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Stengthening of polyphase Si_3N_4 materials through oxidation

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Specimens of various polyphase Si_3N_4 materials fabricated in the Si–Mg–O–N system, and a commercial Si_3N_4 material were subjected to oxidation treatments prior to flexural strength determinations at 1400° C. It was demonstrated that a pre-oxidation treatment could significantly improve the high-temperature strength. The compositional change induced by oxidation which can decrease the volume fraction of the viscous phase present in these materials at high temperatures is believed to be responsible for the observed strengthening.

1. Introduction

The continuous glassy intergranular phase that exists in most (if not all) polycrystalline Si_3N_4 materials plays an important role in both oxidation and mechanical property phenomena [1]. At high temperatures, this intergranular phase becomes viscous and both a path for fast diffusion [2] and a source of stress-induced cavitation. Oxidation phenomena take advantage of this continuous viscous phase for inward and outward diffusion of oxidation reactants and products [2]. The viscous phase is also responsible for mechanical property degradation at high temperatures. Under stress, it is a path for material rearrangement (diffusional creep) [3]. The propensity of the viscous phase to cavitate under stress is responsible for the slow-crack growth phenomena exhibited by polyphase Si_3N_4 at high temperatures [4], and this is also responsible for its strength degradation.

Previous investigations have shown that oxidation resistance [2, 5] creep resistance [3] and high-temperature strength [5] of polyphase Si_3N_4 frabricated in the Si–Mg–O–N system depend on its composition. All three of these properties decrease as the material's composition moves closer to the eutectic composition in the Si_3N_4–Si_2N_2O–Mg_2SiO_4 compatibility triangle [6]. These observations strongly suggest that the volume fraction of the glassy intergranular phase, which governs diffusional flux and cavitational propensity, is determined by the lever rule developed for determining phase content from phase diagrams. That is, the composition of the glassy phase is similar to the eutectic composition (i.e. the last liquid to solidify after fabrication) and its volume content depends on the bulk composition relative to the eutectic composition. Thus, within the limits of the compositions studied, the volume fraction of the glassy intergranular phase appears to increase as the bulk composition moves closer to the eutectic composition.

Discovery that the creep resistance of several different polyphase Si_3N_4 materials could be improved by a pre-oxidation treatment [7, 8] was our first indication that the high-temperature strength may also be improved by the same treatment. During this same period, results of oxidation studies [2] had shown that compositional change is not only exhibited by the formation of a silicate surface scale, but also by a gradient of both the additive cation and the crystalline phases from the surface to the interior. As detailed elsewhere [2], the additive cation and cation impurities that reside in the glassy intergranular phase diffuse to the surface in an attempt to equilibrate the glass composition with the SiO_2 formed by the oxidation of Si_3N_4. This outward diffusion forms a gradient of depleted additive (and impurity) cation(s). Oxygen, in the glassy phase originally

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Figure 1 Oxidized cross-section of a specimen previously oxidized at 1400° C/300 h. White film on parameter is the initial oxide scale. White centre is produced by a thin oxide scale formed on the less resistant composition. Darker zone illustrates the depth of compositional change which is more resistant to oxidation (specimen thickness = 0.3 cm).

associated with the outward diffusing cation(s), is left behind to react with Si_3N_4 to form Si_2N_2O. The volume fraction of the glassy phase is thus reduced by the loss of both the outward moving cation(s) and the oxygen which reacts to form Si_2N_2O.* Thus, the glassy intergranular phase is a fugitive of the oxidation process.

The compositional gradient produced by oxidation can best be visualized by the following demonstration. Oxidize a polyphase Si_3N_4 specimen for a period sufficient to form a relatively thick surface scale. Section the specimen and re-expose the freshly cut surface to a much shorter oxidation period. Upon examination, the sectioned surface will reveal the compositional gradient due to the greater oxidation resistance (and thus thinner scale) of the cation depleted zone. An example is shown in Fig. 1 (initial composition (mole fractions): 0.755 Si_3N_4, 0.120 SiO_2, 0.125 MgO; oxidized for 300 h at 1400° C in air, sectioned and re-oxidized for 0.5 h at 1400° C). Quantitative microchemical and X-ray analysis of this same cross-section as presented elsewhere [2] also shows that the compositional change produced by oxidation extends to the centre of this specimen.

