of 0.25. Fig. 1 indicates the strengths of the three materials to be 185, 235 and 257 MN m^{-2} respectively – values which cannot be adequately represented by a single datum point on a strength/porosity plot. Actual recorded strength levels have indicated that extrapolation of the lines derived in [3] are valid for the two fine powders up to a density of at least 2.5 Mg m^{-3}. In all cases increases in density (decreases in porosity) will lead to further improvements in strength but the finer powders clearly have greater strengths at all extrapolated porosity levels. However, the improvements in properties outlined above represent only control of the starting silicon structure, since nitriding conditions were identical. We have demonstrated that changes in the nitriding process (e.g. use of flowing rather than static nitrogen) can lead to significant changes in strength and the critical defect size [6]. Thus further improvements in strength are likely to be achieved by optimizing reaction procedures although research is necessary to determine the extent of these improvements.

Whilst the above comments have dealt with the improvement of strength, it is important to recognize that an improvement in the consistency of the properties of reaction sintered silicon nitride is of great value both to the economics of production [5] and the application of the material. Most of our recent work has been aimed at this rather than strength improvement. It is also worthy of note that the above comments relate to materials in which the strength is controlled by porosity rather than impurities. In cases where impurities control strength well defined strength/density relationships were not established and the critical defects were easily identified in fracture surfaces.

Finally, we would like to express our reservations concerning the use of data for both hot-pressed and reaction sintered silicon nitride since, as noted by Rice [1], the nature of the fabrication processes, the origin of porosity and indeed the composition of the materials are so different. It should also be noted that whilst the two materials are to some degree competitive, they can also be considered complementary as they represent a trade-off between cost, strength and density. Thus whilst differences in strength between 200 and 250 MN m^{-2} appear small on a semi-log plot constructed to incorporate hot pressed strengths, the 25% improvement in the strength of reaction sintered silicon nitride must be regarded as significant.

Acknowledgement

This letter is published by permission of the Controller, HMSO holder of Crown Copyright.

References

1. R. W. RICE, *J. Mater. Sci.* **12** (1977).
2. B. F. JONES and M. W. LINDLEY, *ibid* **11** (1976) 191.
3. *Idem, Powder Met. Int.* 8 (1976) 32.
4. D. P. ELIAS and M. W. LINDLEY, *J. Mater. Sci.* **11** (1976) 1278.
5. B. F. JONES and M. W. LINDLEY, *ibid* **11** (1976) 1288.
6. B. F. JONES, K. C. PITMAN and M. W. LINDLEY, *ibid* **12** (1977).
7. B. F. JONES and M. W. LINDLEY, *ibid* **11** (1976) 1969.
8. *Idem, ibid* **10** (1975) 967.

Received and accepted 24 September 1976

B. F. JONES
M. W. LINDLEY
Admiralty Materials Laboratory,
Holton Heath,
Poole,
Dorset, UK

Rapid chemical vapour-deposition of Si_3N_4

Pyrolytic Si_3N_4 is expected to have more favourable properties than those of reaction-sintered and hot-pressed Si_3N_4. We have successfully prepared the massive crystalline Py–Si_3N_4 at the deposition rate (the rate of increase in layer thickness x/t) of 0.73 mm h^{-1} using the $SiCl_4 + NH_3 + H_2$ system as the source material [1]. The present work revealed that x/t can be increased to about 1.2 mm h^{-1} by regulating the $SiCl_4$ (vapour) flow rate. This paper describes the conditions for rapid chemical vapour-deposition of Si_3N_4 and its structural characteristics.

The deposition method and the experimental set-up used in the present experiments are similar to those previously reported [2]. The deposition conditions employed are as follows: deposition temperature (T_{dep}), 1400° C; total gas pressure (P_{tot}), 40 and 60 Torr; NH_3 gas flow rate [FR

