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Mechanical properties of Si_3N_4–Al_2O_3 FGM joints with 15 layers for high-temperature applications

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Abstract

"Crack-free" alumina-silicon nitride joints, comprised of 15 layers of gradually differing compositions of Al_2O_3/Si_3N_4, have been fabricated using sialon polytypoids as functionally graded materials (FGM) bonding layers for high-temperature applications. Using flexural strength tests conducted both at room and at elevated temperatures, the average fracture strength at room temperature was found to be 437 MPa; significantly, this value was unchanged at temperatures up to 1000 °C. Scanning electron microscopy (SEM) observations of fracture surfaces indicated the absence of any glassy phase at the triple points. This result was quite contrary to the previously reported 20-layer Al_2O_3/Si_3N_4 FGM samples where three-point bend testing revealed a severe strength degradation at high temperatures. Consequently, we believe that the joining of alumina to silicon nitride using polytypoidally functional gradients can markedly improve the suitability of these joints for high-temperature applications.

Keywords: Ceramics; Joining; Functionally graded materials; High-temperature strength

1. Introduction

The joining of materials is an important process both commercially and technologically. Although there are numerous joining techniques, achieving sound bonding using the functionally graded materials (FGM) method is commonly used because it achieves a gradual compositional change from one type of joint element to the other, thereby avoiding a singularity at the interface. Functionally graded materials consist of a spatially varying composite microstructure designed to optimize performance through a corresponding property distribution.[1] A graded interface can minimize the differences in properties from one material to another. Minimizing such property differences between two joining materials becomes especially pertinent for brittle materials, *i.e.*, when joining two dissimilar ceramics. Since ceramic materials invariably display little or no plastic deformation, small differences in the coefficient of thermal expansion (CTE) during processing can result in cracking and premature failure of the joint. To prevent this problem, FGM joining techniques can be used to create a continuous change in composition from one side of a specimen to the opposite side, with an accompanying gradient of thermal expansion properties. Consequently, the use of such a graded junction, rather than an abruptly changing bond layer, presents a feasible method for the effective joining of dissimilar ceramics with widely differing CTEs. To date, the concept has been successfully demonstrated with the sialon polytypoidal functional gradient joining of Al_2O_3 and Si_3N_4, using 20 individual Al_2O_3/Si_3O_4 layers of gradually varying composition.[2] Across this composition gradient, a phase transformation takes place in the sialon polytypoids nearest to the Al_2O_3-rich area. A transformation from 12H to 15R serves to relieve lattice mismatch stresses. 15R and 12H are different types of sialon polytypoids with distinct faulted structures. These polytypoids are physically and chemically compatible with both Si_3N_4 and Al_2O_3. Because metal–nitrogen bonding is in general more covalent than metal-oxygen, there is freedom to vary the covalent:ionic contributions to the interatomic bonding in a variety of structures.[3] The relationships

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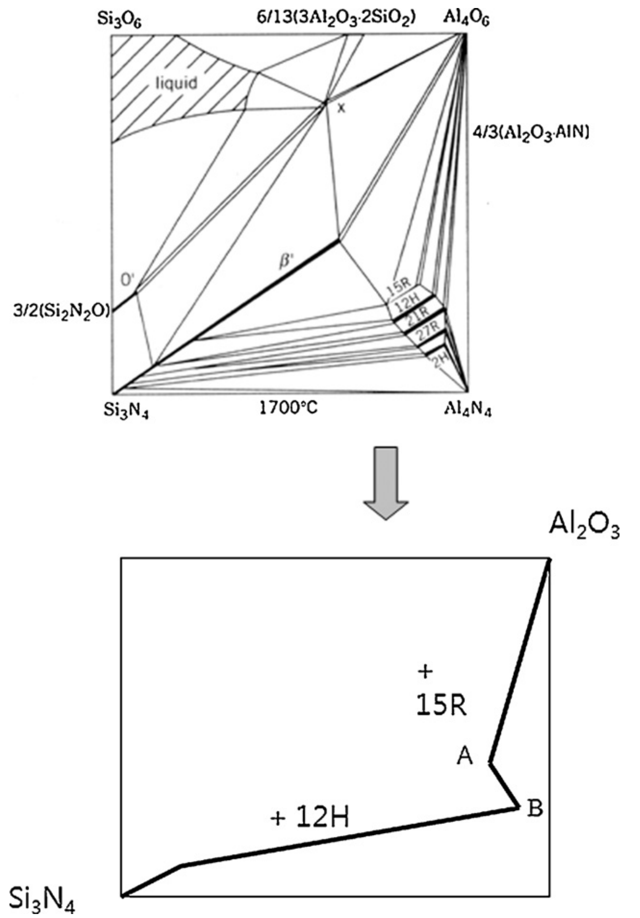