It was therefore concluded that since the detrimental glass phase can be a fugitive of the oxidation process, oxidation could improve the high temperature mechanical properties as first discovered during creep experiments and as it will now be demonstrated through strength measurements.

2. Experimental procedure

The object of this study was to determine the effect of a pre-oxidation treatment on the high-temperature strength of polyphase Si_3N_4. Materials fabricated in the Si–Mg–O–N system were chosen for this study. Since prolonged oxidation is known to produce surface pits in these materials [9, 10] which introduce a detrimental, new flaw population, pre-oxidized specimens were reground to remove the surface pits prior to strength determinations.

The first group of bar specimens examined were diamond cut and ground from 19 different materials which form three series of compositions previously investigated at high temperatures in studies concerning strength [5], creep [3], and oxidation resistance [2]. Materials in each series contained a fixed mole fraction of Si_3N_4 (either 0.91, 0.833 or 0.755) and a given MgO/SiO_2 molar ratio that could range between 0.1 and 11. Fabrication details have been presented elsewhere [5]. All 19 specimens were placed on a reaction-bonded Si_3N_4 setter with raised knife-edge contacts and oxidized together in air at 1400° C for 300 h. The specimens were weighed before and after oxidation, each specimen was separately surface ground until surface pits, formed to various depths on the different materials, were no longer observed by visual inspection with a binocular microscope.

The second group of specimens were cut from a large billet of commercial, hot-pressed Si_3N_4 (NC 132) obtained recently from the Norton Company, which is also fabricated in the Si–Mg–O–N system. This group was separated into different sets. Flexural strength measurements were made at room temperature and 1400° C without a pre-oxidation treatment. The other sets were subjected to oxidation in air at either 1400 or 1500° C for various periods prior to regrinding and strength determinations at either room temperature or 1400° C. The amount of material removed by reginding was dependent on the depth of the surface pits formed during oxidation as discussed above.

All flexural testing was performed on bar specimens (approximate dimensions of 0.3 cm × 0.6 cm × 3.2 cm) using a four-point loading device with inner and outer spans of 1.27 and 2.54 cm,

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*Equilibrium considerations require that the viscous phase maintain its original composition. That is, a portion of the SiO_2 in the viscous phase reacts with the Si_3N_4 to produce Si_2N_2O.

TABLE I Oxidation and strength data for Si–Mg–O–N compositions oxidized at 1400° C/300 h

Initial composition (mole fraction)			MgO/SiO_2 molar ratio	Weight change ($mg\,cm^{-2}$)	Flexural strength (MPa)	Prior flexural strength (MPa)	Change (%)
Si_3N_4	MgO	SiO_2					
0.910	0.020	0.070	0.29	0.93	482	343	+ 40
0.910	0.030	0.060	0.50	1.36	534	339	+ 57
0.910	0.040	0.050	0.80	1.74	445	307	+ 45
0.910	0.055	0.035	1.57	1.78	327	183	+ 79
0.910	0.065	0.025	2.60	2.39	500	269	+ 86
0.833	0.015	0.152	0.10	0.21	452	287	+ 58
0.833	0.030	0.137	0.22	1.40	420	352	+ 19
0.833	0.040	0.127	0.31	2.09	319	341	− 7
0.833	0.052	0.110	0.47	2.02	452	334	+ 35
0.833	0.085	0.082	1.04	3.34	377	211	+ 79
0.833	0.120	0.047	2.55	5.31	350	280	+ 25
0.833	0.144	0.023	6.26	4.72	411	476	− 14
0.755	0.020	0.225	0.09	0.93	405	225	+ 80
0.755	0.055	0.190	0.29	1.92	455	269	+ 69
0.755	0.085	0.160	0.53	3.18	449	279	+ 61
0.755	0.125	0.120	1.04	4.30	338	199	+ 70
0.755	0.155	0.090	1.72	4.41	510	193	+ 164
0.755	0.190	0.055	3.45	4.47	500	414	+ 21
0.755	0.225	0.020	11.25	5.94	324	408	− 16