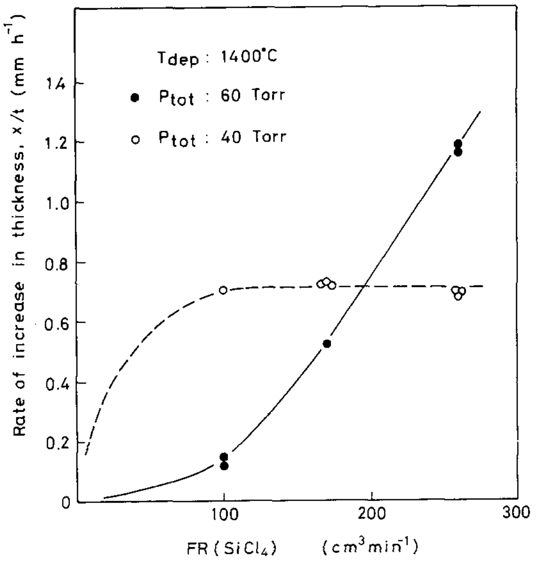

Figure 1 Effect of the $SiCl_4$ (vapour) flow rate on the rate of increase in thickness of Py–Si_3N_4.

$(NH_3)]$, 60 cm^3 min^{-1}; $SiCl_4(v)$ to H_2 gas flow rate ratio $FR(SiCl_4)/FR(H_2)$, ~0.26; $SiCl_4(v)$ flow rate $[FR(SiCl_4)]$, 100, 170 and 260 cm^3 min^{-1}.

Fig. 1 shows the relationship between x/t and $FR(SiCl_4)$. At $P_{tot} = 40$ Torr, x/t ranges from 0.68 to 0.73 mm h^{-1}, while at $P_{tot} = 60$ Torr it increases with increasing $FR(SiCl_4)$ and reaches 1.2 mm h^{-1} at $FR(SiCl_4) = 260$ cm^3 min^{-1}. Above $FR(SiCl_4) = 260$ cm^3 min^{-1}, the deposited layer on the substrate is heterogeneous at $P_{tot} = 60$ Torr.

Structural characteristics of Py–Si_3N_4 formed at $x/t = 1.2$ mm h^{-1} are as follows: the crystal structure is α-type; the lattice parameters are $a = 7.752 \pm 0.002$ Å and $c = 5.622 \pm 0.002$ Å; the density is 3.18 g cm^{-3} (100% of a theoretical density); and the (2 2 2) plane is parallel to the deposition surface.

References

1. K. NIIHARA and T. HIRAI, *J. Mater. Sci.* **11** (1976) 604.
2. *Idem, ibid* **11** (1976) 593.

Received 31 August
and accepted 4 October 1976

TOSHIO HIRAI
KOICHI NIIHARA
TAKASHI GOTO
The Research Institute
for Iron, Steel and Other Metals,
Tohoku University,
Sendai, 980, Japan

Non-unique stress–strain-rate relations during superplastic flow

Isothermal superplastic deformation of a material of constant grain size is usually represented by an equation of the type [1–3]

$$\sigma = k\dot{\epsilon}^m \qquad (1)$$

where σ is the applied stress, $\dot{\epsilon}$ the strain-rate, m the strain-rate sensitivity index, and k an empirical constant. This equation implies that the magnitude of stress corresponding to a given strain-rate is independent of the *path* by which that strain-rate is reached. Further, it has been reported that strain-rate compensated true stress–true strain curves exhibit practically no work-hardening when the grain size is stable [1–3]. The experimental finding [4, 5] that prior deformation at superplastic strain-rates does not alter the mechanical properties also seems to suggest that strain is an unimportant variable during superplastic flow.

"Dynamic" mechanical history, however, has not been considered to date. For example, a given strain-rate of $\dot{\epsilon}_1$ may be reached in case of two nearly identical specimens by elongating them to different lengths l_1 and l_2 at cross-head speeds V_1 and V_2, respectively, such that $V_1/l_1 = V_2/l_2 = \dot{\epsilon}_1$. If Equation 1 represents an equation of state (i.e. is independent of the path by which $\dot{\epsilon}_1$ is approached) the observed stress in either case should be equal, provided necking and grain growth are absent.

Bars of chill-cast Pb–Sn–Cd ternary eutectic alloy were zone-refined using fourteen passes and subsequently rolled at room temperature to produce sheets of approximate thickness 0.8 mm. Thickness of tensile specimens, produced by stamping, varied between 0.74 and 0.86 mm although within each specimen no thickness variation was allowed. The width was constant and equal to 6.5 mm while the gauge length lay between 19.7 and 21.3 mm.

Specimens needed for a series of tests were taken from the same ingot to eliminate grain-size variation. Stability of grain size during deformation, on the other hand, was ensured by heat-