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**JOINING OF SILICON CARBIDE
WITH A CORDIERITE GLASS-CERAMIC**

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Joining of Silicon Carbide with a Cordierite Glass-Ceramic

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Abstract

A method for the joining of silicon carbide using a cordierite glass-ceramic has been developed. Cordierite, with glass-ceramic processing, remains amorphous and wets the SiC substrate to form a strong bond when rapidly fired. Subsequent heat treatment crystallizes a multiphase interlayer with a matching bulk thermal expansion coefficient (CTE). A benchtop tape casting method for depositing joining precursor films of varying thickness is described. The wetting characteristics of cordierite on SiC that are pertinent to the joining process are shown to be highly sensitive to processing atmosphere. Doping with a fluoride ion flux can lower the peak processing temperature without significantly altering the crystallization path. The effect of interlayer thickness is observed by monitoring indentation crack paths and with 4-point bending tests. Controlling the degree of crystallinity is shown to tailor the mismatches in thermal expansion coefficient and elastic moduli to produce joints of high strength ($\sigma_F > 500$ MPa). Characterization is accomplished with XRD, SEM, and TEM.

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I. Introduction

Methods for producing high strength joints of ceramics or metal alloys with silicon carbide (SiC) often require conditions that would degrade the SiC, or damage the material to which it is to be joined. Environmental stability is also of concern, particularly when the joining technique involves the use of a reactive metal, where excess unreacted metal limits the corrosion and oxidation resistance. This may lead to loss of strength under high temperature or irradiative environments.¹⁻⁵

Conventional wisdom dictates that ceramics may not be put in service above the processing temperature, as this can bring about thermodynamic instability. Since the service temperature envisaged for a number of these advanced materials approaches or exceeds 1000°C, and environmental and microstructural effects predominate between 1200-1700°C, a thermal hierarchy is imposed upon the joining process. Furthermore, embrittling chemical reactions and severe thermal stresses accompany higher processing temperatures. Some researchers have suggested reaction bonding with a silicon rich liquid phase to lower the processing temperature.^{6,7} Efforts have been made to produce a low temperature ceramic joint which can withstand a higher service temperature by way of a metallic partial transient liquid phase.^{8,9} Other attempts include the use of a crystallizable glass to improve the refractoriness of the resultant joint.¹⁰⁻¹⁴

In this paper a method is described for obtaining a high strength SiC-to-SiC joint with a process that produces well-adhered, chemically compatible interfacial phases and a matching bulk thermal expansion coefficient using a composite ceramic interlayer. Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), with a high elastic modulus (232 GPa) and strength, as well as a low thermal expansion coefficient ($2.0 \times 10^{-6} / ^\circ\text{C}$ from 0-1000°C) and excellent thermal shock resistance, proved to be a

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good choice in combination with SiC. With glass-ceramic processing it can be made to wet the SiC substrate, filling pores and forming a strong bond. Many additives, such as alkali earth oxides or fluoride ion lower the melting point and viscosity, without significantly altering the crystallization path. In addition, brazing with an oxide provides for intrinsically good oxidative stability for high temperature service. Most significant to this work, however, is the ability to control the final multi-phase microstructure through a crystallization heat treatment which tailors the elastic modulus and bulk thermal expansion coefficient of the final product and relaxes the thermal stresses present at the interface.

Experimental

The cordierite glass-ceramic powder (EG-0221), obtained from Ferro Corp. in Cleveland, Ohio, is a 4.9 μm glass frit containing 52.5% SiO_2 , 32.0% Al_2O_3 , 13.5% MgO , and 2.0% BaO by weight. The SiC (Hexoloy SA) was obtained from Carborundum Co. in Niagara Falls, NY. To establish an optimum processing atmosphere, 1 μm polished SiC substrates, with thick ($> 100 \mu\text{m}$) cordierite coatings, were fired at 1550°C for 30 minutes in air, argon, and vacuum ($6.7 \times 10^{-4} \text{ Pa}$); and the resulting fracture surfaces examined in the SEM. Optimum wetting conditions were assessed with sessile drop studies. The glass pieces used were prepared by melting the glass powders in a platinum crucible in air for 60 minutes at 1550°C , followed by immediate quenching into de-ionized water. Bubble free pieces were chosen and ground flat for the experiments. The SiC substrates were subjected to several surface pretreatments: pre-oxidation (24 hours at 1500°C), kaolin glazing (2 hours at 1300°C), and titanium ion-implantation ($10^{17}/\text{cm}^2$ dose, 150 KeV). The pretreated substrates were thoroughly cleaned in an acetone/isopropanol ultrasonic bath, followed by a final methanol/water rinse, prior to the wetting experiments. The glass pieces were positioned

on the substrates and placed in a graphite element furnace. After evacuating to 6.7×10^{-4} Pa, they were melted using ramp rates ranging from 5 to 60 °C/minute, and held at peak temperatures between 1465 and 1550°C for times ranging from 0 to 60 minutes. The furnace was then cooled in vacuum, flowing argon, and flowing helium gas to establish quench rates between 1400-950°C of 10 to 28°C/minute. Upon removal from the furnace, the wetted substrates were cross-sectioned and examined optically for interfacial void formation, possible reaction zones, and extent of phase separation and/or crystallization in the cordierite. The contact angle, θ , was determined from optical micrographs using the geometric relation

$$\theta = 2 \tan^{-1}(2H/d) \quad (1)$$

where H and d are the height and footprint of the sessile droplet, respectively.