Fig. 1. The Si–Al–O–N system (1700 °C).[13] The diagram below the quarternary phase diagram shows an equilibrium line path of Si_3N_4–12H–15R–Al_2O_3. A and B line refers to the 12H/15R "interface" at the center of the FGM.

between Si–Al–O–N condensed phases are represented by the quaternary phase diagram (Fig. 1) and any point in the square diagram Si_3N_4–Al_4O_6–Al_4N_4–Si_3O_6 represents a combination of 12^+ and 12^- valences where the components adopt their usual valency states (*i.e.* Si^{4+}, Al^{3+}, N^{3-} and O^{2-}). A polytypoid is defined as a faulted structure in which the fault periodicity depends on composition through the cation/anion ratio. Differing fault periodicities lead to changes in the polytypoids' cation/anion ratios, and also result in different coefficients of thermal expansion. Relieving the lattice mismatch has resulted in a macroscopically crack-free FGM. The mechanical properties of these crack-free FGM joints have been tested at room and high temperature.

As materials, ceramics are widely used for many applications that require high melting temperatures, high-temperature strength, good wear resistance, and chemical stability.[4] For structural applications, ceramics often display only minimal degradation in strength and fracture resistance at temperatures up to, and often above, 1000 °C. This behavior is in sharp contrast to most metallic structural materials, which invariably soften at higher temperatures. It is this retention of mechanical properties at elevated temperatures, as compared to ambient, which identifies ceramics as preferred candidate materials for many structural applications, although their limited ductility and toughness at lower temperatures often frustrates their actual use.

Silicon nitride ceramics have often been the preferred candidates for such structural applications owing to their high strength and particularly high toughness relative to most other ceramic materials. To join Si_3N_4 to other ceramics, specifically Al_2O_3, sialon polytypoidal functional gradients can be used since sialon polytypoids are physically and chemically compatible with both materials[5]; moreover, sialon polytypoids are attractive joining materials since they have CTE values between those for Si_3N_4 and Al_2O_3. It is the objective of this study to use such FGM joining techniques to bond Si_3N_4 to Al_2O_3 and specifically to evaluate the strength of the corresponding dissimilar ceramic joints, both at room (25 °C) and elevated (1000 °C) temperatures.

In this paper, we report on the mechanical properties of the bonded ceramics, FGM joined using 15 layers. Resulting room and high-temperature strengths are compared with previously reported results[2] for these two materials where the FGM joining techniques were not optimized. Our ultimate aim is to discern whether such FGM bonding procedures can actually produce Al_2O_3/Si_3N_4 joints suitable for high-temperature structural applications.

2. Experimental procedures

2.1. Material fabrication of optimized joint

The processing and characterization methods used to generate the layered FGM Al_2O_3/Si_3O_4 joints were similar to those described in detail by Lee et al.[6] A powder stacking method was used to produce 15 layers with varying Al_2O_3/Si_3O_4 composition and thickness, prior to hot pressing to sinter the multilayered FGM's. The optimal thickness of each layer was determined using simulation results.[7] 6 wt% Y_2O_3 and 2 wt% Al_2O_3 were added as additives to sinter Si_3N_4; 3 wt% Y_2O_3 was used as a sintering additive for the polytypoid powders.[5] Si_3N_4 powders from Grand C&M with a particle size ranging from 0.3 to 0.5 μm were used, together with Al_2O_3 powders from Tamicron industries with a particle size ranging from 0.16 to 0.3 μm; 12H sialon polytypoid powders were obtained from Novel Technologies. Powders of each composition were mixed in a solvent of isopropanol then agitated using an ultrasonicator to prevent agglomeration. The powders were dried, sieved then stacked layer by layer in a cylindrical 25-mm diameter mold. The green body was pressed using a cold press to 38 MPa for 8 min. The green body was sintered using a hot press at 1700 °C for 2 h at a pressure of 38 MPa in flowing nitrogen gas to prevent decomposition of the Si_3N_4. A schematic of the experimental setup is shown in Fig. 2. Table 1 shows the composition and layer thickness of sintered FGM joint.

