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Reply to "Comments on 'On the background damping in the vicinity of the grain-boundary peak in zinc' "

Povolo [1] has suggested that the interpretation of the strain amplitude dependent damping found in zinc [2] in terms of the Granato–Lücke model was incorrect and has suggested that for torsion, the expression for the strain amplitude dependent damping should be

$$\Delta_t = C_1 \frac{C_2}{\epsilon} g \left(\frac{C_2}{\epsilon}\right) \exp\left(-\frac{C_2}{\epsilon}\right), \quad (1)$$

where $g(C_2/\epsilon)$ is a ratio of polynomials and is plotted in [3]. Over the range of strain amplitudes used in the present experiments, $g(C_2/\epsilon)$ varies from 6 to 2.05, whereas $\exp(-C_2/\epsilon)$ varies from 2×10^{-3} to 120×10^{-3}. Thus the change in Δ_t in Equation 1 produced by a change in $g(C_2/\epsilon)$ is small compared to the change produced by a change in $\exp(-C_2/\epsilon)$. The Granato–Lücke model is only an approximation at the tempertures of interest and since Povolo's equation only produces a small change in the level of damping, it is not inconsistent to use the original Granato–Lücke equation.

Furthermore, Povolo's equation is itself only approximate in that $g(C_2/\epsilon)$ is an approximation for a set of experimental integrals to which data cannot be compared. Povolo gives no estimate of the error introduced by this procedure.

It can be seen from Table I in [2] and Fig. 2a in [1] that the values of C_2 are similar in both cases, supporting the use of the original Granato–Lücke equation. If C_2 from [1] is plotted versus d, as Povolo has done, then similar curves would be obtained. It is obvious from the figures that C_1 increases, but this does not invalidate Equation 10 in [2] as has been suggested by Povolo.

In conclusion, although Povolo's papers have shown possible inadequacies in the Granato–Lücke theory, he has not attempted to evaluate the magnitude of his approximations. Fiore and Bauer [4] have made further comments on this aspect which will not be repeated here but which are also extremely relevant to this paper.

The differences between the analysis of the results in terms of the Granato–Lücke equation and Povolo's equation are minor in relation to the basic underlying theory and data can therefore still be satisfactorily explained by the use of the original equation.

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Comment on "Additional observations on the strength/nitrided density relationship for a reaction sintered silicon nitride"

It is useful to compare the strength versus density data for reaction sintered Si_3N_4 that Jones and Lindley [1] reported in recent correspondence, with other Si_3N_4 data. This comparison and its implications for further improving the strength of reaction sintered silicon nitride are briefly discussed.

