JOURNAL OF MATERIALS SCIENCE 16 (1981) 3099–3104

# Oxidation weight gain and strength degradation of $Si_3N_4$ with various additives

C. CM. WU, K. R. McKINNEY, R. W. RICE, W. J. McDONOUGH,
S. W. FREIMAN*
*Naval Research Laboratory, Washington, DC 20375, USA*

Oxidation behaviour and strength degradation, due to long-term high temperature exposure in air, of $Si_3N_4$ with MgO, $ZrO_2$ or $Y_2O_3$, as densification aids have been studied. It was found that the weight change and strength degradation in the specimens depend largely on the kind of densification aid. Strength degradation, which generally occurred and was greatest at higher additive levels, was related to the generation of pits in the specimen surface. Possible mechanisms for pit formation are discussed.

## 1. Introduction

$Si_3N_4$ is a leading candidate material for increasing operating temperatures and hence improve the efficiency of systems involving heat, e.g. turbine engines. Dense forms of $Si_3N_4$ from hot-pressing, sintering or chemical vapour deposition (CVD), are of particular interest for some of the most demanding cases, e.g. high stress and temperature applications. The latter places particular emphasis on oxidation and its effects on the performance of dense $Si_3N_4$ bodies which commonly have an oxide additive which is used for densification. While oxidation effects have been reported by a number of investigators on their own materials [1, 2] and a few other bodies [2–6] for comparison, no systematic study of the type and amount of additve has been reported. This paper reports such a systematic study of the weight, surface chemical and room-temperature strength changes due to oxidation. A companion paper reports internal compositional changes due to oxidation [7].

## 2. Experimental procedures

A variety of laboratory and commercial hot pressed† and some chemical vapour deposited (CVD) $Si_3N_4$ bodies [8] were studied (Table I). The processing of some bodies was varied as discussed later to study the relationship between oxidation and strength changes. Rectangular cross-section bars about 2.5 mm × 7.5 mm × 40 mm were diamond sawn such that the largest faces were parallel to the original hot-pressing or CVD surfaces. These bars were then diamond ground along their length on all faces using a 180-grit, metal bonded wheel with a typical feed rate of $760\,mm\,min^{-1}$ and 0.025 mm depth of cut. Edges of the bars were then rounded on a $15\,\mu m$ diamond disc.

Oxidation studies were carried out in an alumina tube furnace at 1430° C for 100 h; i.e. to observe effects of substantial oxidation. (The tube itself had previously been aged for several hundred hours at 1430° C.) Bars were set on edge on two $Si_3N_4$ supports near the bar ends in a NC-132 $Si_3N_4$ boat in the tube. The ends of the tube were left open and the specimens were brought to 1430° C in about 3 h; furnace cooling after shut-down typically reached room tempeature of about 22° C in times of the order of 7 h.

After oxidation, weight changes of each of the specimens were measured and the oxidized surfaces were examined. Then 3-point flexure strengths were obtained with a 12.7 mm span and cross-head

---

*Present address: National Bureau of Standards, Washington DC 20234, USA.

†Because of this variety, it was impossible to know or analyse for impurities. However, the focus is on trends with additives, generally at levels beyond those of any impurities. Further, most of the work is based on a few common sources.

0022–2461/81/113099–6$02.60/0

TABLE I Hot pressed $Si_3N_4$ materials

| Additive | Wt % | Vol % | Source |
|---|---|---|---|
| MgO | 0.25 | 0.24 | Naval Research Laboratory* |
| | 0.5 | 0.48 | |
| | 1 | 0.96 | |
| | 2 | 1.92 | |
| | 3 | 2.89 | |
| | 1 | 0.96 | Norton NC132 |
| | 1 | 0.96 | Ceradyne, Ceralloy 147 |
| | 5 | 4.81 | |
| $ZrO_2$ | 2 | 1.19 | Naval Research Laboratory* |
| | 4 | 2.40 | |
| | 8 | 4.88 | |
| | 12 | 7.45 | |
| | 16 | 10.10 | |
| $Y_2O_3$ | 5 | 3.49 | Ceradyne, Ceralloy 147 |
| | 10 | 7.09 | |
| | 15 | 10.81 | |
| | 8 | 5.63 | Norton NCX34 |
| | 13 | 9.31 | Norton NC136 |

*Hot-pressed using AME 85 $Si_3N_4$ powder.

travel rate of 1.27 mm $min^{-1}$ under room conditions, i.e. 22° C and 50% relative humidity. The oxidized surfaces were ground off some oxidized bars to test any effects of oxidation on the room-temperature strength of the bulk material. After strength tests, fracture surfaces were examined in a scanning electron microscope (SEM) to determine the origins of failure. An energy dispersive X-ray analyser (EDAX) in the SEM was used to examine fracture surfaces and qualitatively evaluate changes in concentration of additives as a function of depth below the oxidized surfaces.