In joint fabrication, cordierite films of various thickness were applied by tape casting techniques. The SiC substrates were ground flat to ensure coplanarity, then subjected to various surface treatments before the ceramic films were applied. To limit the amount of organic material introduced (i.e. plasticizer), and subsequent handling during a tape transfer operation, the film was cast directly onto the substrate using a doctor blade on a template made from a surface-ground steel plate (Fig. 1). The basic slip formulation was similar to that described by Richards¹⁵ in the production of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ slips. The solvent was an azeotropic mixture of Ethanol and Methyl Ethyl Ketone (40/60 by weight). Menhaden fish oil (Sigma Chemical Co., St. Louis, MO) was added as a dispersant at 3 wt. % relative to solids. After mixing ultrasonically for 30 minutes, 5% tertiary amide polymer binder (Dow Chemical, Midland, MI) was added and mixing was continued for another 30 minutes. It was important to add the dispersant prior to the binder to prevent agglomeration, as competition for adsorption sites occurs.¹⁶ The slip composition was vacuum

degassed, then deposited directly onto the substrate with the doctor blade. The concentration of solids was kept at 0.6 g/ml and the doctor blade gap height set between 50-200 μm .

The binder was removed by heating in air at 400°C for 4 hours, then the SiC rods (16 mm X 19 mm DIA) with cordierite layers were placed in a graphite die and a 500 gram weight applied to ensure good contact was maintained. The samples were fired in a graphite element furnace evacuated to 6.7×10^{-4} Pa. The ramp rate above 400°C was 60°C/min., sufficiently fast to prevent partial crystallization that would have affected viscosity and impaired wetting. The peak temperature and dwell times were determined by the sessile drop experiments. Vacuum, flowing argon, and flowing helium gas were used to quench to just above the glass transition temperature of 815°C, and nucleation dwell times (for precipitation of the glass-ceramic precursor phase) of 1 and 5 hours were studied. The crystallization time and temperature were set at 1200°C for 2 hours. The heating rate to the crystallization temperature was sufficiently slow (10°C/min.) to prevent deformation of the ceramic skeletal network that can be caused by rapid crystallization.¹⁷ Thermal shock was minimized by slow cooling (5°C/min.) below the lower limit of cordierite crystallization to room temperature.

Microstructural characterization was accomplished with x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and transmission electron microscopy (TEM). An HF (1% in H₂O) etch was used to distinguish phases in the composite ceramic. For the most accurate determination of phase distribution, exposed fracture surfaces were examined whenever possible, as opposed to powders, to account for thermal gradient effects on the crystallization behavior of the glass-ceramic in the sandwich geometry used.

During preliminary investigations, the strength of the interface and the experimental upper bound for joint thickness were assessed by fabricating joints of varying thickness and introducing

low incidence angle (approx. 45°) cracks near the interface using a pyramidal shaped diamond indenter (Vickers) with a 10 kg load. The eventual crack paths were observed in the SEM, especially any tendencies for crack propagation along the interface. Later, the mechanical properties of the final joint were assessed with 4-point beam bending tests. The modulus of rupture was determined using the formula, $\sigma_r = 3sp/bh^2$, with “s” the moment arm, “p” the load, and “b” and “h” the width and height of the sample beam. Beams were cut to 3 X 3 X 30 mm size, and polished on a lapping wheel to 1 μm finish. Weibull statistics were employed to gain a more thorough statistical interpretation of the results.¹⁸

The average residual stress present upon cooling associated with the formation of a thin joint is

$$\sigma = \frac{E(\alpha_i - \alpha_j)\Delta T}{1 - \nu} \quad (2)$$

where E is the elastic modulus for the interlayer, α is the coefficient of thermal expansion, and ν is Poisson’s ratio for the interlayer. Also, there are stress concentrations near the free surface that depend upon the modulus mismatch, and the volume over which these concentrated stresses extend will scale with the layer thickness. In thinner layers a smaller sampling volume reduces the probability of finding a flaw of critical size for crack initiation and propagation, and the joint strength can approach the theoretical cohesive strength of the interlayer (or the interfacial adhesive strength, whichever is smaller). Furthermore, if cracking initiates near the interface the distance within which it can grow with high stress is smaller with a thinner joint. This constrained volume of stress relief reduces the tendency for interface crack advance brought on by the modulus mismatch. As residual stresses are superimposed upon the applied stress, it is most advantageous

to make joints as thin as possible, within the requirements for complete coverage, and to limit the mismatches in elastic moduli and thermal expansion.

The thermal expansion of the multi-phase glass ceramic interlayer was determined using the following rule of mixtures formulation:¹⁹

$$\alpha = \frac{\sum \alpha_i B_i W_i / \rho_i}{\sum B_i W_i / \rho_i} \quad (3)$$

where α is the thermal expansion coefficient, B the bulk modulus, W the weight fraction, and ρ the density of the individual phases. The composition of the interlayer was found with the lineal intercept method on SEM micrographs, in conjunction with direct comparison of several integrated peak intensities from x-ray diffraction scans.²⁰ The variables in the intensity equation were obtained from the program *Powder Cell 1.0*, by W. Kraus and G. Nolze (<http://www.lmcp.jussieu.fr/sincris/logiciel/prg-powdercell.html>).

