Cohesive Energy of Interfaces and Toughness of Fluorine-Doped Si₃N₄/SiC Composites

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フッ素含有 Si₃N₄/SiC 複合材の界面凝集エネルギーと靱性

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Fracture mechanics and electron microscopy studies were systematically conducted on a dense Si₃N₄ material reinforced with high-aspect-ratio SiC platelets. This model system contained only an amorphous SiO₂ phase at the multigrain pockets and along the internal interfaces. Two different procedures (and their empirical combination) were followed to gradually weaken the grain interfaces and, hence, deliberately change the fraction of intergranular fracture within the material upon crack propagation. These procedures were: 1) the gradual addition of a fluorine impurity, which remains segregated at the grain boundaries after sintering, and 2) the adoption of a "quenching" process under high pressure. Quantitative high-resolution and analytical electron microscopy provided fundamental insight into the internal structure of the intergranular SiO₂ phase doped with fluorine and the corresponding microcracking processes. Quantitative fractography allowed to estimate the apparent cohesive energy of the internal interfaces of the composite and to relate it to the macroscopic material toughness.

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1. Introduction

When metals or metallic alloys exhibit segregation of impurities to grain boundaries, a drastic loss of ductility is often observed in fracture testing at room temperature.^{1,2)} This phenomenon has long been known as temper embrittlement since a tempering process is generally needed for grain-boundary segregation to occur (e.g., in the range 350–600°C in steels). In metallic materials embrittled by impurity segregation, fracture occurs by a "brittle" separation of grain boundaries and, as a consequence, the resulting fracture energy may be drastically reduced. According to many systematic studies, the approach to get high toughness in metal systems is generally established as that of improving the grain-boundary cohesive strength to promote transgranular crack propagation, this circumstance allowing to exploit the intrinsic toughness of the metal grains.³⁾

In contrast to the aforementioned metal systems, the strategies established for toughening polycrystalline ceramics and related composite materials at room-temperature, follow a completely opposite direction.⁴⁾ Because of the intrinsic brittleness of the ceramic crystallites, the occurrence of grain-boundary

fracture is generally considered as an imperative requirement to achieve some toughening effect. As a matter of fact, avoiding cleavage fracture of the grains allows to activate extrinsic micromechanisms shielding the crack faces behind a "brittle" (i.e., atomically sharp) crack tip.^{5,6)} The toughening effect obtainable in ceramic polycrystals, which undergo grain-boundary fracture is also proved to be noticeably enhanced by the presence of grains with elongated shape.⁷⁾ It is beyond the scope of this paper to provide a comprehensive description of the micromechanisms of toughening in ceramics, a topic recently reviewed by Evans⁴⁾ and Becher.⁸⁾ It is, however, matter of some concern here that the highest toughness data achieved so far in polycrystalline ceramics (with elongated microstructures) through the reduction of the grain-boundary cohesive strength, although strongly improved with respect to those of the respective single-crystals, are still to be considered quite low as compared to even "brittle" metals, which apparently fail by the same grain-boundary fracture mechanism. As an example, we shall refer to data for high-purity (covalent) polycrystalline ceramics such as Si₃N₄ and SiC, which

have an intrinsic toughness (i.e., the toughness value experienced by the material for a completely transgranular failure mode) of 8–12 J/m^2 ,^{9),10)} while several times higher values have often been reported for both monolithic and composite Si_3N_4 and SiC materials failing by “brittle” separation of grain boundaries.¹¹⁾ These toughness data, however, cannot achieve the level of the most “brittle” metallic alloys. Hence, a striking feature arises in understanding the maximum toughness achievable in polycrystalline ceramics by the “brittle” grain-boundary separation process and, in particular, whether the possibility exists of enhancing the room-temperature toughness of ceramics to the level of brittle metals (i.e., several hundred J/m^2), which would be extremely high among the presently known ceramic and related composite materials.

