Microstructural Studies of Ceramics and Ceramic Composites

M. RÜHLE and E. BISCHOFF*

Materials Department University of California Santa Barbara, CA 93106, USA
Now at: MPI für Metallforschung, Stuttgart, FRG

ABSTRACT

Microstructural studies of ceramics and ceramic composites reveal that interfaces and/or interfacial boundary layers play an essential role in the fracture behavior of these types of materials. Transmission electron microscopy (TEM) observations concerning the chemical stability of interfaces are reported. In addition, crack propagation experiments in whisker reinforced ceramics are described.

INTRODUCTION

Ceramics and ceramic composites are typically capable of withstanding higher temperatures than other materials. However, high temperature degradation phenomena exist that influence performance and reliability. The important degradation processes include creep, creep rupture, flaw generation, diminished toughness and microstructural instability. In this paper some microstructural observations are reported with respect to thermal degeneration and microstructural changes. Additionally, crack propagation studies in ceramic composites are described.

REMARKS ON MICROSTRUCTURE OF CERAMICS AND MECHANICAL PROPERTIES

The strength of a ceramic typically diminishes at elevated temperatures. A dominant microstructural consideration with regard to elevated temperature behavior is the existence of a grain boundary layer. Such boundary regions typically remain amorphous after liquid phase sintering and are silicate-based as elaborated by analytical TEM techniques (Clarke, 1979; Simpson et al., 1986). The grain boundary phase is responsible for rapid mass transport and may dominate the creep, creep rupture and oxidation behavior as well as the microstructural stability (Pask and Evans, 1987). Grain size also represents another important microstructural parameter, since it influences diffusion length.

The addition of SiC whiskers to Al_2O_3 causes significant improvement on mechanical properties (Becher and Wei, 1984; Chokshi and Porter, 1985). However, it has been shown that SiC whisker-reinforced Al_2O_3 is susceptible to thermal oxidation at elevated temperature (Lipetzky et al., 1988). Similarly, SiC fiber reinforced materials are extremely susceptible to annealing in air; consequently, the fracture behavior is changed dramatically at different temperatures

MATERIALS AND EXPERIMENTAL DETAILS

The following materials were used for our studies: (1) SiC whisker-reinforced Al_2O_3 (Greenleaf Corp.) and (2) LAS-fiber reinforced glass ceramics (United Technologies Corp.). The microstructural characteristics of the different materials were evaluated by TEM. Indentation induced cracks were evaluated, and characteristic features of crack resistance were identified.

EXPERIMENTAL OBSERVATIONS AND DISCUSSION

Monolithic Ceramics Many monolithic ceramics are composed of a crystalline phase and an amorphous grain boundary phase. The presence of the grain boundary phase can be detected by different TEM techniques. Large amorphous pockets at triple grain junctions can be crystallized by a post sintering annealing treatment (Bonnell, 1987). However, residual amorphous layers are usually present especially if the crystallized phase possesses a chemical composition which is different from the chemical composition of the amorphous pocket. The residual film is responsible for a high temperature degradation.

Wiederhorn et al.,(1986) showed that high temperature crack initiation and incremental growth occur by a selective cavitation process in which cavitation first occurs within relatively narrow grain boundaries (covered with amorphous film) that are, in case of a tensile experiment, roughly aligned normal to the tensile axis. Subsequently, cavitation occurs within inclined grain boundaries and multi-grain junctions to form a continuous open crack. TEM studies by Wiederhorn et al., (1988) of Al_2O_3 ceramics showed that high temperature cavitation occurs within the glassy portion of the grain boundaries. The microstructural observations have been correlated to mechanical creep rupture data.

Whisker Reinforced Ceramics Various TEM observations have been made of uncracked regions and in the vicinity of indentation induced cracks in SiC reinforced Al_2O_3 (20 vol% SiC whiskers). Far from the indentation, tilting experiments with the use of dark field techniques indicate that the SiC/Al_2O_3 interface consists of an amorphous phase typically about 5nm thick (Rühle et al., 1987). The SiC whiskers are heavily faulted, typical for different polytypes of α–SiC. Strain fields around the whiskers are indicative of thermal expansion induced residual strains.