III. Results and Discussion

(1) *Processing atmosphere and interlayer thickness.*

Processing in vacuum was required to produce a stable film and reduce bubble formation at the interface. Whereas processing in air led to vigorous reaction and a highly irregular film, processing in argon produced a continuous, stable coating; but fracture surfaces revealed the presence of large unwet areas due to bubbles. However, the fracture surface joints processed in vacuum showed the absence of voids due to bubbling. See Figure 2.

The indentation crack path studies (Fig. 3) of SiC/cordierite sandwich joints of thickness between 15 and 35 μm demonstrated the presence of good adhesion at the interface, as none of the low angle impinging cracks preferred the interface over the bulk. Due to the similarity in density and contrast in the SEM between the bulk material and the reaction zone adjacent to the interface,

the presence of a chemically compatible interfacial reaction phase could be inferred. Based on the tendency of cracks to deflect and propagate through the interlayer in thick joints, the maximum thickness for achieving strong joints was taken to be 15 μm .

(2) *Wetting and Contact Angle*

Substrate surface precondition, peak temperature, peak dwell time, the presence of fluoride ion dopant, as well as heating rate and quench rate were variables in the determination of optimum wetting conditions. With no surface preconditioning, the contact angle remained high (110°), after 60 minutes at 1550°C . Preconditioning, in the form of pre-oxidation, kaolin glazing, and titanium ion-implantation all served to decrease the contact angle to below 90° . It is believed that the presence of a reactive layer on the surface assists the spreading of the glass. With the pre-oxidized and ion-implanted substrates, after a sufficient time at peak temperature the reaction phase forming was wet by the liquid droplet. The optimum combination of peak temperature and dwell time that minimized both the contact angle and interfacial void formation due to chemical reaction was found to be 1550°C , 30 minutes for the undoped glass; and 1500°C , 30 minutes for the glass with 1 wt. % CaF_2 flux. 60° contact angles were obtained. The kaolin glazed parts yielded partially crystallized droplets that did not adhere well after cooling. These results were obtained both from direct observation of gas evolution from the furnace viewport, and metallurgical cross-sections of droplets quenched from peak temperature to the glass transition point.

The formation of a strong bond is conditional on the formation at the interface of a thin silicate reaction product or glassy phase which is chemically compatible with both SiC and cordierite. 2° thin-film x-ray scans taken on pre-oxidized substrates with large sessile drops (which were physically removed from the substrates after quenching), revealed low quartz and serpentine, a magnesium silicate hydroxide, formation at the interface. This glancing-incidence

angle technique produces x-ray penetration only in the 1-2 μm surface layer of the specimen, allowing for more sensitive detection of near-interface species over bulk phases. Similarly, 2° thin-film XRD scans of the titanium-ion implanted substrates revealed peaks corresponding to a titanium oxide and an alkali-stuffed silicate.¹⁸

In the reactive wetting scenario involving pre-oxidized substrates, one can propose the formation of serpentine and quartz at the interface by the following reaction

where the reactants are dissolved in the starting glass. Migration of MgO from the glass to the pure SiO_2 scale can be driven by the concentration gradient and the free energy of silicate formation in the surface layer. Since decomposition of SiO_2 into Si and O_2 gas would not yet occur at the vacuum used in this study,²¹ the occurrence of bubbles at the interface may be attributed to reaction of the SiC substrate with the pre-oxide scale to form SiO gas and CO gas.

This reaction has been shown to proceed at the processing temperatures used here in carbon-rich SiC systems (Hexaloy SiC contains residual carbon) at very low oxygen partial pressures,²² as encountered in a graphite element furnace at high vacuum. The depletion of the SiO_2 scale due to the formation of the silicate and the gaseous byproducts of the substrate reaction could account for the reduction in bubbling rate seen after 30 minutes at 1550°C.

For reactive wetting involving titanium ion-implanted substrates, one can propose the following reaction for the formation of TiO_2 and an alumina-stuffed silicate.

In this case the depletion of titanium and/or the increase in diffusion path for SiO_2 to the interface due to titania formation is believed to cause the reduction in bubbling rate observed.

A fast heating rate was required to maintain a homogeneous glass with good flow characteristics and wetting. Sessile droplets of glass heated at 60°C/min. 1550°C, followed by rapid quenching in flowing helium to the glass transition temperature, were clear or slightly opaque, indicating the absence of crystallization or phase separation. In contrast, specimens heated at only 5°C/min. had sessile droplets that did not remain in good contact with the surface after quenching, forming instead a hollow cap of solid. In addition, the milky white color attested to phase separation and/or crystallization, which in turn slowed the spreading of the droplet. Similarly, rapid quenching was necessary to limit phase separation and crystallization upon cooling to the glass transition point, thus allowing for the *controlled* crystallization of cordierite with a subsequent heat treatment. 28°C/min cooling rates were obtained over the primary range of cordierite crystallization (1400-950°C) with a high flowrate of helium gas (which has a thermal conductivity several times higher than either argon or nitrogen).