Despite the extensive efforts addressed to theoretically model the fracture processes in ceramics and related composites, only very few systematic experimental studies have been reported about the role of interfacial cohesive energy on the macroscopic toughness of the material. It is hard to accept that the toughening effect in ceramics is predominantly dictated by the morphology of the grains without emphasis placed on the interfacial properties, as initially treated by some early work on the subject.¹²⁾ Furthermore, it is physically plausible to expect that, by systematically reducing the interfacial cohesive energy, γ_b , the macroscopic toughness of a ceramic polycrystal will first increase through the gradual elimination of cleavage grain fracture (and the effect of crack-wake shielding mechanisms). However, after experiencing a peak value for an appropriate γ_b value, the toughness starts decreasing, the material being ultimately unbonded on the microstructural level or, in other words, already fractured below certain γ_b values.

This report describes an attempt to determine systematically the dependence of the macroscopic toughness values, measured in a polycrystalline $\text{Si}_3\text{N}_4/\text{SiC}$ composite system, on the cohesive energy of its internal interfaces. A model material containing only pure SiO_2 at the grain and phase boundaries was selected as a reference polycrystalline body and systematically doped with increasing amounts of fluorine (F), in order to vary the degree of cohesive bonding developed between the Si_3N_4 and the SiC crystallites during the sintering process. Furthermore, it was empirically found that, in the present composite, a drastic change in the cooling rate after the sintering cycle could alter the fraction of intergranular path during crack propagation, in particular, influence the apparent cohesive strength of the grain boundaries. Fracture mechanics and quantitative fractography data on composites containing different amounts of fluorine and/or cooled down after sintering at different cooling rates, have been used here to clarify the role of γ_b on the macroscopic

toughness of the material.

2. Model $\text{Si}_3\text{N}_4/\text{SiC}$ composites

The composite material examined in this study consisted of a high-purity Si_3N_4 matrix (E-10, Ube Ind. Ltd., Ube, Japan) and 25 mass% α -SiC platelets (Grade M, C-Axis Co., Jonquiere, Canada; average thickness (t) and diameter (H) 3.2 and 26.2 μm , respectively). Sintering was performed without any external addition of densification aids. Complete densification ($>99.5\%$) was achieved at a temperature of 2050°C by hot-isostatically pressing (HIP) the material under 180 MPa for 2h. High pressure was applied in a HIP apparatus via argon gas while the specimen was encapsulated in a borosilicate glass tube evacuated to 0.1 Pa, in order to avoid the infiltration of gas into the powder compact. A detailed description of both the mixing and the sintering process has been reported previously.¹³⁾ Although no extraneous phase was added to the starting $\text{Si}_3\text{N}_4/\text{SiC}$ powder blend, there was an oxygen impurity content of ≈ 1.5 mass% as a consequence of the oxidation process of the Si_3N_4 powder after exposure to the atmosphere. This impurity resulted in the formation of a few mass% of glassy SiO_2 , which remained segregated at the grain boundaries after densification. Chemical analyses have shown that the total amount of impurities other than oxygen present in the sintered body was <1200 ppm.¹³⁾ Microstructural characterization by image analysis techniques monitored the development during HIP sintering of the equiaxed Si_3N_4 matrix grains with an average size of ≈ 1 μm while the SiC platelets were found to obey a three-dimensionally random distribution.¹⁴⁾

In comparison with this “pure” (undoped) $\text{Si}_3\text{N}_4/\text{SiC}$ system, two materials with an identical phase composition but doped with different amounts of F were also fabricated by the same glass-encapsulation HIP process. The sintering temperature to achieve complete densification was 1900°C for the F-doped materials, while the pressure and the holding time conditions were kept constant (i.e., the same as those adopted for the undoped sample). The HIP conditions were slightly modified to ensure that the average size of the matrix grains was comparable to that of the undoped material. The F-dopant was introduced into the composite bodies by adding increasing amounts of pulverized polytetrafluoroethylene (Teflon, E.I. du Pont de Nemours, Wilmington, DE, USA) during the mixing procedure of the raw powders. The mixture was then pre-fired in high vacuum at 1200°C, in order to depolymerize the teflon structure to tetrafluoroethylene C_2F_4 and, successively, to eliminate the CO gas. The choice of teflon as the starting compound for introducing F into the material was made since it does not involve the contemporary incorporation of H into the specimen and, hence, allows an easier modelling of the grain-boundary SiO_2 structure when only F remains

segregated at the grain boundaries.