## 3. Results and discussion

In general, strength of unoxidized, i.e. as-180-grit ground, bars were about 800 MPa, whether they were made with MgO, $Y_2O_3$ or $ZrO_2$ as additives. There was no significant dependence on the amount of additive present. However, the strength of all compositions could be raised considerably by using finer surface finishing, e.g. with 600-grit ground, strengths of 1000 MPa have been reported [9]. Fractographic examinations [9–11] showed that fracture origins of bars in the lower portion of the above strength range were predominately from flaws introduced by grinding. On the other hand, fracture origins of bars in the upper portion of this strength range were from either machining flaws or processing related flaws.

Overall, the most significant effect of oxidation on strength was the large 30 to 60% reduction from the unoxidized strengths for almost all compositions (Figs 1 to 3). One important exception was essentially no loss of strength in the body with 8 wt% $Y_2O_3$. Within this range of 30 to 60% of the oxidized strengths, two trends seem worthy of note. First, for MgO additions, commercial bodies with about 1% MgO retained one of the higher fractions of unoxidized strength but most other compositions with MgO suffered some of the greatest reductions in strength. Second, all compositions showed lower oxidized strengths at higher

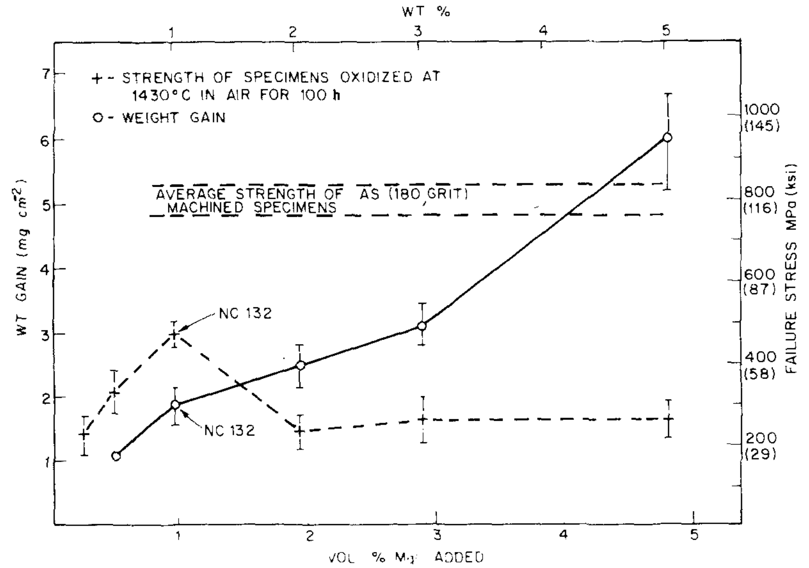

*Figure 1* Strength and weight gain of MgO added $Si_3N_4$ as a function of concentration of MgO. Note the monotonous increase of weight gain.