Fluoride ion as a fluxing agent has long been known to be effective in improving melt homogeneity and reducing glass melting point and viscosity.^{23,28} In this work the effect of minor additions on delaying phase separation and crystallization was also observed. Doping with 1 wt. % CaF₂ delayed the phase separation inherent in the glass, as observed by the near 100°C reduction of the "clearing temperature", or temperature above which the glass becomes optically clear. If phase separation or crystallization occurs, the difference in refractive index of the different phases leads to a cloudy or milky coloration.²⁴ X-ray maps of phase separated droplets showed relative enrichment of Mg, Al, and Ba in some, with a contact angle below 70°, while the higher viscosity high SiO₂-containing droplets displayed a 100° contact angle. In contrast, when the CaF₂-doped glass was heated slowly, no droplet segregation was seen, the glass remained transparent, and a sub-90° contact angle was measured.¹⁸ These observations could be attributed to fluorine's ability

to substitute for oxygen in the glass and preserve a highly disordered network. Precipitation of barium fluoride could also serve to limit the formation of a barium oxide-rich immiscible phase. By maintaining the homogeneous glassy state the flux allows for processing at lower temperatures without compromising the desired wetting characteristics on SiC. Equivalent contact angles were obtained with the 1% flux addition when processed at the lowered peak temperature of 1500°C.

(3) Microstructural Evolution

Microstructural control of the interlayer to improve thermomechanical properties was accomplished with a two step process: heterogeneous nucleation of a precursor phase in the bulk, followed by a crystallization and grain growth heat treatment. Figure 4 illustrates the effect of quench rate on phase morphology. It shows SEM micrographs of joints with slow cooling (10°C/min.) and rapid cooling (25°C/min.) to the glass transition temperature of 850°C, immediately followed by slow cooling (2°C/min.) to room temperature. Slow cooling produced nucleation and growth of large polygonal and elongated dendritic crystals at the SiC interface (Fig. 4a and 4b). EDS analysis showed the relative enrichment of aluminum in the polygonal crystals, indicative of the presence of mullite. Elongated crystals are characteristic of cordierite,^{25,26} which was confirmed with TEM. In contrast, joints with rapid cooling showed no evidence of interface nucleated crystallization in the SEM, and the morphology appears indistinct (Fig. 4c).

Figure 5, thin-film XRD scans of fracture surfaces, shows the loss of preferential crystalline orientation of cordierite with increasing quench rate and nucleation dwell time. In (a), crystallized from slow cooling (15°C/min.) with no nucleation dwell, the x-ray diffraction scan shows the absence of secondary cordierite peaks, indicative of a high degree of crystallographic texturing. It is likely that this microstructure is comprised of interface nucleated grains which grow to impingement in the joint. Grain boundaries are not revealed by the etch in Figure 5a. Without the

etch, the microstructures displayed no contrast by SEM. Since both cordierite and mullite are resistant to the etchant used, when complete conversion to these phases occurred, no contrast was seen. In (b), crystallized from slow cooling with a 5 hour nucleation dwell, secondary cordierite peaks occur, but their intensities are disproportionate to the main peak, and the corresponding microstructure shows elongated grains on the order of 2 μm and larger size. In Figure 5c, crystallized from rapid cooling (28°C/min.) with a 5 hour nucleation dwell, however, no texturing occurred as the proper ratio of cordierite peak intensities was observed. The corresponding microstructure shows equiaxed grains on the order of 1 μm size. These observations suggest that when the quench rate and nucleation dwell are sufficient, heterogeneous nucleation and growth of cordierite in the bulk is favored over interface nucleation.

(4) Cordierite Nucleation and Crystallization

Heterogeneous nucleation of cordierite on magnesium titanate precipitates in TiO_2 doped cordierite glass-ceramic was first demonstrated by Maurer et al.²⁷ In the BaO-doped glass studied here, the barium silicate $3\text{BaO} \cdot 5\text{SiO}_2$ was observed in glass powders removed after the quench and nucleation stages, and prior to crystallization. This is illustrated in the x-ray diffraction scans of Figure 6. In (a), 2° thin-film XRD scan of a joint removed immediately after quench, the barium silicate peak at 3.75 Å is discernible, along with the silica peak at 4.17 Å. The ratio of peak heights, corrected for background, was 0.28. In (b), from a joint removed after quench and 5 hour nucleation, the same peaks occur, with a corrected peak intensity ratio of 0.37. It is likely that the SiO_2 peak noted corresponds to a stuffed alkali silicate structure, as no crystalline silica peak matches it conclusively. The higher silicate : silica peak intensity ratio after 5 hours nucleation demonstrates the more complete phase separation with associated diffusion of barium to form the silicate. The scan in (c) again shows that cordierite crystallization without crystallographic

texturing was possible under these conditions. It was taken on powders to enable a more accurate determination of mullite concentration, since the primary mullite and SiC peaks overlap in the diffractometer scans taken on fracture surfaces.

The absence of an amorphous region in the XRD scan of the fracture surfaces (Fig. 5) and in the powder XRD scan in Figure 6c clearly indicates nearly complete crystallization is taking place. In the equilibrium $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system, cordierite melts incongruently into a mullite containing liquid, and mullite and α -cordierite were detected by XRD and confirmed with TEM. The matrix phase is most likely a stuffed quartz derivative structure, which would have both a low (α , $T < 550^\circ\text{C}$) and a high (β , $T < 900^\circ\text{C}$) polymorph. The peak at $2.61 \text{ \AA}$ ($2\theta = 34.3^\circ$) in Figure 5c is consistent with the most intense peak attributed to a high quartz solid solution.²⁹ This form of distorted quartz containing magnesium and aluminum substituting for silicon would have d-spacings close to those of, and possibly enter into solid solution with, α -cordierite.²⁹⁻³¹

Despite the presence in the pre-oxidized substrates of an interfacial silicate or quartz phase during the glass spreading stage, only cordierite was detected by TEM after full crystallization. In Figure 7 crystalline α -cordierite is identified at the interface, along with a spinel grain in the interlayer. Bright field/Dark field imaging and selected area diffraction showed the same cordierite grain below and adjacent to the spinel grain. Presumably absorption of the interfacial species formed during reactive wetting into the recrystallizing quartz phase to form cordierite is occurring. (No significant amount of spinel was detected by XRD; other investigators have found that it is almost entirely absorbed during the high temperature crystallization anneal.³⁰) Whereas the presence of a brittle intermediate phase or amorphous carbon would lead to a weakly bonded interface,³² a dissolution reaction leading to the formation of a homogeneous interface would act to improve the interfacial cohesive strength.