3. Structure and cracking of interface boundaries

The overall microstructure and the grain-boundary structure as well as the internal cracking of the materials were characterized by both transmission electron microscopy (TEM) and high-resolution (HREM) studies using a 400-kV microscope (Model 4000EX, JEOL Ltd., Tokyo, Japan) whose point-to-point resolution was 0.18 nm. TEM foils were prepared by the usual procedure consisting of grinding, dimpling, and argon-ion-beam thinning. A light carbon coating was performed to avoid charging during TEM observation. In all the materials investigated, the fluorine dopant was systematically found to be segregated at grain boundaries after sintering. No fluorine could be detected within the Si_3N_4 or the SiC grains. The respective amounts of F in the glassy- SiO_2 intergranular film of the sintered bodies were determined by both energy-dispersive X-ray spectroscopy (EDX) and by electron energy-loss spectroscopy (EELS). EELS analyses indicated a rather homogeneous distribution of fluorine along the SiO_2 boundaries, while quantitative EDX data showed an average amount of 2.4 and 5.8 mass% of F in the SiO_2 glass structure of the two doped composites, respectively. Further details about EELS and EDX microanalyses have been given elsewhere.¹⁵⁾ According to a previously established technique,¹⁶⁾ the grain-boundary film thickness of the sample with 5.8 mass% fluorine in the glassy- SiO_2 phase was accurately measured and found to slightly increase to 1.1 ± 0.1 nm, as compared to the thickness of

1.0 ± 0.1 nm measured in the undoped sample.¹⁷⁾ The structural characteristics of the grain boundary are shown in the HREM micrograph of Fig. 1, which represents the glassy- SiO_2 film in the sample containing the higher F content. This sample was slowly cooled down from sintering temperature (i.e., 1900°C) at a cooling rate of 100°C/h. A typical EELS spectrum, revealing the presence of both fluorine and oxygen in the amorphous film, is also shown together with a proposed model of the SiO_2 glass structure containing F. This simplified structural model was drawn according to previous models reported in the literatures¹⁸⁾⁻²⁰⁾ and under the assumption that no nitrogen from the Si_3N_4 grains is dissolved in the glass. It should be borne in mind that TEM inspection of grain boundaries in a specimen containing the same starting amount of teflon but "quenched" from the sintering temperature at a rate of $\approx 650^\circ\text{C/h}$, failed to individuate structural differences as compared to the slowly cooled sample.

As shown in Fig. 1, a peculiarity of the F-doped SiO_2 structure may reside in the presence of non-bridging Si-F bonds which result from the replacement of one O^{2-} ion by two F^- ions to compensate for ionic valency. Although F and O atoms have almost identical ionic radii (0.132 nm against 0.133 nm), the incorporation of two F^- ions for each O^{2-} ion is likely to lead to the detected (slight) increase in grain-boundary film thickness. Important micro-mechanical consequences can be related to the modification of the SiO_2 -glass structure by F. Non-bridging Si-F bonds may weaken the cohesive strength of the interfaces leading to easier cracking.

Fig. 1. HREM micrograph of the Si_3N_4 - Si_3N_4 grain boundary in the composite containing 5.8 mass% F in the intergranular SiO_2 phase (cooling rate 100°C/h). EELS analysis revealed the presence of F segregated at the boundary film. A simplified structural model of the SiO_2 glass including only Si, O, and F atoms is also shown (see inset).

Fig. 2. TEM image of a cracked Si_3N_4 -SiC phase boundary observed in the composite containing 5.8 mass% F in the SiO_2 glass structure and cooled down at $100^\circ\text{C}/\text{h}$. Note that F was also detected at the phase boundaries by EELS analysis. Arrows indicate the phase-boundary crack.