Simulations were performed to determine the optimum thickness of each layer necessary to minimize residual stresses and CTE mismatch across the FGM joint.[7] The composition and thickness of each layer is presented in Table 1. As a result of this optimization, the Si_3N_4–polytypoids–Al_2O_3 FGM could be processed crack free (Fig. 4).

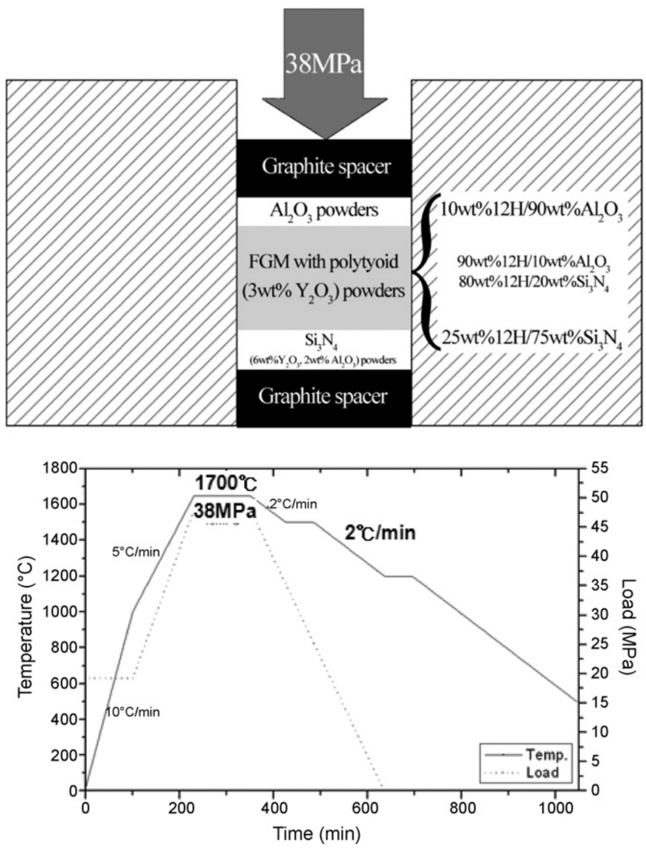

Fig. 2. (a) Experimental setup used to fabricate the crack-free joints using hot pressing. (b) Temperature and loading cycle used in such hot pressing procedures.

Transmission electron microscopy (TEM) [JEM-3010, used voltage at 300 keV] was used to examine the microstructures, specifically to identify different phases at the various regions along the interface of the dissimilar ceramic joint.

2.2. Strength characterization

Three-point bend tests were conducted at room (25 °C) and high temperatures (1000 °C) to determine the strength of the joint as a function of temperature. The test jig was designed specifically for testing unnotched rectangular cross-section beam specimens which were 3 mm × 4 mm × 10 mm and employed an upper loading span length of 8 mm (Fig. 3).

Table 1
Composition and layer thickness for the 15-layered FGM joint.