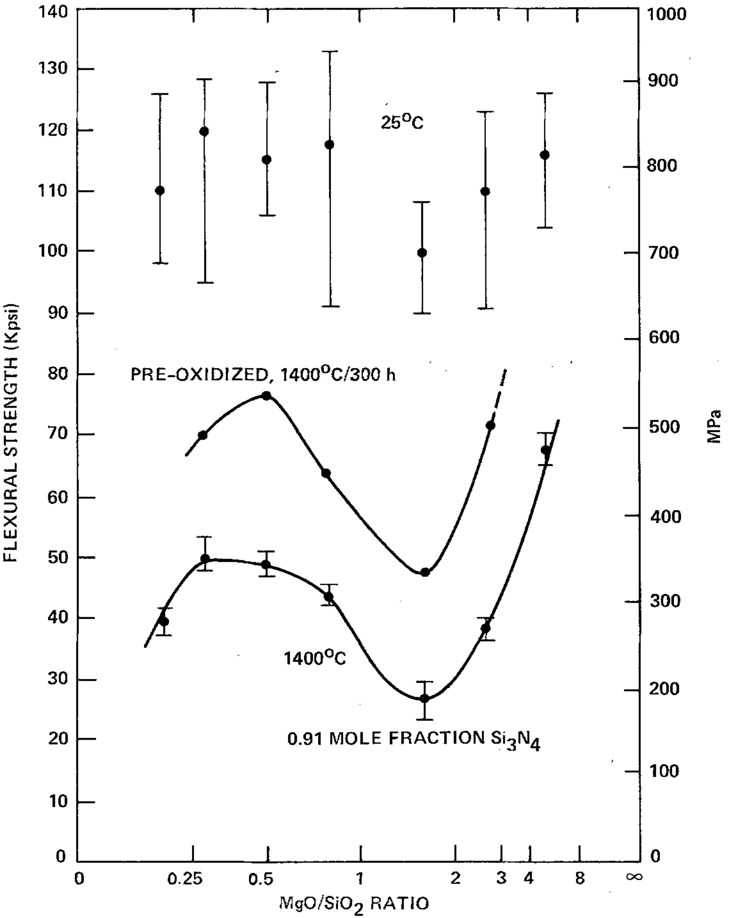

Figure 2 Flexural strength data for the series containing 0.91 mole fraction Si_3N_4 fabricated with different MgO/SiO_2 molar ratios. Data include the 5 specimens subjected to a 1400° C/300 h pre-oxidation treatment.

respectively and a crosshead speed of 0.05 cm min^{-1}. X-ray diffraction analysis was used to determine the crystalline phase content of the surfaces of the unoxidized and oxidized, reground specimen. The intensity ratio of (1 1 1) Si_2N_2O and (2 0 0) Si_3N_4 diffraction peaks determined by an area analysis was used to report compositional changes.

3. Results

3.1. Compositions with various MgO/SiO_2 ratios

Table I lists the specimens, their initial compositions, their weight gain during oxidation per unit area, and their flexural strengths (1400° C in air) after the 1400° C/300 h oxidation treatment. The second from last column lists the per cent change in strength due to the pre-oxidation treatment. Fig. 2 illustrates, for comparative purposes, the strength data (room temperature, 1400° C, and pre-oxidized, 1400° C) for the series containing 0.91 mole fraction Si_3N_4.

Both Table I and Fig. 2 illustrate that a pre-oxidation treatment can significantly improve the high-temperature strength of polyphase Si_3N_4 materials. Within each series, the largest increase occurs for compositions with a MgO/SiO_2 molar ratio between 1 and 3. Also, compositions with $MgO/SiO_2 > 4$ exhibit a strength decrease after oxidation.

Flexural strength calculations assumed an elastic stress–strain behaviour. Data obtained previously for unoxidized specimens tested at 1400° C with an MgO/SiO_2 ratio ranging between 1 to 3 exhibited a nonelastic behaviour upon stressing to failure, indicative of lower strengths than reported in Table I and Fig. 2. On the other hand, all pre-oxidized specimens did exhibit an elastic stress–strain response to failure. Thus, the strength difference for compositions within this range of MgO/SiO_2 ratios is even greater than that reported in Table I.