Moreover, with increasing temperature, the viscosity of the SiO_2 film may significantly be reduced owing to the presence of F.²¹⁾ We have been concerned with this latter phenomenon in a separate paper,¹⁵⁾ where internal friction and creep data of the present composites were discussed in detail. Here, emphasis is placed on the weakening of the interfacial cohesive energy, which leads to easy cracking of the phase boundaries. Figure 2 shows a TEM image of one of the several cracked $\text{Si}_3\text{N}_4/\text{SiC}$ interfaces observed in the specimen containing 5.8 mass% F at the boundaries and slowly cooled down at $100^\circ\text{C}/\text{h}$. These cracks seem to be easily formed inside the specimen by applying even small loads. No microcracks were found by TEM inspection in the as-sintered undoped specimen for any cooling rate condition.²²⁾

4. Cohesive energy of interfaces and toughness

In previous fracture mechanics and fractography studies on the undoped composite,^{23),24)} it was empirically found that a quenching process with a cooling rate of $\approx 650^\circ\text{C}/\text{h}$ (i.e., analogous to the tempering process in metals) from the sintering temperature, while maintaining high externally applied pressure, leads to a noticeable increase of the fraction of transgranular crack propagation with the consequence of a macroscopic embrittlement of the material. On the other hand, specimens slowly cooled down at $100^\circ\text{C}/\text{h}$ showed relatively high toughness values. So far, the physical origin of such a fracture behavior remains uncertain, being possibly related to residual compressive microstresses developed at the interfaces by the quenching process under HIP pressure²⁴⁾ or to internal cracking/dislocation pile-up in the basal plane of the α -SiC reinforcing crystallites.^{25),26)}

Quenching the composites doped with F also produced a reduction in toughness. However, some interesting features were revealed by quantitative

fractography. The work of fracture (WOF) of the materials, measured in bending geometry on chevron-notched specimens, was determined from the areas under the stable load-displacement curves and the respective ligament areas.^{13),27)} Profilometric analyses of the fracture surfaces were performed by a three-dimensional scanning image analyser (3D-SIA), which allowed to automatically determine surface roughness, R_L , over the entire fractured area of the notched bars with a resolution on the order of μm .^{23),24)} Figure 3 shows the respective fractions of transgranular and intergranular crack propagation for the composites containing different amounts of F in the SiO_2 glass boundary and cooled down after sintering at different rates. The fraction of intergranular crack propagation, ξ , was determined according to the following equations:

$$\xi = (R_L - 1) / (R_L^0 - 1) \quad (1)$$

$$R_L^0 = 1.125 + 0.25 \left\{ \left[(H+t)/\Delta \right] - \left[t/\Delta (\pi/2 - \theta_L) \right] \int_{\theta_L}^{\pi/2} (1/\tan \theta) d\theta \right\} \quad (2)$$

where R_L and R_L^0 are the roughness value experimentally measured and the maximum roughness theoretically computed for a completely intergranular crack path, respectively. Δ and θ are the center-to-center near-neighbours distance and the acute angle between the platelet and the main fracture plane, respectively. The first numerical term on the right hand side of Eq. (2) represents the maximum theoretical roughness increase due to the matrix (volume fraction 75%) under the hypothesis that it is constituted by a regular array of hexagonal grains whose apothem is equal to the average grain size. The second numerical term accounts for the maximum roughness increase related to a crack path circumventing a 25 vol% fraction of randomly oriented platelets. In a previous report,¹⁴⁾ the parameter Δ was measured as a function of the SiC-platelet content of the present geometry, giving an average H

Fig. 3. Average fractions of intergranular and transgranular fracture propagation as calculated from the respective roughness data (obtained by 3D-SIA) through Eqs. 1 and 2. Amounts of F dopant in the grain boundary SiO_2 phase and cooling rates are also given.

value (for the addition of 25 vol%) of $24.2 \mu\text{m}$. In the present calculation, the lower boundary of integration was assumed as $\theta_L = \pi/90$. The accuracy of the ξ values determined by solving Eqs. (1) and (2) was checked by comparing them with the ξ values experimentally obtained on crack profiles observed by TEM in two of the present composites.²⁴⁾