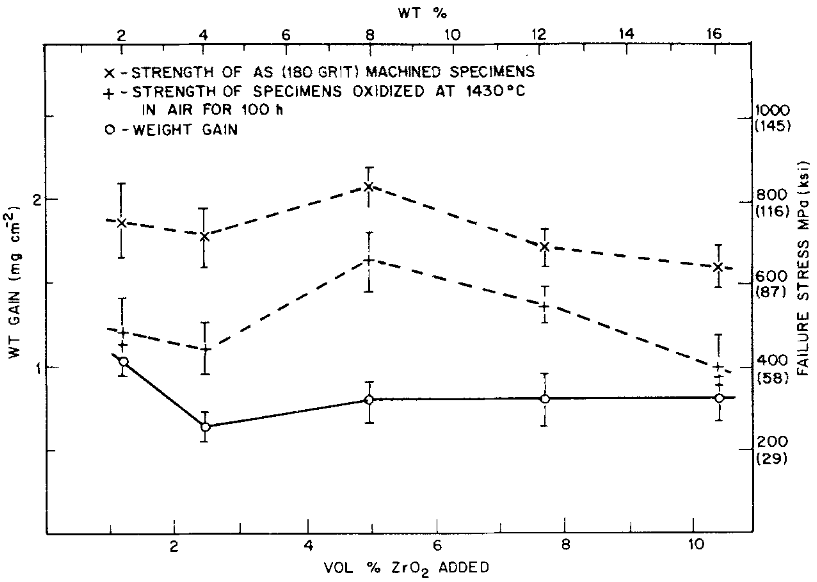

*Figure 2* Strength and weight gain of $ZrO_2$ added $Si_3N_4$ as a function of concentration of $ZrO_2$. The weight gain remained essentially constant over the range of concentration investigated.

additive contents than at most lower additive contents.

The behaviour of CVD $Si_3N_4$ was in marked contrast to this. Although strengths were low (170 MPa), due to the large (~ 20 $\mu$m) grain size, oxidation did not decrease strengths. In fact, strengths after oxidation increased, e.g. by about 10%.

Fractographic examination of oxidized specimens after strength testing showed that the sources of failure were typically oxidation pits in the surface of all bars with oxide additions, but not CVD $Si_3N_4$. This corroborates previous findings [12] for bodies made with MgO, and shows that pit formation is also the basic mechanism of strength degradation in $Si_3N_4$ hot pressed with $ZrO_2$ or $Y_2O_3$ additions (Fig. 4). Strengths generally correlated with pit size. Thus, for MgO materials, pits as large as about 1 mm have been observed.

Removal of the oxide layer and the oxidation pits by grinding resulted in the same strengths as in unoxidized specimens. Thus oxidation did not change the room-temperature strength or fracture

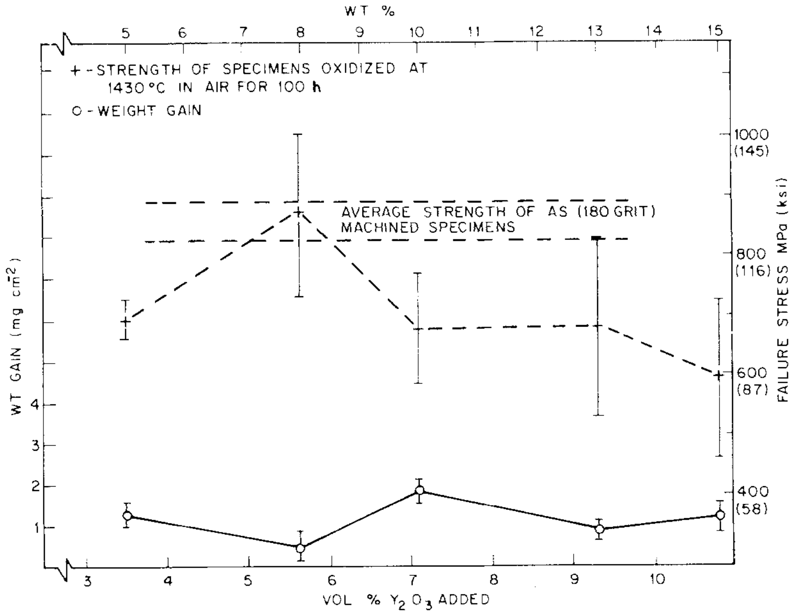

*Figure 3* Strength and weight gain of $Y_2O_3$-added $Si_3N_4$ as a function of concentration of $Y_2O_3$. The weight gain is about constant over the entire range of concentration studied.