Layer composition	Layer thickness (μm)
100% Si_3N_4	1056.0
75% Si_3N_4/25% 12H	956.0
50% Si_3N_4/50% 12H	1000.0
25% Si_3N_4/75% 12H	1111.1
20% Si_3N_4/80% 12H	667.0
10% Al_2O_3/90% 12H	440.0
20% Al_2O_3/80% 12H	390.0
30% Al_2O_3/70% 12H	330.0
40% Al_2O_3/60% 12H	330.0
50% Al_2O_3/50% 12H	330.0
60% Al_2O_3/40% 12H	330.0
70% Al_2O_3/30% 12H	330.0
80% Al_2O_3/20% 12H	330.0
90% Al_2O_3/10% 12H	440.0
100% Al_2O_3	440.0

Loading was performed in displacement control at constant displacement rates of 0.6 mm/min and 6 mm/min with an MTS 810 computed-controlled servo-hydraulic testing machine equipped with a Centorr Testorr furnace. Elevated temperature tests were conducted in an overpressure of gaseous argon to prevent degradation of the Si_3N_4. Samples were heated at 10 °C/min, and held at 1000 °C for 1 h to allow for thermal homogenization in the sample. Five separate samples were evaluated for each data set. All measured strength data were compared with those for the previous 20-layered FGM Al_2O_3/Si_3N_4 samples.[2]

After testing, all fracture surfaces were observed using a scanning electron microscopy (SEM) [Hitachi S-4800, secondary electron mode].

3. Results and discussion

3.1. The optimized crack-free joint

Fig. 4 shows an optical image of the optimized crack-free joint with 15 layers. TEM images of this FGM sample are shown in Fig. 5(a) and (b). In the Si_3N_4-rich region, only Si_3N_4 and 12H polytypoid were found, whereas in the Al_2O_3-rich region, only Al_2O_3 and 15R polytypoid were found. The average size of a 12H polytypoid grain is approximately 0.3 μm in width and 1.3 μm in length. The average size of a Si_3N_4 grain is ~0.3 μm in width and ~1 μm in length, similar to that of the 12H polytypoid.

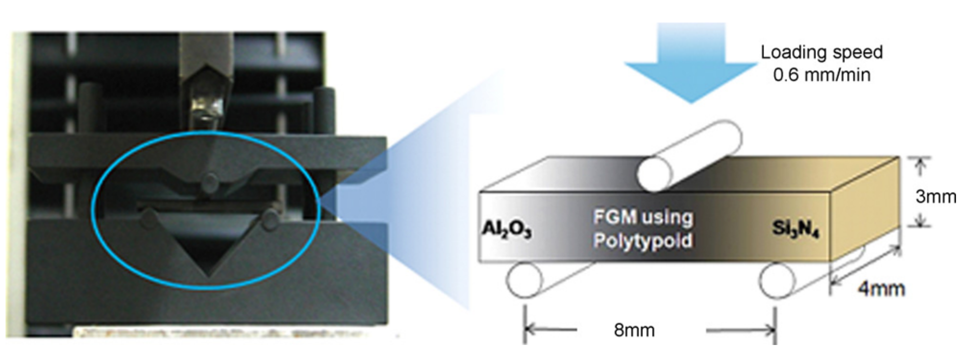

Fig. 3. Sample position and test jig geometry used for three-point bend testing.

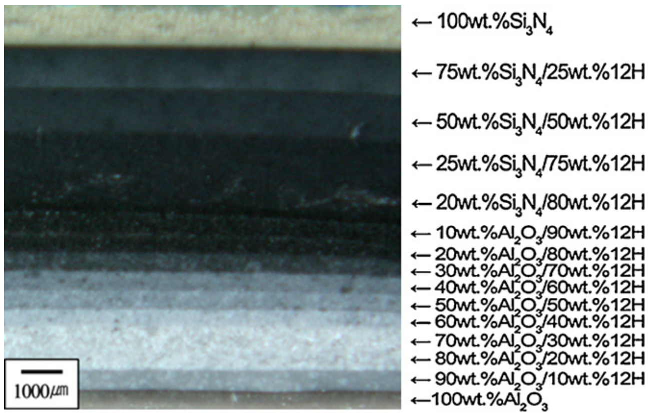

Fig. 4. Optical microscopy image of the crack-free FGM structure.

Table 2
Strength test results, as a function of temperature, of optimized the 15-layered FGM joint (5 samples were tested for each set).