The average cordierite grain size in the joint, determined by a lineal intercept technique from SEM micrographs, was approximately 1 μm , and the volume fraction of the preferentially etched phases (quartz and residual glass) was found to be 34%, as determined by the lineal intercept method described by Kingery, *et al.*³³ This also was in agreement with the cordierite : stuffed-quartz peak intensity ratio obtained from the thin-film XRD scan of the fracture surface in Figure 5c. The ratio of cordierite to mullite concentration was determined by direct comparison of the integrated peak intensities of the (111), (110), and (121) mullite peaks with the (102), (202), and (211) α -cordierite peaks in Figure 6c. These peaks were chosen because they are distinctly resolvable in the spectrum (no overlapping peaks), and have I/I_0 ratios ≥ 0.5 . The 12 weight % fraction of mullite, W_{mull} , assumed to be precipitating upon quenching or during the recrystallization process, was found from the relation

$$W_{\text{cord}} + W_{\text{mull}} = (1 - W_{\text{quartz} + \text{glass}}) \quad (7)$$

once the ($W_{\text{cord}} / W_{\text{mull}}$) is known. The assumption that no preferential crystallographic orientation is present is based on the near-theoretical ratios of x-ray diffraction peaks in the cordierite and mullite phases in Figures 5c and 6c. Deconvolution of the cordierite/mullite overlapping peak at $\sim 3.37 \text{ \AA}$ in the XRD scan of the fracture surface in Figure 5c and analysis of TEM micrographs yielded similar results. Table 1 lists the composition of the polycrystalline joint material, as determined by these methods. The final room-temperature microstructure obtained in Figure 8 is likely to be composed of α -cordierite, mullite, and a distorted α -quartz, with a small amount (~ 2 wt. %) of residual barium-rich silicate glass. Both were crystallized at 1200°C for 2 hours after a 5 hour nucleation dwell at 850°C . The interconnected microstructure is suggestive of the coalescence of discrete second phase particles during coarsening. Such effects have been documented in complex silicate systems.^{34,35}

(5) Processing and Thermomechanical Properties

Using the rule of mixtures and the data shown in Table 2, the coefficient of thermal expansion of the interlayer was calculated at $5.1 \times 10^{-6} / ^\circ\text{C}$ (550-900°C), and $6.2 \times 10^{-6} / ^\circ\text{C}$ (25-550°C), assuming a polymorphic transformation from β - to α -quartz upon cooling. All properties used in the calculation, unless otherwise noted, were obtained in a materials handbook.³⁶

It is clear from these properties that the easiest way to tailor the thermal expansion coefficient of the composite interlayer, and thus improve mechanical properties, is to change the extent of cordierite crystallization. The process map depicted in Figure 9 assists in visualizing the procedure by which this was accomplished in this study. The SiC/cordierite joints are heated at a sufficient rate (60°C/min.) to prevent partial phase separation or crystallization in the melt (which would adversely affect flow properties and wetting), and held at the optimum combination of peak temperature and dwell time (1500°C, 30 minutes for 1% CaF₂-doped glass) for minimizing the contact angle and interfacial void formation due to the reactive wetting process. A fast quench (28°C/min.) to 850°C (just above the glass transition point) prevents the formation of large interface-nucleated cordierite and mullite grains. After holding for a sufficient time at the nucleation dwell (5 hours was used) a 2-phase dispersion of barium-rich silicate glass and cordierite glass is formed. Upon further heating crystallization of the cordierite glass to a stuffed β -quartz derivative phase, possibly nucleated on barium silicate precipitates, precedes the formation of α -cordierite. 12 weight % mullite is also precipitated throughout the joint layer. During crystallization slow heating is essential (10°C/min. was used) to prevent deformation of the glass-ceramic and maintain a rigid skeletal network. Once in the primary range of cordierite crystallization (950-1400°C) the time and temperature at which α -cordierite is formed out of the β -quartz reservoir determines the resulting phase distribution, and therefore the thermomechanical

properties of the composite. This is illustrated with the schematic process zone yielding interlayers of acceptable CTE's in Figure 9. Given that a crystallization heat treatment of 1200°C for 2 hours produced CTE-matched joints with high strength, processing in this zone, while preserving the lever rule between cordierite and quartz, should yield similar microstructures. Longer hold times at the crystallization temperature would lower the CTE (as well as decrease the modulus mismatch with SiC) by furthering cordierite grain growth at the expense of the quartz phase. The toughness of the material would also be increased by providing more frictional sliding surface area for grain pullout and crack deflection. Since larger grains also provide for larger flaw initiation points, however, a proper trade-off between strength and toughness is necessary to optimize the mechanical integrity of the joint.