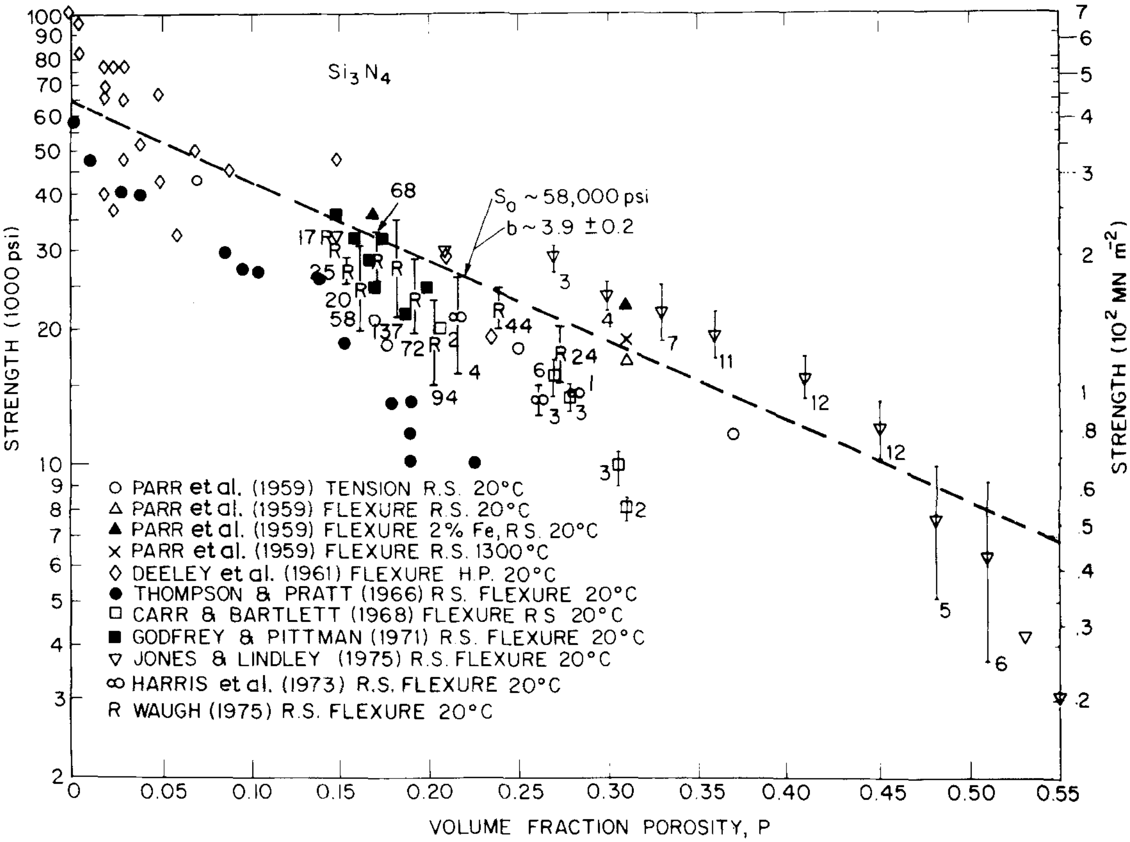

Figure 1 Semi-logarithmic plot of the strength of Si_3N_4 as a function of porosity. Note the parameters S_0 and b are shown for the set of data not including that of Waugh and Harris. Addition of these data lowers b by a limited amount.

First, as shown in Fig. 1, Jones and Lindley's data are generally consistent with data compiled by the present author for a variety of Si_3N_4, both hot pressed and reaction sintered, bodies made by various investigators. In this figure, as semilogarithmic plot of strength as a function of the volume fracture porosity rather than density has been made. This allows application of the widely used exponential form of porosity dependence ($S = S_0 e^{-bP}$, where S = strength at volume fraction porosity P, and S_0 = strength at $P = 0$), and comparison to the porosity dependence of other materials. The S_0 and b (i.e. slope) value for this equation were first determined to be 65 000 psi* and 5.3 [2] before data of Jones and Lindley [1], and Waugh [3] were available. The addition of Jones and Lindley's data changed these values to some extent, as shown in Fig. 1. Subsequent addition of data of Harris *et al.* [4] and especially those of Waugh [3], clearly shift the curve downward (i.e. a larger slope value) closer to the earlier curve. The exact values of these parameters are not necessarily significant, e.g. since differences in test technique and pore character are factors in their variation. However, it is significant that these b values are consistent with an overall average b value of 4 ± 2 that the present author has found in an extensive survey of the porosity dependence of strength of a wide variety of ceramic materials [2]. Furthermore, increasing the amount of data, especially by increasing the range of porosity tends to give b values closer to this average as is the case for the above Si_3N_4 data. Incidentally, while extrapolation of strength porosity data to 0 porosity is often somewhat tenuous because of possible changes in failure

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*10^3 psi = 6.89 N mm^{-2}.

mechanisms, and in the case of silicon nitride because of the use of additives in dense material, it is worthwhile to note that the linear dependence of strength on density proposed by Jones and Lindley extrapolates to about 350 MN m^{-2} (about 50 000 psi) at 0 porosity. This is 20% or so lower than the extrapolated value from the exponential dependence which again indicates better agreement of the latter with existing data.

Jones and Lindley suggested that the variation of strength well below the average strength at any porosity may, in turn, imply that there are unidentified parameters, control of which could lead to higher than their maximum strengths at any porosity. Unfortunately, the chances for this speculation being true appear limited. This basically stems from the fact that strength is a weak link process so that there are many more opportunities for decreasing strength than for increasing it. Thus, in the specific case where strength is dominated by porosity, the strength of a body having a given amount and type of porosity will typically be a maximum when that porosity is homogeneously distributed.

Inhomogeneities in the distribution of the porosity will reduce Young's modulus (E) [5] and probably the fracture energy (γ), by providing lower density crack paths and increase the flaw size (C) due to pore agglomeration. If one reduces the size of the pores for a given porosity higher strength may be obtained due to greater overall homogeneity raising E and probably γ; however, the chances of having local clusters of pores to increase C can often counter much, or all, of these possible increases. Also, even if one is successful in reducing the average size of the pores without significantly increasing the chance of pore clustering, one often has a few remaining larger pores that will limit strengths. The dominating effect of porosity on strength strongly suggests variations in strength are due mainly to variations in porosity, barring unusually low strengths due to poor (e.g. incomplete) nitriding, impurities, etc. Furthermore, the statistical nature of the distribution of silicon particle sizes, packing, and impurities which can affect resultant pore structures all indicate limited opportunities to improve the homogeneity of pore size, shape, and spatial distribution. Thus, while there may be other microstructural factors affecting the strength of the nitrided bodies and, while some improvement in strength by reducing the pore size may be feasible, the chances for further increases appear limited. While test parameters may also be a factor, the fact that Jones and Lindley's data show among the highest strengths for a given density indicates that they have made substantial progress, but this is no guarantee of further progress. What is clearly needed is extensive characterization of developmental samples, especially of their porosity, with particular attention to characterization of fracture origins. Preliminary analysis of fracture origins of test samples kindly supplied by Waugh supports the above observations, i.e. while some specimens of intermediate or lower strengths have a readily identifiable inhomogeneity (e.g. larger particles) at the fracture origin, most specimens do not. Thus, achievement of higher densities appears to be the main route to higher strengths in further development of reaction sintered Si_3N_4.