Fig. 3 shows the Si_2N_2O/Si_3N_4 ratio determined on ground surfaces of both unoxidzed (1400° C/300 h) specimens. This ratio is plotted as a function of the initial MgO/SiO_2 molar ratio. Data for the unoxidized specimens are representative of the material's bulk. But because oxidation produces a gradient in the Si_2N_2O/Si_3N_4 ratio [2], data for specimens subjected to oxidation are only representative of the depth for which material was removed by grinding to eliminate surface pits. Although data for the oxidized specimens are not representative of its bulk, it does show that compositional changes as outlined in the introduction did take place, i.e. the average bulk composition decreases its MgO/SiO_2 ratio shifts toward the Si_3N_4–Si_2N_2O tie line. Note that the larger changes occur for materials with an initial MgO/SiO_2 molar ratio between 0.5 and 3.0.

3.2. Commercial Si_3N_4 material

Table II lists the oxidation treatments for the specimens of NC 132. As shown, most of the specimens were subjected to various periods of oxidation at 1400° C prior to regrinding and strength testing. After it was discovered that excessive periods (> 500 h) at 1400° C were required to achieve modest strength gains at high temperatures, the remaining specimens were oxidized at 1500° C. As indicated in Table II, significant strengthening can be achieved by a pre-oxidation treatment at 1500° C. It was also demonstrated that such a treatment did not impair the room temperature strength. A detailed description of these results now follows.

Flexural strength measurements of unoxidized specimens at 25 and 1400° C resulted in an average strength of 878 and 282 MPa, respectively. The load-deflection response of these specimens at 1400° C was nonlinear indicating extensive creep during strength testing. Although the strength of these specimens at 1400° C is listed as 282 MPa, the authors recognize that the material's true strength could be significantly lower due to the extensive creep and the use of an elastic solution to calculate strength [11]. In addition, the area of subcritical crack growth could easily be distinguished as previously reported [12], i.e. the fracture area traversed by the slowly moving crack can be distinguished by the rougher topography caused by extensive cavitation.

Short periods of oxidation (50 h) prior to strength testing resulted in a nearly linear load-deflection response. After a pre-oxidation period of 100 h, the load-deflection response was linear to fracture. Judging the first results obtained on the materials fabricated by the authors, high-temperature strengthening was expected for oxidation periods of ~ 300 h at 1400° C. But contrary to this expectation, modest strengthening was not observed until the oxidation period at 1400° C was increased to 548 h. It then became obvious that significant strengthening could be

