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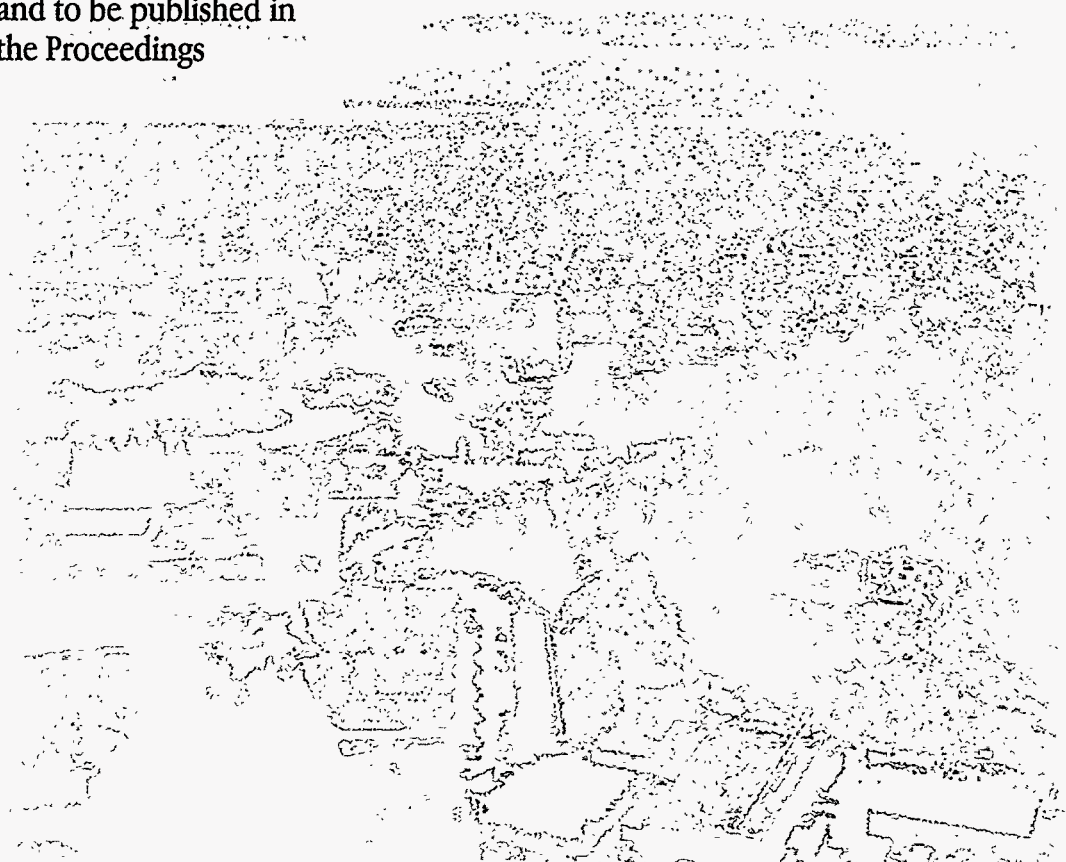
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**Indentation and Oxidation
Studies on Silicon Nitride Joints**

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Materials Sciences Division

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**INDENTATION AND OXIDATION STUDIES ON
SILICON NITRIDE JOINTS**

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ABSTRACT

Silicon nitride ceramics have been joined with a yttrium oxide - silicon dioxide interlayer. A 1:2 molar ratio of Y₂O₃ to SiO₂ was chosen to obtain the desired Y₂Si₂O₇ stoichiometry, which should give the interlayer better oxidation resistance compared to other interlayer materials. Mechanical characterization of the joints performed by indentation shows it to have good room temperature strength.

INTRODUCTION

A key technological challenge to be overcome for ceramics to be used as high temperature structural materials is the ability to join them [1,2]. One of the routes involves the use of a joining interlayer, and is referred to as brazing when the interlayer is metallic. Usually, these joints do not have good high temperature strength and have poor oxidation resistance. The interlayers to join ceramics can also be glasses and ceramics. A class of ceramics that has been used to join Si₃N₄ ceramics contain sintering aids such as MgO, Al₂O₃, and SiO₂. These sintering aids, which are present in the bulk product as secondary and grain boundary phases, show good chemical and physical compatibility with the Si₃N₄ grains. This

compatibility can be expected to exist when the sintering aids are used as the interlayer between pieces of bulk Si_3N_4 . Measurements on joints prepared with these chemicals show them to have high room temperature strength [3-5].