The dependence of the measured WOF of the materials on the (average) interfacial cohesive energy, γ_b , is shown in Fig. 4. The γ_b values were calculated from the fractographic data, given in Fig. 3, according to the following equation:²⁸⁾

$$\gamma_b = (E'_m/E'_b) \gamma_m \cos^4(\xi\pi/2) \quad (3)$$

where $E' = E/(1-\nu^2)$ is the elastic modulus for plane strain conditions, ν is the Poisson's ratio and the subscripts m and b refer to matrix grains and grain boundary, respectively. In the calculation, E_m , ν_m and γ_m were assumed equal to 312 GPa, 0.23²⁹⁾ and 10.7 J/m^2 ,¹⁰⁾ respectively. On the other hand, $E_b = 72 \text{ GPa}$ and $\nu_b = 0.16$ were assumed for the SiO_2 glass-boundary film.³⁰⁾ In the present approximate procedure, it was assumed that no variation of the bulk elastic properties of the SiO_2 glass occurred with the incorporation of F. As shown in Fig. 4, within a certain range of the (apparent) grain-boundary fracture energy, the measured macroscopic WOF value increases with decreasing γ_b value. This is clearly due to the development of interface microcracking and debonding processes just ahead of the crack tip, which leads to the gradual elimination of cleavage fracture of the individual grains and, consequently, allows the SiC platelets to be circumvented and, thus, to operate toughening mechanisms in the crack wake. In this range of γ_b , although the internal interfaces of the materials are still sufficiently bonded to ensure microstructural integrity, the weakening of their cohesive strength can produce some beneficial effect on the overall fracture resistance of the composites. On the other hand,

despite the high fraction of intergranular crack propagation, which can be produced by combining the effect of F addition and quenching process, a reduction in toughness is noticed. This embrittlement was also found to be accompanied by a noticeable change in shear modulus which decreased for about 20% from 140 GPa to 110 GPa. This latter data strongly suggests the presence of large portions of unbonded interfaces which cannot transmit internal microstresses and lead to the observed decrease in the macroscopic stiffness. The present data also envisage that, for γ_b values below a certain lower limit, spontaneous cracking of the internal interfaces may occur and the material, virtually unbonded on the microstructural level, easily undergoes fracture on the macroscopic scale.

5. Conclusion

In conclusion, the present study provides clear evidence that segregation of impurities, which is thought to produce non-bridging bonds and act as structural modifiers of the intergranular glassy phase in Si_3N_4 ceramics (e.g., fluorine in SiO_2), can remarkably weaken the cohesive strength of internal interfaces. This phenomenon promotes debonding processes ahead of the crack tip and, thus, leads to some crack-wake toughening effect, once intact elongated grains are left unfractured behind the tip of the advancing crack. Optimum interfacial cohesive energies for toughening were found to be comprised within the range of $1\text{--}5 \text{ J/m}^2$, namely a about 0.5–10 times lower value compared to the intrinsic fracture energy of the individual grains of the polycrystal. The benefit in toughness arising from weakening the interfacial strength, however, appears to be physically limited to an increase of about one order of magnitude (in WOF), as compared with a completely transgranular crack path (i.e., to the bulk WOF value of the individual grains of the polycrystal). Furthermore, the approach for pursuing high toughness by weakening the internal interfaces in Si_3N_4 -based ceramics seems to be incompatible with the high stiffness values which are often required in structural applications.

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References

- 1) C. J. McMahon, *Temper Embrittlement in Steel*, ASTM STP, 407, 127–35 (1968).
- 2) M. Guttman, Residuals, "Additives and Materials Properties", Philos. Trans. R. Soc. Lond. A295, Cambridge University Press (1980) p. 151.
- 3) C. T. Liu, C. L. White, C. C. Koch and E. H. Lee, "High

Fig. 4. Measured WOF values as a function of the (average) interfacial cohesive energy, γ_b . One sample represents one data point. The fraction of F at the interfaces and the cooling rates after sintering are specified.