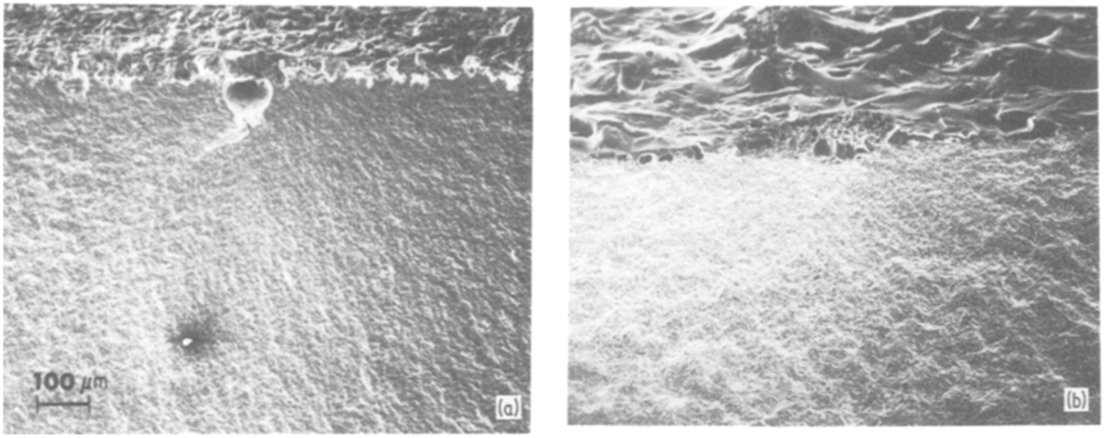

*Figure 4* Strength degradation in hot-pressed $Si_3N_4$ due entirely to the formation of oxidation pits upon prolonged exposure at high temperature in air: (a) NC132, and (b) Ceralloy 147. Note the difference in the sizes of pits.

toughness of the bulk material, even though there are bulk compositional changes [7].

It has been suggested [13] that pit formation in NC132 is related to W impurities introduced by milling $Si_3N_4$ powders with WC mills and media, or the latter alone. In this study, different batches of $Si_3N_4$ specimens with 3 wt% MgO additions were milled in plastic containers with WC, $ZrO_2$ or $Al_2O_3$ media. Upon oxidation, bars from these three bodies showed no difference in average flexural strength, weight gain or size and distribution of oxidation pits. Thus, mechanisms other than reactions with W impurities must be sought for the mechanism of the formation of strength degrading pits. Also, since pits formed in bodies with $ZrO_2$ or $Y_2O_3$ additions, the mechanisms cannot be tied to one particular additive.

On the other hand, since no pits formed in CVD $Si_3N_4$ bodies, pit formation may be dependent on the additives. Consideration of additive vaporization suggests correlations with the rate of pit formation; i.e. slower in $ZrO_2$ and $Y_2O_3$ against MgO containing bodies. At 1430° C, MgO already has an appreciable ($\sim 1.5 \times 10^{-6}$ atm) vapour pressure. (Resultant depletion of MgO from the oxidizing surface should enhance diffusion of Mg from the interior toward the outside surface, creating a Mg gradient in the specimen. Such a Mg gradient was observed by EDAX, corroborating the suggested MgO vaporization.) Although the vapour pressure of $ZrO_2$ is not available for these temperatures, the fact that the temperature of appreciable volatility for $ZrO_2$ ($< 2300°$ C) is much higher than MgO ($\sim 1600°$ C) indicates that $ZrO_2$ would have much less vapour pressure than MgO at 1430° C. A similar argument is expected to be true for $Y_2O_3$ since Wygant and Kingery [14] have indicated higher stability for $Y_2O_3$ than either $ZrO_2$ or MgO. Thus, the rate of pit growth and strength degradation appear to vary directly with vaporization of the additive. Clearly, much or all of the additives do not retain their identity but react to form various compounds. However, many of these compounds may vaporize incongruently and thus there may be a correlation between their vaporization and that of a major constituent such as MgO.

The weight change per unit surface area due to the oxidation is shown as a function of the amount of additives in Figs 1, 2 and 3, respectively, for MgO, $ZrO_2$ and $Y_2O_3$ additives. Note that while the weight gain of bodies with $ZrO_2$ or $Y_2O_3$ additions was relatively low ($\sim 1$ mg cm$^{-2}$ or less) and essentially independent of the amount of additive, the weight gain of bodies made with MgO additions increased with the amount of MgO used. In contrast to this, for CVD $Si_3N_4$, the weight gain is significantly lower ($\sim 0.15$ mg cm$^{-2}$).