The drawback of using the above mentioned sintering aids is that they can induce poor oxidation resistance. While all Si_3N_4 grains are covered with a layer of SiO_x , which should give the ceramic good oxidation resistance, at high temperatures the silica reacts with the sintering additives to form a flux which provides enhanced oxygen transport to the Si_3N_4 surface resulting in an increase in the oxidation rates [6]. A secondary phase that can provide good oxidation resistance is one in equilibrium with both SiO_2 and Si_3N_4 . Such a phase is found in the Y-Si-N-O system, and has the stoichiometry $\text{Y}_2\text{Si}_2\text{O}_7$. Experimental measurements in bulk Si_3N_4 sintered with Y_2O_3 and SiO_2 show it to have an improved oxidation resistance [7]. Further work by Cinibulk *et al.* [8-10] confirmed the benefit of sintering using a range of rare earth oxides with SiO_2 on oxidation, creep and high temperature strength, as a result of formation of the intergranular $\text{RE}_2\text{Si}_2\text{O}_7$ phase.

We present here a report on the joining of silicon nitride ceramics using Y_2O_3 and SiO_2 . Preliminary results show that joints have good mechanical strength at room temperature and good oxidation resistance.

EXPERIMENTAL PROCEDURE

Bulk Si_3N_4 specimens (Toshiba Corporation) were polished to a surface finish of 1 μm . The interlayer was formed by dip coating the bulk ceramic in a slurry which was prepared using the chemicals given in Table 1. The initial powder composition was determined by the desired chemical phase, hence a molar ratio of 1 part of Y_2O_3 to 2 parts of SiO_2 was used. The powders were mixed in an attritor mill with isopropyl alcohol as the solvent, then dried, ground and sieved.

Table 1
Chemicals used to form slurry for dip coating

Chemicals	Quantities
Powders	0.5 grams
Isopropyl alcohol	8 ml
Binder (XUS 40303, Dow Chemicals)	0.015 grams
Dispersant (Triton X-405, Aldrich)	12 drops
Plasticizer (Glycerol, Aldrich)	24 drops

To process Si_3N_4 , special precautions were taken. At the high processing temperatures, Si_3N_4 decomposes to form SiO and N_2 [11]. The decomposition can be minimized by embedding the samples in Si_3N_4 powder and maintaining a positive nitrogen pressure. Unfortunately, the available furnace could not accommodate positive pressures, hence a N_2 pressure of 1 atmospheres was used. Furthermore, since the processing is done in a graphite furnace, Si_3N_4 can partially react to form SiC . This reaction was minimized by using a boron nitride crucible.

The specimens were placed inside the experimental set up and heated at 5°C per minute to 1800°C , for 1-2 hours, and cooled at 5°C per minute. Through the lid of the crucible, a small pressure was applied (~ 0.1 MPa) to maintain interfacial contact during the joining process.

A preliminary assesment of the mechanical integrity was made by indentation. The specimens were polished down to a $1\ \mu\text{m}$ surface finish and Vickers indented at a load of 9 kilograms. The interaction of the resulting crack with the interphase was observed to obtain information about the mechanical properties of the joint.

Oxidation studies were conducted by heating the specimens at 10°C per minute to 1300°C , for 24 hours, and cooled at 10°C per minute. The back of the specimen was then notched and the specimen broken to observe oxide scale.

RESULTS

Figure 1 is a scanning electron micrograph of the joint. The picture shows the joining compound to have completley wet the susbstrate and form a continuous bond with the bulk ceramic. The image also shows a Vickers indent and the cracks induced by it. The crack approaches the joint and is not deflected by it, suggesting a strong joint. If the joint were weak, the crack would have been deflected into the joint and would have propagated along it [12].

At shallower incident angles (Figure 2), the crack is deflected by the joint. This behavior is consistent with fracture mechanics analysis of crack deflection at interfaces [13,14]. These analyses consider the energies for deflection and penetration through the interface. When the crack impinges on the interface at an oblique angle, the deflection process is energetically favored. The SEM image also shows the presence of ligaments that bridge the crack. These ligaments may be due to the formation of elongated Si_3N_4 grains that have grown across the joint during the processing [15].