- Temperature Materials Chemistry II", Ed. by Z. A. Munir and D. Cubicciotti Pennington, New Jersey, The Electrochemical Society (1983) p. 32.
- 4) A. G. Evans, *J. Am. Ceram. Soc.*, **73**, 187–98 (1990).
 - 5) D. S. Dugdale, *J. Mech. Phys. Solids*, **8**, 100–05 (1960).
 - 6) G. I. Barenblatt, "Advances in Applied Mechanics", Vol. 7, Academic Press, New York (1962) p. 55.
 - 7) F. F. Lange, *J. Am. Ceram. Soc.*, **56**, 445–53 (1973).
 - 8) P. F. Becher, *J. Am. Ceram. Soc.*, **74**, 255–75 (1991).
 - 9) A. Ghosh, M. G. Jenkins, K. W. White, A. S. Kobayashi and R. C. Bradt, Proceedings of the 3rd International Symposium on Ceramic Materials and Components for Engines, American Ceramic Society Columbus, Ohio (1988) pp. 592–97.
 - 10) G. Pezzotti, I. Tanaka and T. Nishida, *Philos. Mag. Lett.*, **67**, 95–100 (1993).
 - 11) E. Tani, S. Umebayashi, K. Kishi, K. Kobayashi and M. Nishijima, *Am. Ceram. Soc. Bull.*, **65**, 1311–18 (1986).
 - 12) K. T. Faber and A. G. Evans, *Acta Metall.*, **31**, 565–77 (1983).
 - 13) G. Pezzotti, *J. Am. Ceram. Soc.*, **76**, 1313–20 (1993).
 - 14) G. Pezzotti, *Acta Metall. Mater.*, **41**, 1825–42 (1993).
 - 15) G. Pezzotti, K. Ota, H.-J. Kleebe, Y. Okamoto and T. Nishida, *Acta Metall. Mater.*, in press.
 - 16) H.-J. Kleebe, M. K. Cinibulk, R.M. Cannon and M. Rühle, *J. Am. Ceram. Soc.*, **76**, 1969–81 (1993).
 - 17) H.-J. Kleebe, M. K. Cinibulk, I. Tanaka, J. Bruley, J. S. Vetrano and M. Rühle, "Tailoring of Mechanical Properties of Si_3N_4 Ceramics", Ed. by M. J. Hoffmann and G. Petzow, Kluwer Academic Publ., The Netherlands (1944) pp. 259–66.
 - 18) W. J. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841–45 (1932).
 - 19) W. D. Kingery, H. K. Bowen and D. R. Uhlmann, "Introduction to Ceramics", 2nd ed., Wiley & Sons, New York (1976) p. 97.
 - 20) K. Awazu, *J. Ceram. Soc. Japan*, **102**, 1060–66 (1994).
 - 21) M. Ohashi, M. Tateda, K. Tajima and K. Shiraki, *Electr. Lett.*, **28**, 1008–12 (1992).
 - 22) G. Pezzotti, B.-T. Lee, K. Hiraga and T. Nishida, *J. Mater. Sci.*, **28**, 4787–97 (1993).
 - 23) G. Pezzotti, K. Noda, Y. Okamoto and T. Nishida, *J. Mater. Sci.*, **28**, 3080–89 (1993).
 - 24) G. Pezzotti, B.-T. Lee, K. Hiraga and T. Nishida, *J. Mater. Sci.*, **29**, 1786–95 (1994).
 - 25) G. Pezzotti, *J. Ceram. Soc. Japan*, **101**, 1113–19 (1993).
 - 26) G. Pezzotti, R. Hiesgen and T. Nishida, *Philos. Mag. Lett.*, **68**, 45–49 (1993).
 - 27) G. Pezzotti, K. Niihara and T. Nishida, *J. Testing Eval.*, **21**, 358–65 (1993).
 - 28) A. Krell, J. Woltersdorf, E. Pippel and D. Schulze, *Philos. Mag.*, **51**, 765–77 (1985).
 - 29) G. Pezzotti, I. Tanaka and T. Okamoto, *J. Am. Ceram. Soc.*, **73**, 3039–44 (1990).
 - 30) S. Sakka, T. Sakaino, K. Takahashi and N. Soga, "Glass Handbook", Asakura Shoten (1980) p. 657.