d_\beta}{d_\alpha}. \tag{1}$$

In this relation, β' is a correction factor close to unity and d_β and d_α are the second phase and matrix grain-size, respectively.

In his analysis Arieli referred, among other binary systems, to Cu–Zn alloys with different compositions and he concluded that there is an excellent correlation between flow stress, σ_f and Z, as shown in Fig. 1 (which corresponds to Fig. 2 of his paper). For all his calculations, the data were taken from the paper by Suery and Baudelet [3].

The aim of this paper is to re-analyse the data obtained in the case of superplastic α/β brasses on the basis of the parameter Z, to discuss the calculations done by Arieli and finally to demonstrate that his conclusion is wrong at least for the Cu–Zn system.

All the data which were used for the determination of the constitutive equation for α/β brasses in the superplastic range [3] are given in Table I. They were obtained from tensile tests at constant strain rate on four α/β brasses with different phase proportions. The stress was calculated at a strain equal to 0.4, after the attainment of an approximately equiaxed structure, the α and β grain sizes being determined at this strain from metallographic observations. In the table values of the parameter Z are also given, this parameter being calculated by considering as matrix the phase with volume fraction higher than 0.5.

So for an α-phase volume fraction α smaller than 0.5, Z is given by:

$$Z = \frac{9}{4}\beta'\alpha\frac{d_\beta}{d_\alpha}, \tag{2}$$

and for α greater than 0.5, by:

$$Z = \frac{9}{4}\beta'(1-\alpha)\frac{d_\alpha}{d_\beta}.$$

The correction factor β' is taken equal to 1.

The calculation shows that the parameter Z always lies between 0.95 and 1.20 with no systematic difference between all the alloys tested. This means that in this system, the experimental second-phase volume fraction is always close to that required for maximum grain-size stability with no significant deviation from it. No correlation can then be found between the flow

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