Temperature	Strength (MPa)
Room temperature (25 °C) (loading rate 0.6 mm/min)	437 ± 102
High temperature (1000 °C) (loading rate 0.6 mm/min)	437 ± 50
High temperature (1000 °C) (loading rate 6 mm/min)	380 ± 20

Table 3
Strength test results, as a function of temperature, for the 20-layered FGM joint.[2].

Temperature	Strength (MPa)
Room temperature (25 °C)	581 ± 60
High temperature (1000 °C) (loading rate 0.6 mm/min)	262 ± 20

In the Al_2O_3-rich areas, the average size of a 15R polytypoid grain is ~0.1–0.2 μm in width and 1 μm in length, as shown in Fig. 5(b). These micrographs indicate that no undesirable reaction took place between the Si_3N_4, the Al_2O_3 or the polytypoids, which agrees with the behavior expected from the Si–Al–O–N quarternary phase diagram.[6] As shown in Fig. 1, 15R is the most chemically similar polytypoid to Al_2O_3 and the most similar polytypoid to Si_3N_4 is 12H. This trend in the polytypoid transformation from 12H to 15R as the ratio of cation to anion for those polytypoids decreases, is exactly as predicted from the phase diagram (Fig. 1). The present approach can be applied to a wide range of ceramic systems including superconductors.[8] The center of the FGM sample where 12H/15R interface is located (A–B line from Fig. 1), may in fact be mixtures of these polytypoids. Therefore, a sharp interface at the center of the FGM could not be resolved.

3.2. Strength characterization

Flexural strengths at room temperature and at 1000 °C were obtained in three-point bending. The displacement rate used at room temperature was 0.6 mm/min, while tests were performed at 1000 °C at displacement rates of 0.6 and 6 mm/min. The average measured strength at room temperature was found to be 437 MPa; this was unchanged at 1000 °C for the same displacement rate (Table 2). This result is contrary to the findings of Lee et al. on their unoptimized 20-layer FGM joints where they found a 50% reduction in fracture strength at high temperatures caused by softening at glassy triple junctions (Table 3).[2] Frac-

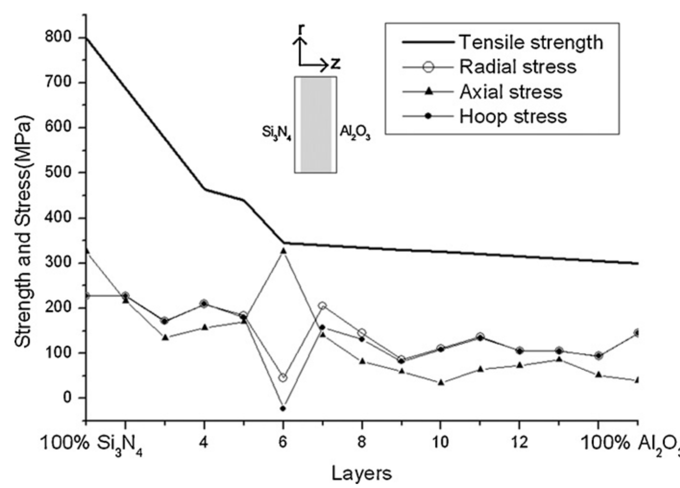

Fig. 6. Comparison of the computed radial, axial and hoop stresses with critical failure strength for crack-free FGM sample calculated by the numerical analysis method.