If the thermal expansion of the interlayer exceeds that of the base material, residual tensile stresses develop upon cooling which can weaken the joint when placed in tension. Conversely, if the interlayer has a lower expansion than the substrate, the joint will be left in compression, which could tend to strengthen the joint when placed in tension. In addition, when the polycrystalline joint material is comprised of low CTE phases (e.g. mullite and cordierite) embedded in a matrix of higher CTE (quartz), compressive hoop stresses and tensile radial stresses can develop at interfaces which serve to toughen the composite.³⁸ With the cordierite/SiC joints studied here, the range of acceptable thermal expansion mismatch which will optimize the two aforementioned effects is controlled by the relative phase distribution of cordierite, mullite, and quartz via the heat treatment process.

(6) Mechanical Strength

Given the process parameters described here, the modulus of rupture, as determined by 4 point beam bending tests, was found to be most sensitive to the extent of coverage in the interlayer.

The main secondary effect was interlayer thickness. The thickness effect is essentially due to three factors; 1) a smaller sampling volume reduces the probability of finding a flaw of critical size for crack initiation and propagation; 2) more and/or larger imperfections due to processing exist in thicker layers, due to the lesser control of particle distribution during tape casting, and a 3% volume contraction associated with crystallization of this material, and 3) a constrained volume of stress relief reducing the driving force for interface crack propagation caused by the elastic moduli mismatch. Test beams with strengths above the quoted modulus of rupture for cordierite (290 MPa) are not unexpected in thin joints with total coverage and can be attributed to the aforementioned effects. A maximum strength of 540 MPa was measured for a specimen with the pre-oxidation surface treatment; this sample fractured into the bulk ceramic (Fig. 10).

For joints, the Weibull shape factor is not a direct indication of the quality of a particular material system, but rather a measure of the overall workmanship of the entire process (including control of wetting coverage and interlayer thickness), which determines the largest flaw size. In the Weibull plots of Figures 11 through 13, two sets of data are presented (for parts with less than 10 μm interlayer thickness), one for the pre-oxidized substrates and one for the titanium ion-implanted substrates. Figure 11 shows that the highest strength values were obtained with the pre-oxidized substrates, where fracture occurred in the base material. Upon examination of fracture surfaces, a direct correlation between the upper and lower strength distributions in the plot and wetting coverage could be made (the high strength parts had coverage > 85%). Figures 12 and 13 show the higher mean fracture strength attained with the titanium ion-implanted parts, although with a lower maximum value. With these specimens, failure usually occurred along the interface. However, the Weibull shape factor for the ion-implanted parts was superior, indicating better wetting coverage. Also, the higher shape factor obtained with rougher surface finish is suggestive of a more tortuous

crack path along an interface with greater mechanical interlocking. However, for the sample set with a high degree of wetting coverage, the fine polished substrates performed better (Weibull shape factor 5.7, compared to 3.9), due to smaller flaw initiation points present at the 1 μm interface. These effects should in general apply to the pre-oxidized substrates as well.

IV. Conclusions

A high strength room temperature SiC/SiC joint, in excess of 500 MPa, has been demonstrated by controlling the bulk thermal expansion coefficient and elastic modulus of a cordierite based glass-ceramic interlayer. The CTE for an interlayer composed of 55% α -cordierite, 31% stuffed quartz, 12% mullite, and 2% residual glass was estimated to be $6.2 \times 10^{-6}/^{\circ}\text{C}$ (25-550 $^{\circ}\text{C}$) and $5.1 \times 10^{-6}/^{\circ}\text{C}$ (550-900 $^{\circ}\text{C}$). This close match with α -SiC effectively limited thermal strain upon cooling and resulted in a joint of high mechanical strength. Contact angles of 60 $^{\circ}$ were achieved during sessile drop experiments with a reactive wetting process. Minor additions (1%) of fluxing agent CaF_2 improved spreading of the glass on the SiC substrate and allowed for a lower temperature processing route, without significantly altering the crystallization path. Since conventional dilatometry is not sensitive enough to accurately measure CTE's in such thin joints, this method of estimated the thermal expansion by way of microstructural control may prove useful in the design of high strength joints. Future work should focus on improving wetting coverage and reducing the processing temperature further through the use of additives such as fluxes or alkali oxides.

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References

- ¹R. W. Rice, "Joining of Ceramics," pp. 69-111 in *Advances in Joining Technology*. Edited by J. Burke, A. Gorum, and A. Tarpinian. Brook Hill Pub. Co., Chestnut Hill, Massachusetts, 1976.
- ²M. M. Schwartz, *Ceramic Joining*. ASM International, Materials Park, OH, 1990.
- ³M. Ferraris, C. Badini, M. Montorsi, P. Appendino, and H. W. Scholz, "Joining of SiC_f/SiC Composites for thermonuclear fusion reactors," *J. Nuclear Materials*, **212-215** 1613-16 (1994).
- ⁴D. P. Stinton, A. J. Caputo, and R. A. Lowden, "Synthesis of fiber-reinforced SiC composites by chemical vapor infiltration," *Am. Ceram. Soc. Bull.*, **65** [2] 347-50 (1986).
- ⁵J. J. Cao, W. J. MoberlyChan, L. C. DeJonghe, C. J. Gilbert, and R. O. Ritchie, "In Situ Toughened Silicon Carbide with Al-B-C Additions," *J. Am. Ceram. Soc.*, **79** [2] 461-69 (1996).
- ⁶B. H. Rabin, "Joining of fiber-reinforced SiC composites by in situ reaction methods," *Mat. Sci. Eng.*, **A130** L1-L5 (1990).
- ⁷B. H. Rabin and G. A. Moore, "Reaction processing and properties of SiC-to-SiC joints," pp. 197-203 in *Joining and Adhesion of Advanced Inorganic Materials*, Proceedings of the Materials Research Society Symposium (1st: San Francisco, CA, 1993). Edited by A. H. Carim, D. S. Schwartz, and R. S. Silbergliitt, Materials Research Society, Pittsburgh, PA, 1993.
- ⁸B. J. Dalgleish, A. P. Tomsia, K. Nakashima, M. R. Locatelli, and A. M. Glaeser, "Low Temperature Routes to Joining Ceramics for High-Temperature Applications," *Scripta Metallurgica et Materiala*, **31** [8] 1043-48 (1994).
- ⁹M. L. Shalz, B. J. Dalgleish, A. P. Tomsia, and A. M. Glaeser, "New Approaches to Joining Ceramics for High-Temperature Applications," *Ceramic Transactions*, **35** 301-22 (1993).

