

The mechanism of inducing uniaxial anisotropy in the plane of the films will be the subject of separate investigations. Analysis of the changes of the type of anisotropy in annealed films needs supporting with structural investigations. Investigations of the influence of high temperature annealing of films on their anisotropy and domain structure have been undertaken.

Acknowledgement

This work was supported financially by the Institute of Inorganic Chemistry and Rare Elements Metallurgy of the Technical University in Warsaw.

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Received 30th September and
accepted 4 November 1977.

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Strength versus nitrified density and microstructural design of reaction-bonded silicon nitride

This letter is intended to add information and direction to the comments of Rice [1] on the observations of Jones and Lindley [2, 3], which were published in this journal. Reaction-bonded silicon nitride (RBSN) is a brittle material and as such its strength is a strong function of the size and distribution of flaws. It is agreed that reducing the overall volume fraction of porosity will result in an increased strength. There is, however, disagreement as to whether the strength can be significantly increased by reducing the average pore size and controlling inhomogeneities in the distribution of pores without changing the volume fraction of porosity.

Rice contends that although a reduction in the size of pores at a given volume fraction porosity could lead to an increase in strength by increasing Young's modulus and the fracture energy, there will be no overall improvement because pore clustering and occasional oversized pores will continue to control strength. In other words, no significant reduction in the size of the weak links can be re-

alized by controlling microstructure. Rice states that except for unusually low strengths (due to poor nitriding, impurities, etc.) variations in strength are simply due to variations in volume fraction porosity.

On the other hand, Jones and Lindley have compiled evidence showing that nitrified density, regardless of green density, is directly related to strength. Since a particular nitrified density may contain different volume fractions of porosity depending on green density (and therefore different volume fractions of porosity can lead to a constant strength), they suggest that improvements in strength using microstructural design are very possible.

Baumgartner [4] points out that there is apt to be a maximum green density which can successfully be nitrified without unreacted Si cores remaining. Thus beyond the limiting higher density, efforts other than increased density (e.g. microstructural design or flaw size distribution control) must be employed.

We are in agreement with Jones and Lindley and Baumgartner here. The very complexity of RBSN makes it a material most susceptible to

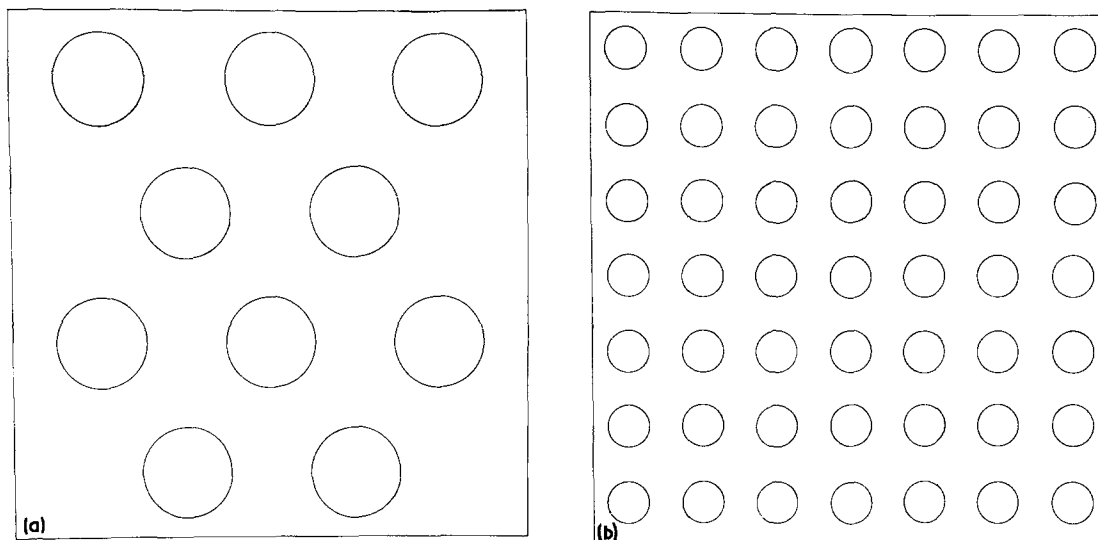


Figure 1 (a) 0.22 volume fraction porosity; assuming constant pore size r_1 , spherical pore shape, regular pore distribution. (b) As in (a) but with constant pore size $r_2 = 0.45 r_1$.

microstructural design and control. Processing parameters [5–9] such as initial powder size and purity and reaction conditions allow accurate control over the resultant microstructure – including flaw size distribution. Therefore it is necessary to combine this microstructural design with densification improvement and reduction of flaws to achieve optimum strength in RBSN.