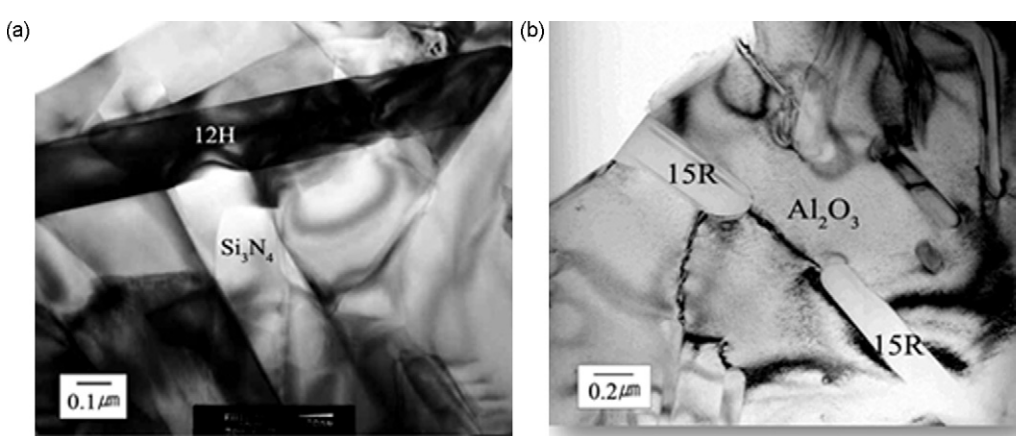

Fig. 5. (a) TEM image of the microstructure in the Si_3N_4-rich side of the FGM joint. Only the Si_3N_4 and 12H phases were detected. (b) TEM image of the microstructure in the alumina-rich side of the FGM joint. Only alumina and 15R phases were detected.

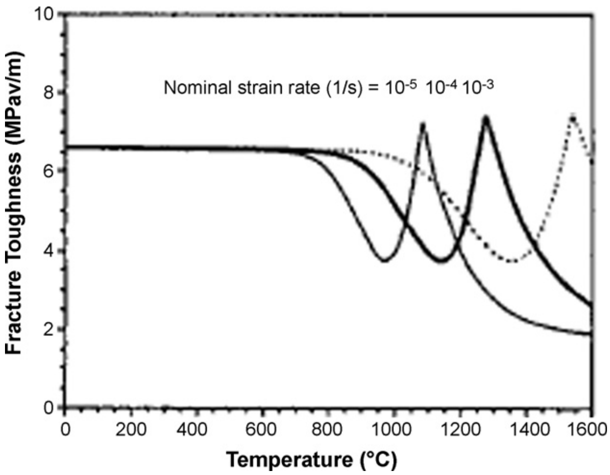

Fig. 7. Fracture toughness of Si_3N_4 as a function of temperature and strain rate. Grain pullout is a dominant strengthening mechanism at low and high (1200–1400 °C), but softening of glassy grain boundaries leads to a decrease in toughness. Though the data presented measures toughness, an analogous argument can be made for the effects of temperature and strain rate on strength. After Chen et al.[9]

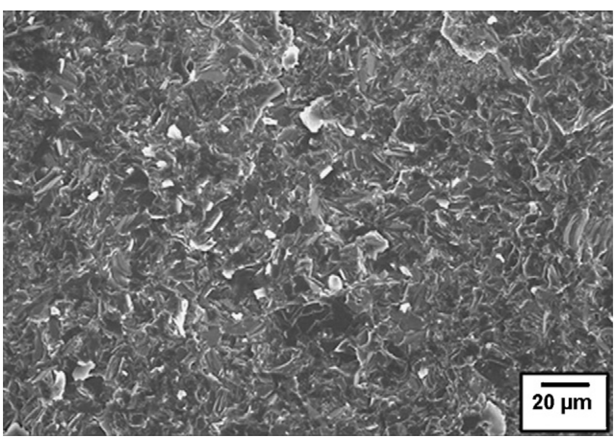

Fig. 8. SEM image of room temperature fracture surface of a 15-layered FGM sample.

tures at both temperatures occurred within the interface between 20% Si_3N_4/80% 12H polytypoid and 25% Si_3N_4/75% 12H polytypoid which is approximately in the middle of the sample. This result agrees with the modeling result where calculated residual stresses in each layer do not exceed the critical strength for failure but axial stress in the joint is the highest in the middle of the sample (Fig. 6). This explains how our 15-layered FGM sample came out macroscopically crack free but has the weakest point in the middle of the sample.