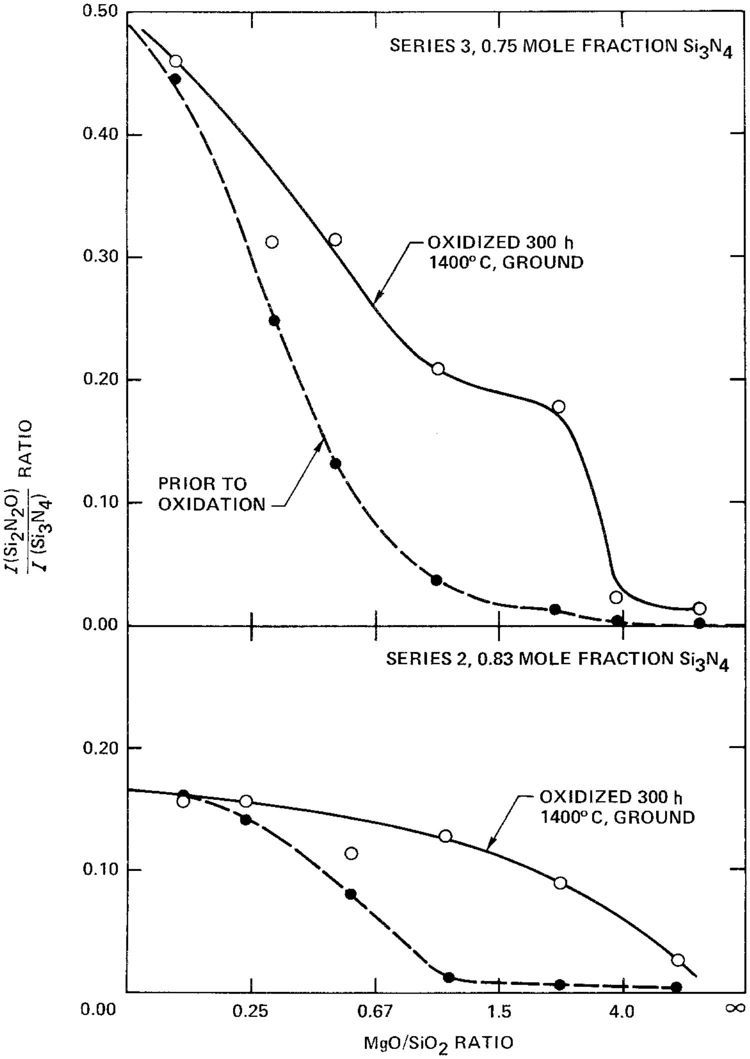

Figure 3 Ratio of X-ray diffraction intensities of Si_2N_2O and Si_3N_4 prior to and after the 1400° C/300 h pre-oxidation treatment as plotted against the initial MgO/SiO_2 molar ratio.

TABLE II Flexural strength results for commercial Si_3N_4

Oxidation treatment		Test temperature (° C)	Number	Weight gain/area (mg cm^{-2})	Depth removed (cm)	Average strength (MPa)	Weight parameters	
Temperature (° C)	Time (h)						m	σ_0 (MPa)
None	None	25	7	–	–	878	8	924
None	None	1400	8	–	–	282	(± 4%)†	
1400	50	1400	3	1.61	0.015	254	(± 4%)	
1400	100	1400	3	2.13	0.020	256	(± 7%)	
1400	256	1400	4	–	–	288	(± 8%)	
1400	332	25	8	2.39	0.020	982	15	1014
1400	332	1400	8	2.39	0.020	280	24	286
1400	548	1400	3	–*	0.020	376	(± 5%)	
1500	206	25	7	–*	0.050	805	11	834
1500	206	1400	7	–*	0.050	482	17	496
1500	306	1400	5	–*	0.050	571	(± 3%)	

*Scale flaked off during oxidation.

†Numbers in brackets denote per cent difference of either maximum or minimum strength values from the average.

achieved within a more reasonable period by increasing the oxidation kinetics by increasing the oxidation temperature. It was thus demonstrated that a pre-oxidation treatment of 300 h at 1500° C could raise the 1400° C strength of NC 132 from < 30% to 70% of its room temperature value. It is expected that longer periods at 1500° C or higher temperatures will result in further strengthening.

Another objective was to determine if the pre-oxidation treatment might influence the lower temperature strengths. As indicated in Table II, room temperature strength measurements were obtained with reground specimens after oxidation treatments of 1400° C/332 h and 1500° C/206 h. Data obtained after the 1400° C/332 h treatment indicates a modest strengthening (~ 12%), and as shown in Fig. 4, a narrower strength distribution. As shown in Fig. 4, the 1500° C/206 h treatment resulted in a strength distribution similar to that obtained at room temperature for specimens that were not subjected to a pre-oxidation treatment.

Fig. 4 also reports the Weibull strength statistics of the high-temperature data where a linear load-deflection response was observed. Table II reports the two Weibull parameters for these data. As indicated, minimal strength scatter is observed for all high-temperature results. This is indicative of slow-crack growth as first pointed out by Charles [13]. It should be noted that although slow-crack growth was prevalent at high temperatures, the fracture surface did not reveal any topographical difference between the slow and fast crack growth regions.

Attempts were made to obtain oxidation kinetics through weight change measurements. As shown in Table II, data was limited to the shorter periods at 1400° C. The oxide scale flaked off at longer periods and during the 1500° C treatments. Table II also shows that the surface pits were deeper for longer oxidation periods or higher temperatures. One oxidized specimen (1400° C/332 h) tested at 1400° C without regrinding resulted in a strength of 165 MPa. This much lower strength was due to fracture initiating at a deep surface pit.