- ¹⁰W. A. Zdaniewski, P. M. Shah, and H. P. Kirchner, "Crystallization Toughening of Ceramic Adhesives for Joining Alumina," *Advanced Ceramic Materials*, **2** [3A] 204-08 (1987).
- ¹¹D. N. Coon, "Vitreous joining of SiC fiber reinforced SiC composites," DOE Technical Report NTIS DE90-01295, 1989.
- ¹²N. Tamari, M. Honda, and M. Ebata, "Joining of SiC Ceramics with $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3\text{-MgO}$ mixture, Yogyo-Kyokai-Shi, **94** [10] 1087-91 (1986).
- ¹³R. D. Watkins and R. E. Loehman, "Interfacial Reactions Between a Complex Lithium Silicate Glass-Ceramic and Inconel 718," *Advanced Ceramic Materials*, **1** [1] 77-80 (1986).
- ¹⁴H. L. McCollister and S. T. Reed, "Glass-Ceramic Seals to Inconel," U.S. Patent No. 4,414,282, 1983.
- ¹⁵V. L. Richards, "Adsorption of Dispersants on Zirconia Powder in Tape-Casting Slip Compositions," *J. Am. Ceram. Soc.*, **72** [2] 325-27 (1989).
- ¹⁶R. Moreno, "The Role of Slip Additives in Tape Casting Technology: Part II-Binders and Plasticizers," *Am. Ceram. Soc. Bull.*, **71** [11] 1627-57 (1992).
- ¹⁷P. W. McMillan, chapters 1 and 2 in *Glass-Ceramics*. Academic Press, New York, 1964.
- ¹⁸T. J. Perham, M. S. Thesis, University of California at Berkeley (1996).
- ¹⁹W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, p. 604 in *Introduction to Ceramics*, 2nd ed. John Wiley and Sons, New York, NY, 1976.
- ²⁰B. L. Averbach and M. Cohen, *Trans. AIME* **176** 401 (1948).
- ²¹F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst.*, **160** 261 (1948).
- ²²N. S. Jacobson, K. N. Lee, and D. S. Fox, "Reactions of SiC and SiO_2 at Elevated Temperatures," *J. Am. Ceram. Soc.*, **75** [6] 1603-11 (1992).
- ²³P. W. McMillan, pp. 71-74 in *Glass-Ceramics*, Academic Press, New York, 1964.

- ²⁴R. H. Doremus, pp. 49-53 in *Glass Science*, John Wiley & Sons, New York, 1973.
- ²⁵K. Watanabe, E. A. Giess, and M. W. Shafer, "The crystallization mechanism of high-cordierite glass," *J. Mat. Sci.*, **20** 508-515 (1985).
- ²⁶M. D. Glendenning and W. E. Lee, "Microstructural Development on Crystallizing Hot-Pressed Pellets of Cordierite Melt-derived Glass Containing B₂O₃ and P₂O₅," *J. Am. Ceram. Soc.*, **79** [3] 705-13 (1996).
- ²⁷R. Maurer, *J. Appl. Phys.*, **33** 2132-39 (1962).
- ²⁸W. A. Zdaniewski, "DTA and X-Ray Analysis Study of Nucleation and Crystallization of MgO-Al₂O₃-SiO₂ Glasses Containing ZrO₂, TiO₂, and CeO₂," *J. Am. Ceram. Soc.*, **58** [5] 163-69 (1975).
- ²⁹W. A. Zdaniewski, "Microstructure and Kinetics of Crystallization of MgO-Al₂O₃-SiO₂ Glass-Ceramics," *J. Am. Ceram. Soc.*, **61** [5-6] 199-204 (1978).
- ³⁰A. G. Gregory and T. J. Veasey, "Review: The Crystallization of Cordierite Glass," *J. Mat. Sci.*, **6** 1312-1321 (1971).
- ³¹Z. Strnad, chapter 2 in *Glass-Ceramic Materials*. Elsevier Science Publishing Co., New York, NY, 1986.
- ³²R. Chaim and A. H. Heuer, "Carbon Interfacial Layers Formed by Oxidation of SiC in SiC/Ba-Stuffed Cordierite Glass-Ceramic Reaction Couples," *J. Am. Ceram. Soc.*, **74** [7] 1663-67 (1991).
- ³³W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, chapters 7 and 11 in *Introduction to Ceramics*, 2nd ed. John Wiley and Sons, New York, NY, 1976.
- ³⁴W. Haller, "Rearrangement Kinetics of the Liquid-Liquid Immiscible Microphases in Alkali Borosilicate Melts," *J. Chem. Phys.* **42** [2] 686-93 (1965).