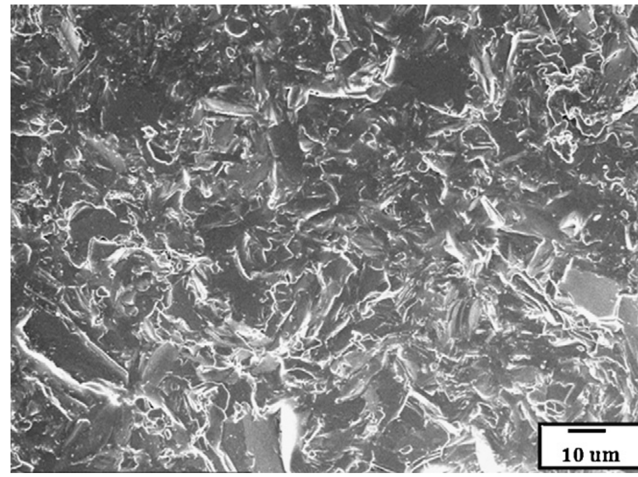

Fig. 10. SEM image of room temperature fracture surface of a 20-layered FGM sample.[2]

Although investigating the weakest part of an FGM joint is best accomplished using four-point bending, the authors were prevented from doing so by sample size limitations. Modeling of the joint was used to calculate the weakest points in the sample which were found to be at the interfaces near the center of the sample.[7] In this situation, three-point bending yields useful results for comparison of fracture strengths. It is apparent that the joints presented here maintained their strength at high temperatures, while the unoptimized joints tested previously[2] did not.

In the unoptimized, 20-layer joints studied previously,[2] glassy phases were found at grain boundaries and triple points.[2] Softening of these glassy phases can increase the fracture strength of ceramic materials if grain pullout is a dominant failure mechanism; however, the temperature range at which these samples were tested is likely a region where grain pullout is not as dominant.[9] At intermediate temperatures[9] (*i.e.* ~1000 °C for Si_3N_4), softened grain boundaries increase the incidence of transgranular fracture, lowering the fracture strength. As the temperature increases further (1200–1400 °C), grain-boundary sliding again becomes an important strengthening mechanism. The flow stress of the softened grain-boundary

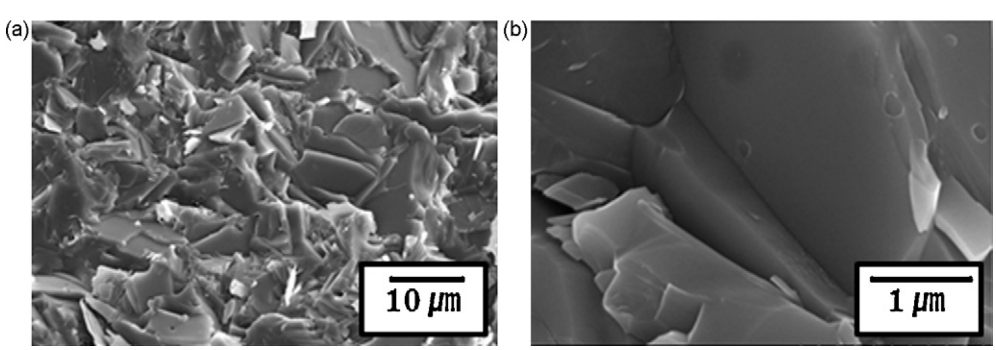

Fig. 9. (a) SEM image of the fracture surface of a 15-layered FGM sample tested at a temperature of 1000 °C; (b) SEM image at the grain boundary used to detect the presence, if any, of any deformed intergranular phases. The image shows no presence of glassy phase at the boundary.

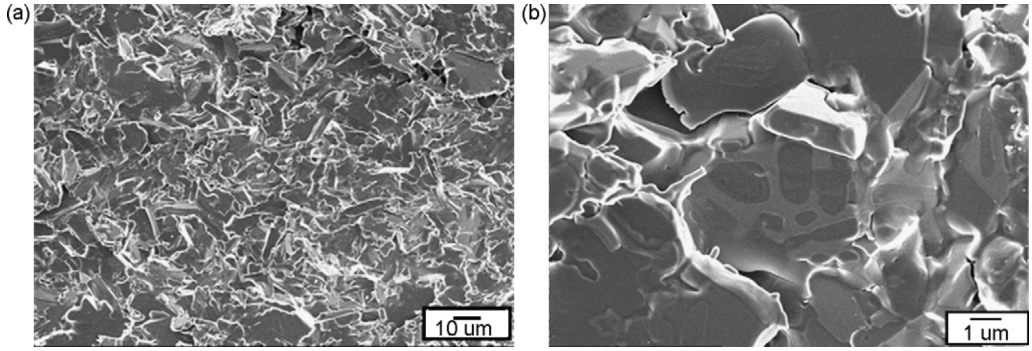

Fig. 11. (a) SEM image of the fracture surface of a 20-layered FGM sample tested at high temperature; (b) SEM image of high-temperature fracture surface with presence of viscously deformed intergranular phase indicated.[2]