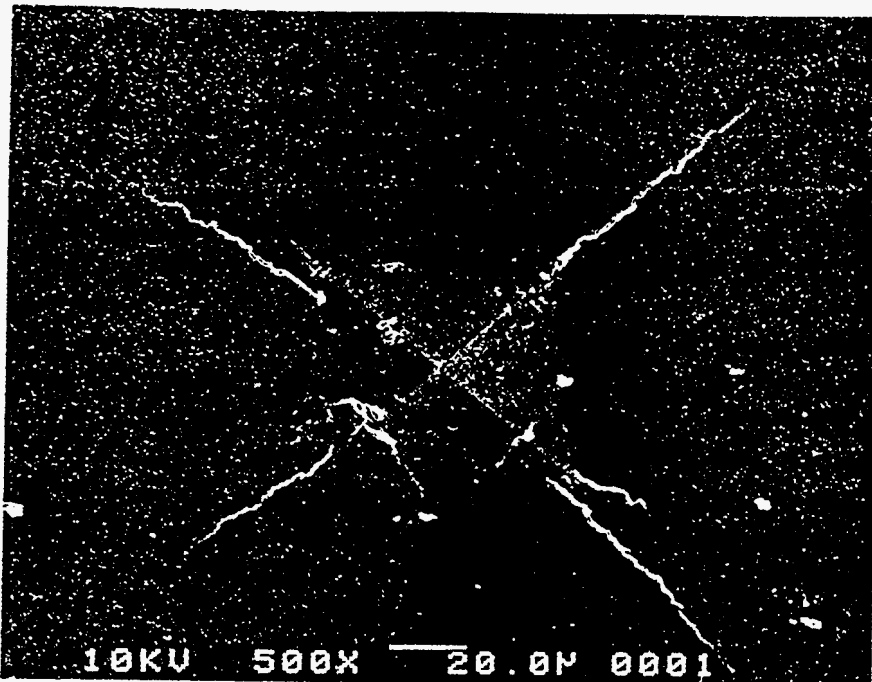


Figure 1

Crack induced by Vickers indent is not deflected by the joint

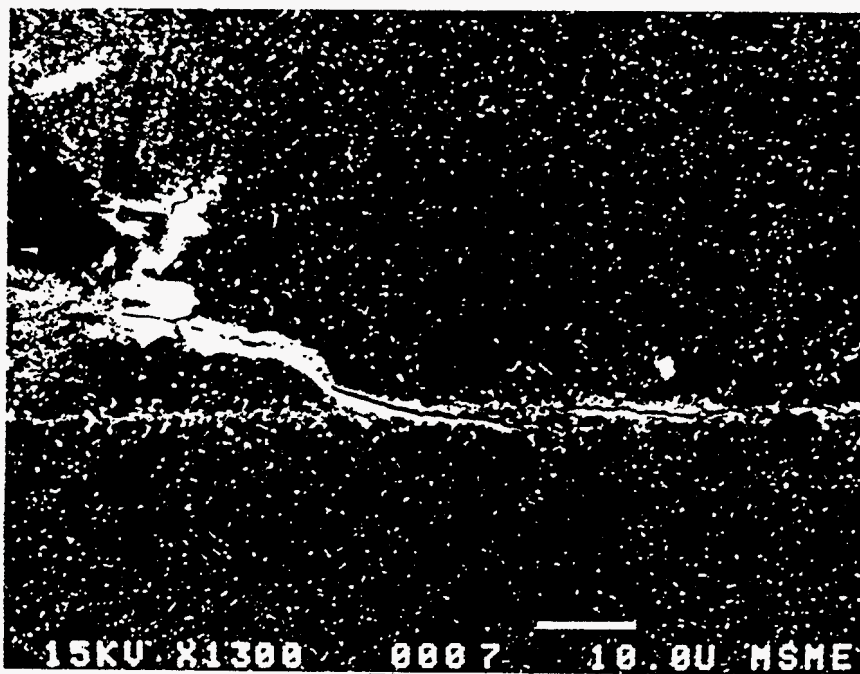


Figure 2

Crack is deflected by joint at shallower incident angles

The morphology of the ligaments formed could also be controlled by the stress fields that cause the cracks to propagate along specific paths. The shape of the cracks is sigmoidal and is similar to that obtained during delamination of interlayers [16,17]. The model proposed is that the crack initiates from the indent, reaches the interface and travels across the interlayer. It then stops at the opposite interface and re-initiates on the side of the indent and again traverses the interlayer. This process goes on till the stress fields are no longer strong enough to cause crack nucleation or growth.

Figure 3(a)-(d) show the results of the oxidation study. Figure 3(a) is a schematic sketch showing the specimen and the regions from which the SEM images were taken. In the lower half of the specimen, the joint was imperfect and could be seen in the SEM (Figure 3(b)). However, near the oxidized surface, the joint could not be distinguished from the bulk. The joint was determined to be the region directly above the imperfection seen in Figure 3(b). Upon comparing the images of the oxide layers, we can see that the oxide thickness is much smaller in the joint region (Figure 3(c)) than in the bulk (Figure 3(d)). This can be attributed to the formation of the oxidation resistant $\text{Y}_2\text{Si}_2\text{O}_7$ secondary phase as discussed earlier.