Oxidation removed all traces of the original grinding marks, but left different surface morphologies and oxide layer thicknesses depending on the additive. For MgO materials (Fig. 5a), there was always a white porous coating. The porosity of the oxidized layer, i.e. a significant amount of homogeneous porosity, with many of the pores being fine, is consistent with the correlation with the high vapour pressure of MgO at these temperatures, as discussed above. The thick-

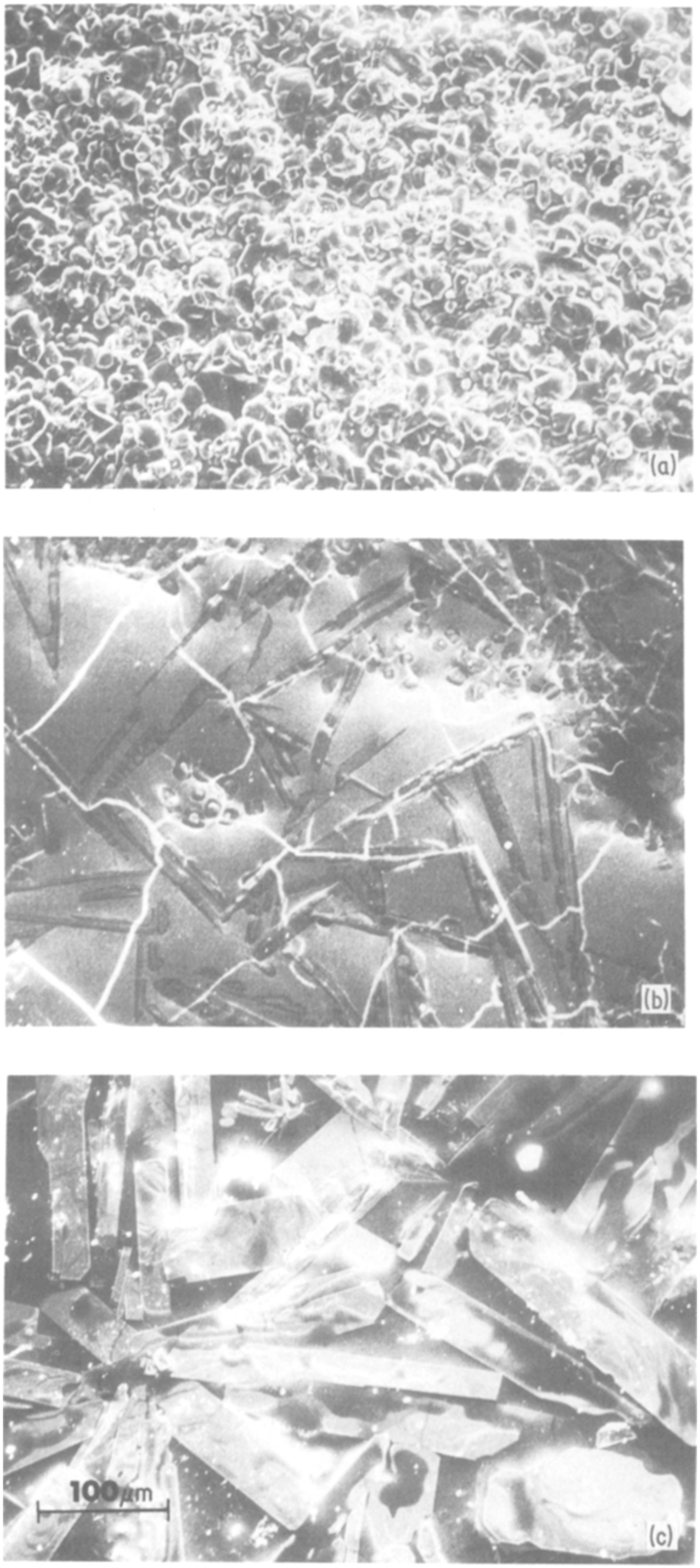

*Figure 5* Surface appearance of oxidized $Si_3N_4$ with various additives: (a) MgO, (b) $ZrO_2$, and (c) $Y_2O_3$.

ness of this layer showed a similar increase with MgO content as the weight gain data showed. On the other hand, thin glassy-like coatings were observed in materials with $ZrO_2$ and $Y_2O_3$ additions (see Fig. 5b and c). Under the SEM, distinctly different surface features were seen for each kind of material. While bodies with MgO additives were covered with nodules, those with ZrO additives have needle-like structures embedded in the glassy coating and platelets were seen in the coating of $Y_2O_3$-added bodies. Cracks were also observed in the glassy layers near the interface with the bulk material. Presumably these cracks formed after oxidation, during cooling to room temperature and have not been observed to extend into the bulk bodies. Hence, they do not contribute to the degradation of the strength of materials.