glassy phase is low enough that grains can readily slide, leading to grain pullout and an increase in intergranular fracture. The strength increases achievable by this method have their limit, as continued softening of the grain-boundary phase at ultra-high temperatures contributes to rapid degradation of the strength of the joint. The same effect can be achieved by increasing the strain rate at a given temperature (Fig. 7).

Figs. 8 and 9 show a mixture of intergranular and transgranular fracture for failures at both room and high temperatures. In the present system (Fig. 8), no glassy phases or glassy triple junctions could be detected consistent with the lack of any strength degradation at high temperatures. However, it should be noted that the room temperature fracture strength of the 20-layer joint was significantly higher, implying that grain pullout may be a dominant strengthening mechanism for these joints (Fig. 10). As expected, the fracture strength for the optimized, 15 layer joints at 1000 °C is lower for a faster displacement rate, but again the drop-off is much less dramatic than for the 20-layer FGM joint. This result also confirms that no softening of intergranular glassy phases took place for this optimized crack-free joint. Therefore, the current optimized 15-layered crack-free joint led to a significantly reduced amount of glassy phases such that no strength degradation was observed at high temperature, in contrast to the severe degradation observed in 20-layered FGM as shown in Fig. 11. This difference might be due to the reduction in number of layers in the Si_3N_4-rich area. It was reported that Si_3N_4 sintered with $Al_2O_3 + Y_2O_3$ has grain boundaries with poor resistance to softening at 1000 °C.[10,11] In these liquid-phase sintered ceramics, grain boundaries and triple junctions often contain an amorphous phase which can soften, resulting in grain-boundary sliding and cavitation. In the current work, for optimization 5 layers were removed from the Si_3N_4-rich area to make a 15 layer joint. As removing 5 layers in the Si_3N_4-rich area reduces the amount of Al_2O_3 and Y_2O_3 used in the FGM fabrication, the strength degradation caused by these sintering additives was minimized significantly as shown in this paper. Indeed previous high-resolution TEM studies by Van Tendeloo et al.[12] on polytypoids in AlN–SiO_2 also showed no glassy phase on the grain boundaries between two polytypoid grains. It is clear that polytypoids allow for glass-free interfaces, which account for greater strength retention at high temperatures.

4. Conclusions

Macroscopic crack-free joining of heterogeneous silicon nitride and alumina ceramics has been optimized to 15 layers by the use of sialon polytypoids as functionally graded materials (FGM), as defined by the phase diagram for the system Si_3N_4–Al_2O_3. The lattice mismatch was accommodated by transformation of the polytypoids to better match the properties of the material with which it was in contact. Moreover, this trend in the polytypoid transformation from 12H to 15R as the ratio of cation to anion decreases (*i.e.* the transition from Si_3N_4 to Al_2O_3), is exactly as predicted from the phase diagram (Fig. 1). The thickness and compositions of each layer of the Si_3N_4–Al_2O_3 bond were controlled to minimize residual stresses. This result was confirmed by three-dimensional modeling of the residual stresses caused by differential shrinkage, which showed that the calculated residual stresses did not exceed the critical strength for failure of the joint. The average fracture strength was found to be 437 MPa at room temperature, with no reduction at high temperatures (1000 °C). A mixture of transgranular and intergranular fractures occurred at both temperatures within the 20%Si_3N_4/80%12H polytypoid and 25% Si_3N_4/75%12H polytypoid interfaces, which is approximately in the middle of the sample. The retention of the strength at 1000 °C showed that the optimized FGM joint had been successfully fabricated and that the FGM-based bonding could be considered as a suitable technique for joining dissimilar ceramic materials for high-temperature structural applications.

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