WORK IN PROGRESS

Current work is being directed towards characterizing the joint using transmission electron microscopy. Work is also being done to determine the strength of these joints using 4-point bending. Future work will be directed towards using rare-earth oxides (such as Yb_2O_3) instead of Y_2O_3 . The advantage is that the rare-earth disilicates crystallize during the cooling process [8]. It is therefore expected that the joints would not become viscous at high temperatures and would retain their strength.

CONCLUSIONS

Si_3N_4 ceramics have been successfully joined using a mixture of Y_2O_3 and SiO_2 . SEM analysis shows the interlayer to have wet the bulk Si_3N_4 and formed a continuous uniform joint. Indentation studies which reveal crack-interlayer interaction shows that these joints have good strength at room temperature. Oxidation studies show that the joint layer oxidizes less compared to the bulk material due to the formation of the $\text{Y}_2\text{Si}_2\text{O}_7$ phase.

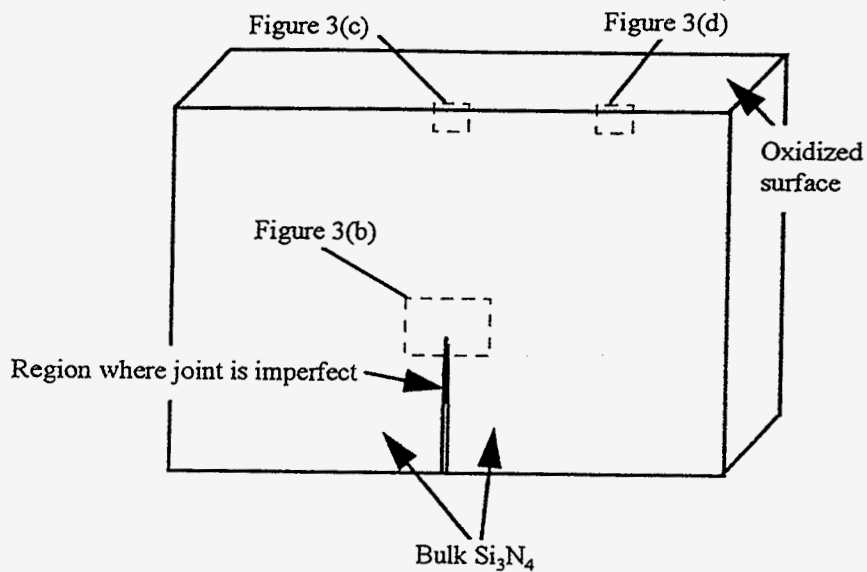


Figure 3(a)
Schematic sketch of specimen used for oxidation study

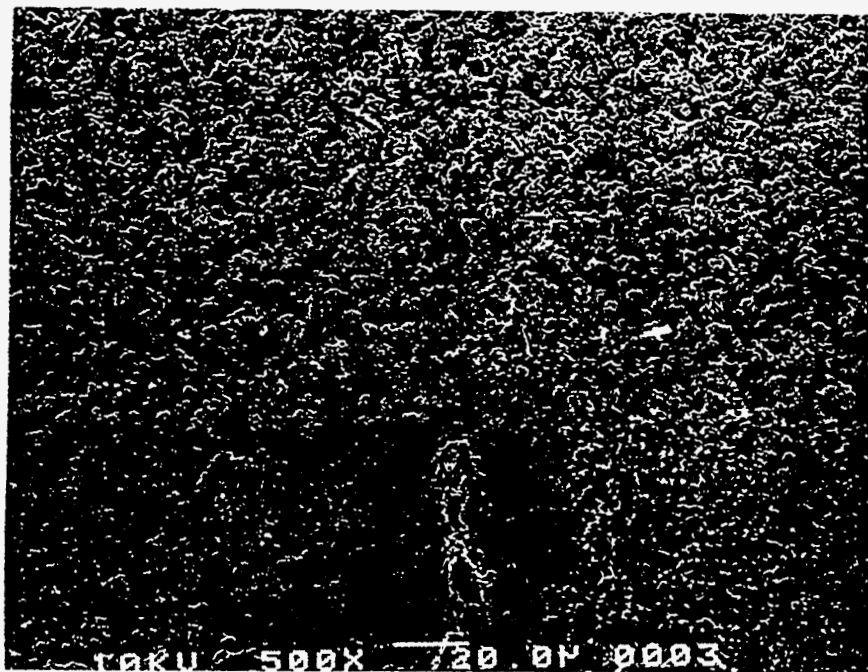


Figure 3(b)
Imperfect joint in the lower half of the specimen

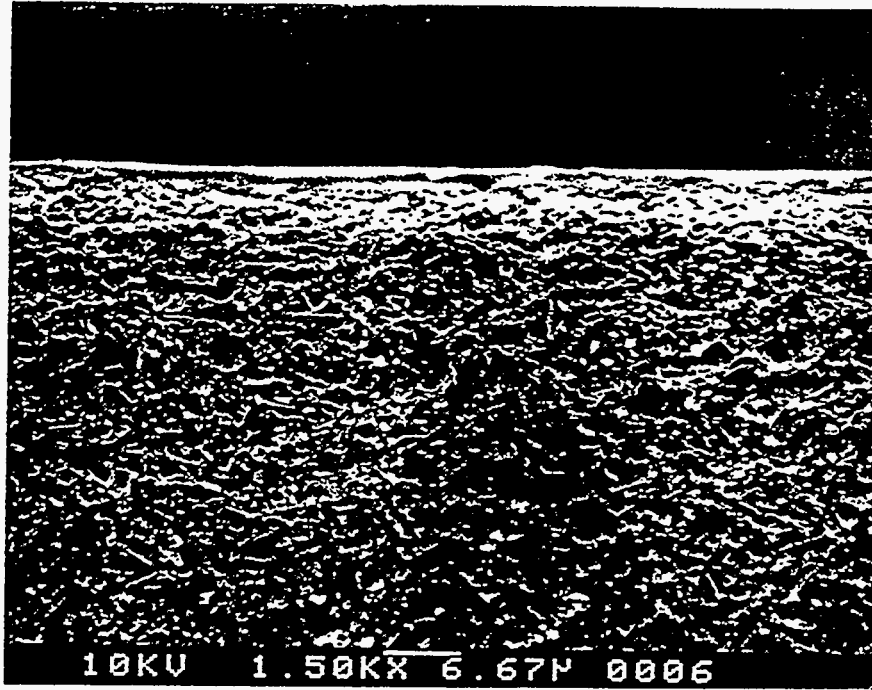


Figure 3(c)
Oxide scale formed on the joint region

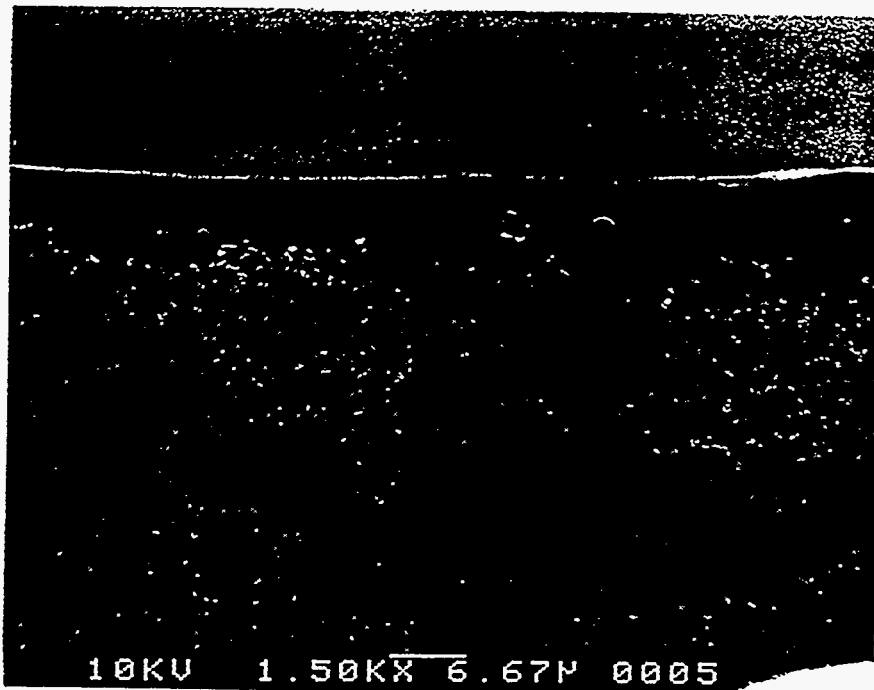


Figure 3(d)
Oxide scale formed on the bulk specimen

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