Direct evidence has been obtained in our laboratory [10]. Specimens with nitrified density of 2.44 g cm^{-3} were made from green compacts of density 1.5 g cm^{-3} . This produced specimens with 0.22 volume fraction porosity (this can be calculated theoretically knowing that the volume of solid increases by 22% during reaction and experimentally from micrographs) corresponding to 94.0% fully reacted material. Processing parameters were controlled to produce various microstructures [5, 10] whose transverse rupture strength varied between 17 and 43 KSI*. In these specimens flaw size was found [10] to be closely related to strength. Average pore size (which is strongly related to the largest pore size observed [10]) was varied between $6 \times 10^{-6} \text{ m}$ and $32 \times 10^{-6} \text{ m}$ using microstructural control. This effect of varied pore size can be seen schematically in Fig. 1 where two pore size distributions are given, each with constant pore content of 0.22 volume fraction porosity. In this representation it is assumed that the pore size

*117 and 297 MPa.

is constant and the distribution is uniform. Neither of these assumptions are observed in practice, yet are made here to simplify the figure. The high strength specimens (43 KSI) are substantially above the strength predicted by Rice [1] on volume fraction porosity data alone.

This illustrates that strength is not only a function of overall volume fraction porosity but also a strong function of the details of the microstructure (such as pore size distribution). It would be prudent to utilize densification, flaw control, and microstructural control in conjunction with one another to improve the strength of RBSN.

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Received 25 October
 and accepted 14 November 1977.

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On the continuous transition between two structure types in the zirconia – gadolinia system

A continuous transition between the fluorite and type C rare earth oxide structures at high temperature has been reported by Perez y Jorba *et al.* [1, 2] in the systems ZrO_2 with Gd_2O_3 , Dy_2O_3 and Yb_2O_3 . At low temperatures there was a miscibility gap between the fluorite and type C phases, while at intermediate temperatures two type C phases coexisted. Similar results were reported in the ZrO_2 – Y_2O_3 system [3], but these were later shown to be artefacts arising from imperfect equilibration [4]. The continuous structural transition has also been observed directly by Rouanet using high temperature X-ray diffractometry in the systems ZrO_2 with Y_2O_3 , Er_2O_3 or Yb_2O_3 [5].

Since a continuous change of equilibrium structure with composition or temperature would be of theoretical interest, it was decided to re-examine one of the cases cited above. The ZrO_2 – Gd_2O_3 system was selected as it is well documented, and the relevant regions of the phase diagram are readily accessible experimentally.

The general techniques used have been described previously [3, 4]. Oxides of 99.9% purity were used, and samples were prepared by mixing the oxides, by arc melting mixed oxides, and by coprecipitation. Pellets weighing about 250 mg were equilibrated in air for 2 weeks at 1450°C or for 4 days at 1650°C, or in a gas-fired furnace for 5 h at 1850°C; they were then removed quickly from the furnaces.

A single composition was studied, ZrO_2 :80 mol % $GdO_{1.5}$, since this should exhibit the three regimes indicated by Perez y Jorba *et al.* at 1450, 1650 and 1850°C respectively. In fact, X-ray diffraction patterns recorded with a Guinier camera using both Cu and $CrK\alpha_1$ radiations, the latter to

avoid GdL fluorescence, showed that all the samples were essentially mixtures of fluorite and type C phases. In general the patterns were very sharp, indicating little if any phase separation during cooling. However the samples equilibrated at 1850°C did show, in addition to the sharp fluorite and type C reflections, some weak, diffuse reflections corresponding to a second type C phase, and also contained a trace of B- Gd_2O_3 phase.

The lattice parameters and estimated compositions of the major phases found are given in Table I: There were no significant variations attributable to the different initial sample preparations so that the values are the means for the three types. Compositions were estimated by linear interpolation between the cell volumes of the pure components as proposed by Zen [6] for example. This was justified here by measurements on 70 and 90 mol % $GdO_{1.5}$ samples, which were single phase fluorite and type C respectively: In both cases the difference between the nominal and estimated compositions was less than 0.5 mol %.

The limits of the two phase field based on these results are shown in Fig. 1, which also indicates

TABLE I Phase data determined at room temperature for ZrO_2 : 80 mol% $GdO_{1.5}$ equilibrated at high temperature

Equilibrium temperature (°C)	Lattice parameter (Å)		Composition (mol% $GdO_{1.5}$)	
	Fluorite	Type C*	Fluorite	Type C
1450	5.322	5.367	69.9	86.1
1650	5.328	5.368	72.0	86.4
1850†	5.340	5.371	76.5	87.4

Standard deviations of lattice parameters are about 0.001 Å.

*The parameter quoted is that of the fluorite sub-cell, i.e. half that of the type C cell.

†A trace of B- Gd_2O_3 solid solution was present also.