³⁵T. P. Seward, D. R. Uhlmann, and D. Turnbull, "Development of Two-Phase Structure in Glasses, with Special Reference to the System BaO-SiO₂," *J. Am. Ceram. Soc.*, **51** [11] 634-43 (1968).

³⁶CRC Handbook of Materials Science and Engineering. Edited by J. F. Shackelford and W. A. Alexander. CRC Press, Inc., Boca Raton, FL, 1992.

³⁷Ferro Corp., EG-0221 product data.

³⁸A. G. Evans and T. G. Langdon, "Structural Ceramics," *Prog. Mater. Sci.*, **21** [3-4] 196 (1976).

Figure Captions

1. *Figure 1* Tape casting process for depositing joining precursor films of varying thickness.
2. *Figure 2* SEM micrographs of cordierite film on SiC processed in a) air, b) argon; and matching fracture surfaces when processed in c) argon, d) vacuum. In vacuum voids due to bubbling are absent. b, c, and d taken at 45° tilt angle.
3. *Figure 3* Indentation crack paths in joints of increasing thickness; a) 15 μm thick interlayer, b) 20 μm thick interlayer, and c) 35 μm thick interlayer. The incidence angle with the interface in each case was 45°. Although no interface debonding was seen, the 35 μm joint cracked even when the indent did not reach the interface.
4. *Figure 4* Effect of quench rate on phase morphology. Slow cooling (10°C/min.) resulting in a) mullite nucleation; and b) cordierite nucleation at the interface. Rapid quench (25°C/min.) resulting in mostly amorphous joint, (c). Samples were examined prior to crystallization heat treatment.
5. *Figure 5* Evolution of fine-grained equiaxed microstructure obtained with high quench rate and 5 hr. nucleation dwell time. (a) 15°C/min. quench, no nucleation dwell; (b) 15°C/min. quench, 5 hr. nucleation dwell; (c) 28°C/min. quench, 5 hr. nucleation dwell. All specimens crystallized 2 hr. at 1200°C. C = α -cordierite, M = mullite, Q = stuffed-quartz. E = enstatite, B = BaO.
6. *Figure 6* Thin-film XRD scan (2°) of joint, a) removed after quench; b) removed after quench and 5 hr. nucleation dwell; and c) XRD scan of powder removed after full process. S = silicon oxide, B = $3\text{BaO} \cdot 5\text{SiO}_2$, C = cordierite, M = mullite.
7. *Figure 7* TEM of cordierite/SiC interface crystallized 2 hr. at 1200°C after a 5 hr. nucleation dwell at 850°C. α -cordierite is identified at the interface after the crystallization anneal.

8. *Figure 8* SEM micrograph of cordierite/SiC joint after full process (25°C/min. quench, 5 hr. nucleation dwell at 850°C, and 2 hr. crystallization at 1200°C).
9. *Figure 9* Process map of the cordierite/SiC joining process, illustrating the heating schedule utilized and the phases present in each region. Dashed lines indicate approximate location of the cordierite crystal growth regime.
10. *Figure 10* Fracture surface of cordierite/SiC joint illustrating a) faceted cordierite fracture; and b) failure in ceramic on opposing SiC beam surfaces.
11. *Figure 11* Weibull distribution of rupture strength of SiC/Cordierite joints with pre-oxidized substrates, depicting two distributions dependent upon surface coverage.
12. *Figure 12* Weibull distribution of rupture strength of SiC/Cordierite joints with titanium ion-implanted substrates, showing higher mean strength for 1µm surface finish.
13. *Figure 13* Weibull distribution of rupture strength of SiC/Cordierite joints with titanium ion-implanted substrates, showing sample set with > 85% wetting coverage.

Tables

Table 1 Composition of Interlayer Material

Phase	Weight Fraction (%)
α -cordierite	55
Stuffed quartz	31
Mullite	12
Barium rich residual glass	2

Table 2 Parameters for determination of coefficient of thermal expansion

<i>Phase</i>	<i>CTE ($\times 10^6$, 0-1000°C)</i>	<i>Bulk Modulus (GPa)</i>	<i>Elastic Modulus (GPa)</i>	<i>Poisson's Ratio</i>	<i>Density (g/cc)</i>
α -cordierite	2.0 ³⁷	133	232 ³⁷	0.21	2.67 ³⁷
α -quartz	22.2	76.9	151	0.20	2.40
β -quartz	14.58	76.9	151	0.20	2.50
Mullite	5.1	308	484	0.238	2.93
Residual glass	4.3 ³⁷	76	150	0.17*	2.2*
α -SiC	5.1	340	637	0.19	3.21

* Obtained for vitreous silica

Figure 1 Tape casting process for depositing joining precursor films of varying thickness.

Figure 2 SEM micrographs of cordierite film on SiC processed in a) air, b) argon; and matching fracture surfaces when processed in c) argon, d) vacuum. In vacuum voids due to bubbling are absent. b, c, and d taken at 45° tilt angle.

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Figure 13 Weibull distribution of rupture strength of SiC/Cordierite joints with titanium ion-implanted substrates, showing sample set with > 85% wetting coverage.

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