The X-ray diffraction analysis results obtained from the ground surfaces of specimens subjected to various oxidizing treatments are shown in Fig. 5. Conversion of the Si_2N_2O/Si_3N_4 intensity ratio to weight per cent Si_2N_2O was carried out according to the calibrated method described by Mencik and Short [14]. This analysis, as used here, assumed no other phase present other than either Si_2N_2O or Si_3N_4. As shown in Fig. 5, the Si_2N_2O content increases rapidly for short periods of oxidation at 1400° C and then levels off at longer periods. Oxidation at 1500° C promotes a greater compositional change.

4. Discussion

As detailed above, the high-temperature strength of polyphase Si_3N_4 materials can be significantly

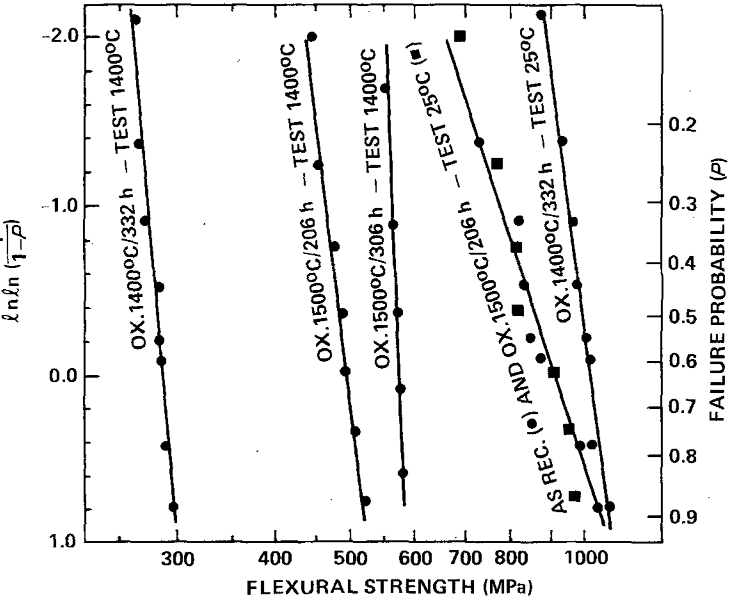

Figure 4 Statistics for the flexural strength data of NC132 Si_3N_4 material subjected to different pre-oxidation treatments.