Note added in proof. Recent fractographic examination of a number of commercial reaction sintered bars (Norton NC-435, supplied by Dr R. Ruh of the Air Force Materials Laboratory) showed that many of these failed from machining flaws. The room temperature strengths of these specimens averaged between 24 000 and 34 000 psi for expected porosities of 20 to 25%; in good agreement with the main trend of the data of Fig. 1. This substantiates the expectation that improvement of the microstructural homogeneity beyond a certain limit is not of practical value since other sources of failure become effective; in this case machining flaws from typical finishing of ceramic components. When pores no longer are the failure causing flaws, then porosity effects strength only through its effects on E and γ, where effects of the amount of porosity are typically substantially more important than the type of porosity.

Acknowledgement

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Reply to "Comment on 'Additional observations on the strength/nitrided density relationship for a reaction sintered silicon nitride'"

We have read with interest Rice's comment [1] on our recent communication [2] and endorse in general his interpretation of the influence of porosity on the strength of ceramic materials. We submit, however, that his apparent pessimism concerning our speculation that further improvement in the strength of reaction sintered silicon nitride is possible, does not take account of the unique nature of this material compared to most other ceramics. It is because of the more complex formation mechanism of reaction sintered silicon nitride that its microstructure has not been systematically optimized. More recent studies have revealed that the unidentified parameters to which we referred [2] are those factors which influence the size of pores and structure of the silicon nitride. The complication arises because the ultimate pore size is dictated not only by the initial structure of the green silicon compact [3] but also by the details of the process by which the silicon is converted to silicon nitride [4–6]. The details of the nitriding process dictate the proportion of silicon nitride formed which contributes to the continuous silicon nitride network which controls the effective size of pores [6, 7].

We are not sure of the manner in which Rice [1] has treated our data for a coarse silicon powder because all of our materials were *incompletely* nitrided and consequently the computation of their porosity levels is rather complicated [8]. Nevertheless a single relationship between strength (or log strength) and volume fraction porosity as advocated by Rice [1] suggests that strength at a particular porosity is dependent on the green density of the silicon compact and independent of the starting powder. However, it has been clearly demonstrated [3, 8] that for a particular silicon powder the linear relationship between strength and nitrided density is *not* dependent on the green density of the silicon compact, i.e. strength at a particular porosity is independent of green density. Additionally, significantly different strength/density relationships have been demonstrated for reaction sintered silicon nitride prepared from different powders [3] showing that the assumption of a single strength level at a given porosity level is an oversimplification. For example, consider the data we have published [3] for three silicon powders with median particle sizes of 25, 11 and 6 μm. Assume that these powders have been selectively compacted and nitrided under identical conditions to yield three fully converted materials with a density of 2.4 Mg m^{-3}. Assuming the theoretical density of silicon nitride to be 3.2 Mg m^{-3}, all products have a volume fraction porosity

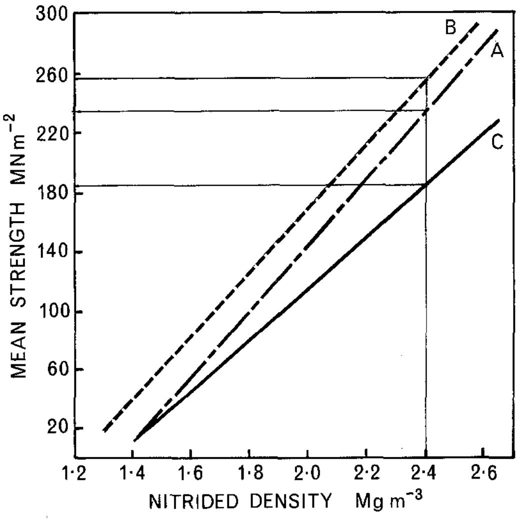

Figure 1 Strength/nitrided density relationships for silicon powders with median particle sizes of 6 μm (B), 11 μm (A) and 25 μm (C) [3].

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

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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