Letters

Pressureless sintering of aluminium nitride to high density

The preparation of dense bodies from AlN powder has been the subject of many investigations. However, attempts to prepare very dense (above 95% of the theoretical density) and strong AlN bodies by standard sintering techniques even at high temperature were unsuccessful [7]. Therefore the standard technique employed today is hot-pressing. By usual ceramic techniques, i.e. by successive pressing and sintering, only 84 to 88% of the theoretical density is achieved [2]. Recently it was shown that the rate of sintering of AlN is strongly influenced by the particle size of the raw powder [3], but even in the case of the finest powder used, very high density was not achieved. The maximum achieved density, quoted in patent literature, is 95% of the theoretical density [4]. In the present work, we report on the activation of AlN sintering by means of small addditions of Ni.

Two types of AlN powder were used in the present study. A fine powder was analysed by standard BET technique and found to have a surface area of about 30 m^2/g, while a coarse commercial powder had a surface area of 1 m^2/g. Nickel was added (1 to 10 wt%) to the AlN powder in two different forms – either as a powder (Koch-Light) or in the form of alcoholic $Ni(NO_3)_2$ solution. Uniform dispersion was achieved by ball-milling in alcohol for several hours.

From the powder, pellets with diameter 16 mm and height 5 mm were pressed under a pressure of 400 Mn/m^2 without binder addition. The pellets were placed in a graphite crucible and coated with AlN powder to prevent contamination from graphite and the atmosphere. Samples were heated in an electric furnace with a graphite heater in a N_2 atmosphere. The rate of heating was about 1500°C/h and the pellets were kept for 1 h at temperatures between 1600 and 2000°C. The time and temperature of sintering were quite critical. Extended heating above 2000°C resulted in porous products.

For X-ray analyses, samples with larger amounts (20 wt%) of Ni were prepared and fired under the same conditions. Densities were measured with mercury in a vacuum pycnometer. The microstructure of sintered pellets was investigated by metallography. The preparation of samples was difficult due to a strong tendency to chipping. Grinding and polishing of samples with alumina powder of different grain sizes gave the best results. Polished samples were etched with the 1:1:1 solution of glycerol, HNO_3 and HF.

The influence of the addition of nickel on the sintered density of aluminium nitride samples is shown in Fig. 1; sintering conditions were 1 h at 2000°C in a nitrogen atmosphere. It can be seen that the addition of nickel activates sintering of AlN, and that the activating influence is limited to small additions, up to 1 to 2 wt%, since aluminium nitride samples with higher amounts of nickel sintered to lower density. The activating influence of Ni on the sintering of AlN is observed only with very fine grained AlN powders. Activation of the original commercial powder with a specific surface area of 1 m^2/g was unsuccessful, whereas activation of milled AlN with a specific surface area of 30 m^2/g proved to be very effective. The homogenous distribution of Ni additions within the sample greatly improved the reproducibility of the results. Best results were achieved by the addition of Ni in the form of alcoholic $Ni(NO_3)_2$ solution. Sintering was carried out after drying and reduction in H_2 at 600°C. The specific examples are compared in Table I.

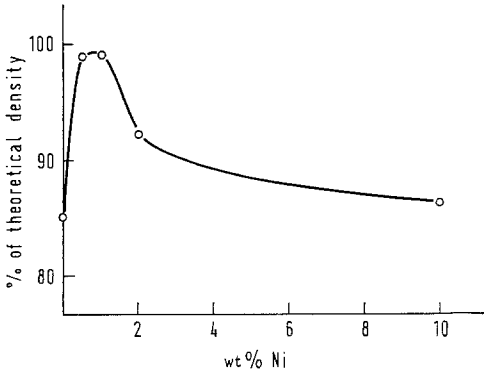

Figure 1 Densities of AlN with Ni additions sintered at 2000°C for 1 h. Ni was added as $Ni(NO_3)_2$ solution.

TABLE I

Sample	Density after sintering at 2000°C (g/cm³)*
Commercial AlN + 1 wt % Ni powder	2.47 ± 0.05
Milled AlN + 1 wt % Ni powder	3.25 ± 0.07
Milled AlN + 1 wt % Ni added as $Ni(NO_3)_2$	3.29 ± 0.04

*Results are the average of ten samples.

Fig. 2 shows the microstructure of an etched AlN specimen, sintered with 1 % Ni addition for 1 h at 2000°C in a nitrogen atmosphere. The density of the sintered specimen was 99.5 % of the theoretical value. An unetched sample (Fig. 3) shows Ni (or Ni-Al phase, formed during the sintering, see below) as white spots. The elongated AlN grains are approximately 10 μm in length. It is interesting to note the similarity of the microstructure presented with the micro-

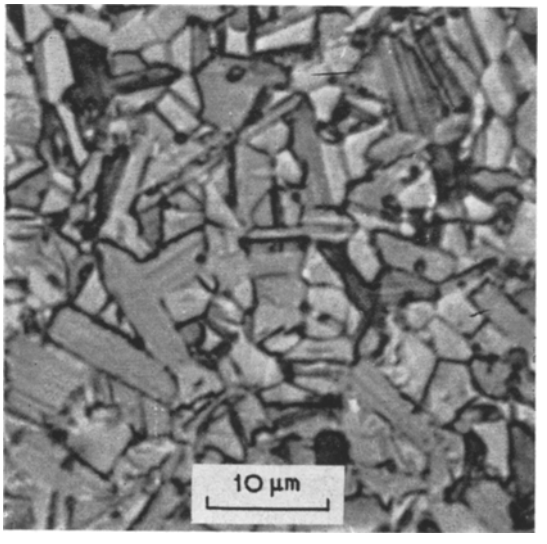

Figure 2 Microstructure of the system AlN + 1% Ni sintered to 99.5% of theoretical density etched.

structure obtained during sintering of a mixture of AlN and Y_2O_3 powders [5], where the tendency of AlN to form a fibrous structure is especially pronounced.

The sintering of AlN-Ni mixtures occurs in the presence of liquid phase, since the sintering

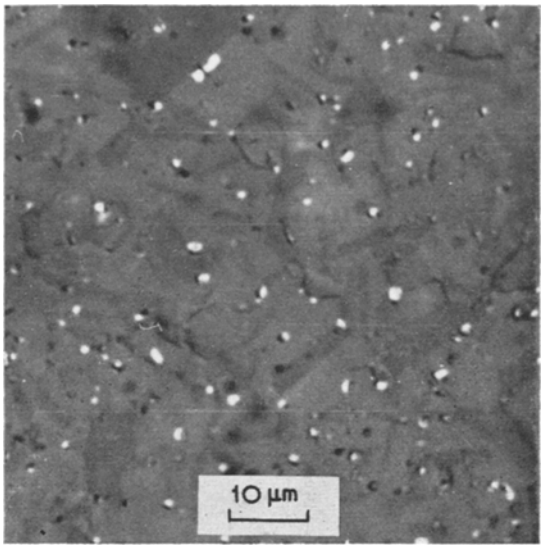

Figure 3 Microstructure of the system AlN + 1% Ni sintered to 99.5% of theoretical density as polished.

temperature is above the melting point of Ni or any compound in the system Al-Ni. However, the activated sintering should not be ascribed, without further evidence, merely to the appearance of a liquid phase, since chemical reactions occurring during the sintering of AlN-Ni mixtures must be taken into account. Preliminary experiments with sintered samples composed of 20 % Ni-80 % AlN showed the formation of $AlNi_3$, which could be detected by X-ray analysis.

References

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