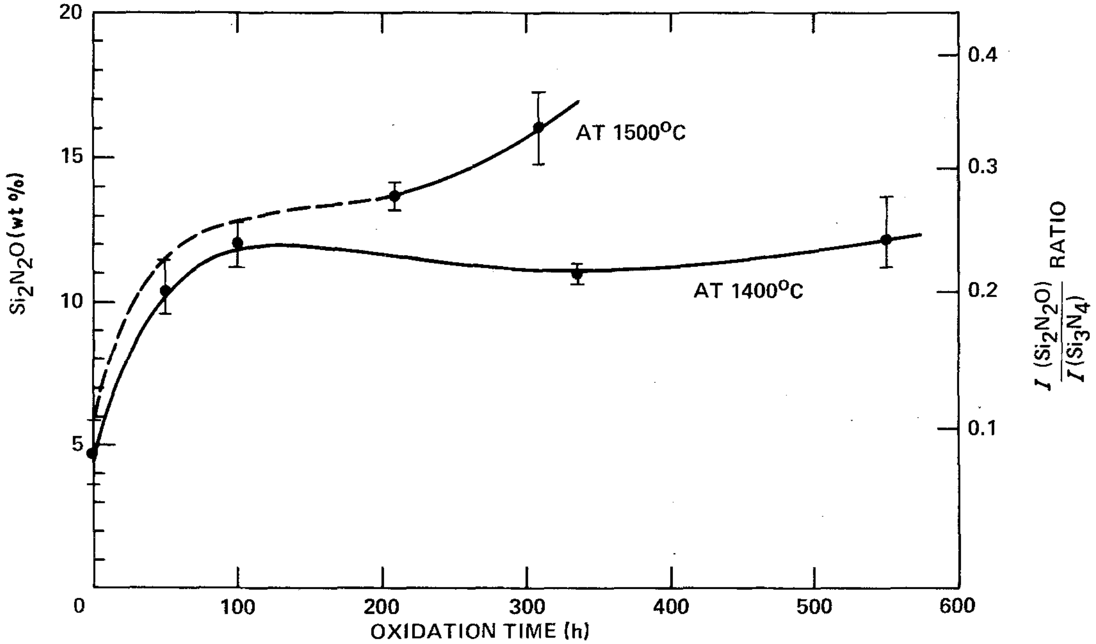

Figure 5 Si_2N_2O content of NC 132 reground surfaces subjected to pre-oxidation treatments at 1400 and 1500° C as a function of treatment period.

improved by an oxidation treatment. For the system chosen for examination here, which develops surface pits during oxidation due to localized surface reactions with iron-type inclusions [10], surface regrinding is necessary to realize these strength improvements. It is expected that for other material systems that do not exhibit surface pitting (e.g. materials in the Si_3N_4–Si_2N_2O–$Y_2Si_2O_7$ system), regrinding may not be necessary.

The strength improvements can be related to the compositional changes induced by oxidation. Oxidation shifts the average bulk composition toward Si_2N_2O. This compositional shift changes the volume content of the liquid in equilibrium with the crystalline phases. Most of the materials studied here had initial compositions within the Si_3N_4–Si_2N_2O–Mg_2SiO_4 compatibility triangle, which contains the lowest melting eutectic of the two compatibility triangles in which Si_3N_4 is an equilibrium phase [6]. For these materials any compositional shift toward the Si_3N_4–Si_2N_2O tie line will decrease the volume content of the eutectic melt and thus result in a strengthening. On the other hand, for compositions in the Si_3N_4–Mg_2SiO_4–MgO compatibility triangle ($MgO/SiO_2 > 2$), a small compositional shift toward the Si_3N_4–Si_2N_2O tie line would move the composition into the Si_3N_4–Si_2N_2O–Mg_2SiO_4 compatibility triangle to increase the volume fraction of the eutectic melt (and therefore the residual glass phase) and thus result in a strength decrease. This is observed for the two materials in series 2 and 3 (Table I) with the highest intial MgO/SiO_2 ratios. Further oxidation resulting in a greater compositional shift should produce a strengthening for these two materials.

The extent of the oxidation required to produce a desired strengthening will depend on the material's initial composition, which controls its initial oxidation kinetics [5], and on temperature, which also controls oxidation kinetics. Impurities must also be included in considering the material's composition. Impurities not only help govern the eutectic composition, its melting temperature and its volume fraction, but they can also diffuse to the surface during oxidation [2]. Thus a specific oxidation treatment scheduled, cannot be presently recommended for an arbitrary composition without analytical relations between oxidation kinetics, compositional change and residual glass phase contents.

The question of to what depth from the surface an oxidation treatment can produce the compositional change required for significant strengthening has not been answered here. Previous experiments [2] involving quantitative compositional measurements show that for specimens of the size used here (~ 0.3 cm thick), a significant compositional change does occur at the centre of the specimen after ~300h at 1400° C. For the specimens treated here, the thickness was reduced by 15 to 35% by surface grinding. Judging from the compositional profiles obtained from the previous studies, it appears that much of the steep portion of the compositional gradient was removed. This suggests that the compositional changes reported in Figs. 3 and 5 are nearly representative of the specimen's centre.

Another interesting result was the slight strengthening obtained at room temperature after the 1400° C/332h treatment. Oxidation reactions produce both molar volume changes and compositional gradients. Either one or both of these phenomena will produce residual surface stresses as detailed experimentally in the Appendix. The reaction $2Si_3N_4 + 1.5\ O_2 \rightarrow 3Si_2N_2O + N_2$ results in a molar volume increase of ~20%. Although most of the compressive stresses produced by this volume increase are expected to relax during oxidation, some remain to produce the apparent room temperature strengthening observed after the 1400° C/332h treatment.