## 4. Summary

The oxidation and resultant strength behaviour of $Si_3N_4$ bodies hot-pressed with various additives showed definite dependences on the additives. White porous layers were formed on bodies with MgO additions, with both the weight gain and the thickness of the layers increasing with MgO additive level. On the other hand, the continuous glassy layers formed on $ZrO_2$ or $Y_2O_3$ additive materials seemed to remain constant regardless of the amount of additive. CVD $Si_3N_4$ showed the least weight gain.

Strength degradation was often 30 to 60% and generally was greatest for higher levels of oxide additions. However, important exceptions were commercial compositions containing about 1 wt% MgO and 8 wt% $Y_2O_3$, the latter showing very limited strength degradation. Strength degradation that occurred was due to the formation of oxidation pits. The sizes of pits were largest in most MgO additive bodies and hence they suffered the most severe strength loss. On the other hand, CVD $Si_3N_4$ actually increased in strength upon oxidation. Resurfacing of the oxidized materials results in the same strength as before oxidation showing no bulk changes in strength due to oxidation.

While the formation of oxidation pits is not completely understood, the presence of W impurities is not a general cause, but a trend for larger pit formation with increasing oxide vapour pressure; i.e. in order $Y_2O_3$, $ZrO_2$ and MgO was indicated.

## References

1. F. F. LANGE, *J. Amer. Ceram. Soc.* **61** (1978) 53.
2. J. A. PALM and C. D. GRESKOVITCH, *Amer. Ceram. Soc. Bull.* 59 (1980) 447.
3. W. C. TRIPP and H. C. GRAHAM, *J. Amer. Ceram. Soc.* **59** (1976) 399.
4. S. C. SINGHAL, *J. Mater. Sci.* **11** (1976) 500.
5. D. CUBICCIOTTO, K. H. LAU and R. L. JONES, *J. Electrochem. Soc.* **124** (1977) 1955.
6. D. CUBICCIOTTI and K. H. LAU, *J. Electrochem. Soc.* **126** (1979) 1723.
7. W. J. McDONOUGH, C. CM. WU and P. E. D. MORGAN, *J. Amer. Ceram. Soc.* **63** (1981) C-45.
8. R. A. TANZILLI; J. J. GEBHART, J. D'ANDREA, C. DULKA, J. HANSON and R. KREITZ, General Electric technical report No. 79SDR2324, "Processing Research on Chemically Vapour Deposited Silicon Nitride," Dec. 1979.
9. C. CM. WU and K. R. McKINNEY, in "*The Sciences of Ceramic Machining and Surface Finishing, II,*" NBS special publication 562 (National Bureau of Standards, Washington DC, 1979) p. 477.
10. S. W. FREIMAN, A. WILLIAMS, J. J. MECHOLSKY and R. W. RICE in "Ceramic Microstructure '76" edited by R. M. Fulrath and J. A. Pask (Westview Press, Boulder, Colorado, 1977) p. 824.
11. R. W. RICE, S. W. FREIMAN, J. J. MECHOLSKY, R. RUH and Y. HARADA, in "Ceramics for High Performance Applications, II" edited by J. J. Burke, E. N. Lenoe and R. N. Katz (Metals and Ceramics Information Center, 1978) p. 669.
12. S. W. FREIMAN, C. CM. WU, K. R. McKINNEY and W. J. McDONOUGH, Metals and Ceramics Information Center Report Proceedings of the 1977 Defense Advance Research Project Agency/Navy Sea System Command Programme Review, edited by J. W. Fairbanks and R. W. Rice (Battele Columbus Laboratories, Columbus, Ohio, 1978) p. 655.
13. N. TIGHE, *Ceram. Bull.* 57 (1978) 320.
14. J. F. WYGANT and W. D. KINGERY, *ibid.* **31** (1952) 251.

Received 15 July 1980 and accepted 27 April 1981.