In conclusion, it has been shown that a pre-oxidation treatment can significantly increase the high-temperature mechanical properties of dense, polyphase Si_3N_4 without affecting their low-temperature strength. Oxidation resistance is also significantly improved by this treatment. This observation suggests that Si_3N_4 compositions that can easily be sintered because of a large amount of a liquid phase, but have poor high-temperature properties, can be improved by a post-fabrication oxidation treatment.

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Appendix: Surface compressive stresses arising during oxidation of Si_3N_4

As documented elsewhere [15], the compressive surface stresses which arise due to molar volume changes accompaning oxidation can be qualitatively assessed by measuring the apparent critical stress intensity factor with an indentation technique. The apparent critical stress intensity factor (K_a) is proportional to the magnitude of the compressive surface stress and the depth to which this stress extends into the material.

Polished specimens of a Si_3N_4 material (0.833 Si_3N_4, $MgO/SiO_2 = 2.55$) were oxidized for different periods at 1400° C. The friable outer scale was removed by light sand-blasting. Indentations were made (20 kg) at room temperature to obtain K_a of the sub-scale surface material. The results illustrated in Fig. A1 show that compressive

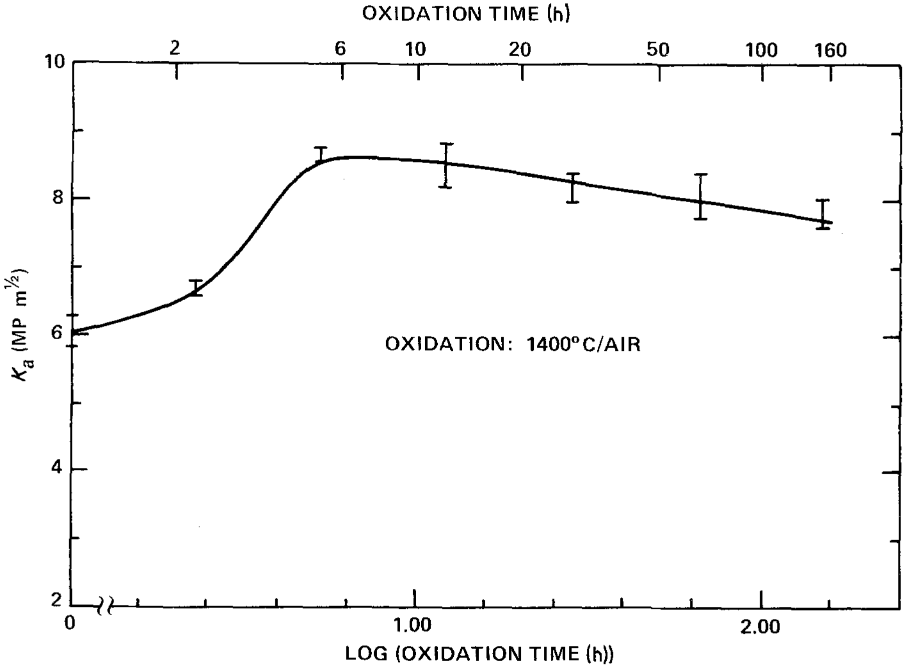

Figure A1 Apparent critical stress intensity factor against oxidation period at 1400° C.

stresses do arise during oxidation, namely, within a period of ~ 5 h, K_a increases from 6 to 8.7 MPa m$^{1/2}$. As oxidation proceeds beyond 5 h, K_a decreases from its maximum value consistent with the observation (see text) that the compositional gradient (one factor that governs the magnitude of the compressive stress) decreases with increasing oxidation time.

It can be concluded that compressive stresses do develop in the sub-scale material due to oxidation. One might suspect that the large molar volume increase (21.5%) due to the oxidation of Si_3N_4 to Si_2N_2O could be responsible for these compressive surface stresses, most of which are relieved by creep during oxidation. Since the thermal expansion of Si_2N_2O (the predominant sub-scale phase) is greater than that of Si_3N_4, one could rule out thermal expansion mismatch as a cause for the compressive surface stresses.

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