Observations by the use of TEM in the region near an indentation have revealed considerable dislocation activity and associated microcracking, especially along SiC/Al_2O_3 interfaces. These processes presumably dominate the abrasion and erosion resistance of the composite causing material removal by the coalescence of deformation induced microcracks.

Crack tip studies (Rühle et al., 1987) at room temperature in the TEM have demonstrated that the observed behavior is appreciably influenced by foil thickness as compared with the diameter of SiC whiskers. In situ studies may have limited scope, especially when small foil thicknesses are used. The effects of a thin foil can be limited by using an indentation approach. Specifically, a crack was introduced by the use of a Vickers indenter and a thin foil was prepared in the plane strain region around the crack tip by back thinning of the specimen after the indentation was introduced.

In those foils having a thickness appreciably larger than the whisker diameter, the crack tip structure typically has the features depicted in Fig. 1. To analyze the essential characteristics it is important to separately appreciate the following features. When the whiskers fracture, the crack is invariably planar and normal to the whisker axis (see A in Fig. 1). Conversely, fracture in the alumina matrix tends to occur along grain boundaries (see B in Fig. 1). With this background, a sequence of views of the region depicted in Fig. 1, taken over a range of tilt angles ($\pm$ 45° in different directions), allows the following conclusions regarding the crack tip zone (see C in Fig. 1). The whiskers remain intact over a narrow bridging zone near the crack tip. To achieve this, the crack extends in the matrix around the whiskers, as evident from the non-planarity of the crack in the bridging region. The residual matrix crack tip opening in the bridging zone is very small (< 2nm). The associated bridging zone size, l, depends on the local orientation of the whiskers. When the whiskers are normal to the crack, the ratio is $l/R \sim 6$, where R is the radius of the whisker.

The present observations indicate that crack bridging is an important contribution to the whisker toughening of Al_2O_3. The micromechanics of toughening by whiskers is established, although important effects inherent to whisker toughening have yet to be thoroughly addressed. Strength and toughness of a composite can be evaluated by the use of micromechanics in

Fig 1. A TEM micrograph, of SiC/Al₂O₃ composite, near a Vickers indent. The crack path is clearly visible, and the crack tip is indicated by an arrow. Region A shows that the whisker fracture occurs normal to the whisker axis. Region B indicates that fracture in the alumina matrix occurs along grain boundaries. Region C describes the bridging zone near the crack tip.

combination with experimental TEM observations. For a volume fraction, f, of whiskers where f=0.2, an experimentally determined bridging zone of $1/R = 6$ results in an increase of the toughness by a factor of about 2.5 compared to the non whisker reinforced material. These results agree with fracture toughness measurements of the bulk composite (Rühle et al., 1987).

Composites of SiC whisker-reinforced Al_2O_3 are extremely susceptible to thermal oxidation due to a series of reactions in which SiC is oxidized, and the oxidation product (SiO_2) reacts with Al_2O_3 to form a whisker-free layer of mullite and silicate glass. The kinetics of the scale growth on the surface of the $SiC-Al_2O_3$ has been analyzed after annealing in air at 1500°C for different annealing times. The porous whisker-free layer can easily be identified and the scale thickness measured. Annealing for 50h at 1500°C results in a scale of about 80μm in thickness. Detailed reaction rate kinetics studies revealed a parabolic time dependence of the scale thickness. This implies that the reaction rate is controlled by a diffusion process. A quantitative study of the reaction kinetics resulted in a measured activation energy of E~ 600kJ/mol .The atomistic mechanisms of the scale growth are not yet evaluated. It is expected that analytical TEM with high spatial resolution of cross-sectional specimens will provide the necessary data for an evaluation of the data.

Extensive creep studies of composites have been performed by Chokshi and Porter (1985). They demonstrated that true steady state creep does not develop in SiC/Al_2O_3 composites, creep rates continue to decrease with increasing creep strain. Also, an anelastic strain recovery is observed on load removal at creep temperatures. Existing creep models are inadequate to explain these observations. The development of the appropriate creep models for composites will require measurements to be made with the use of specimens with systematically varied microstructure.

Fiber Reinforced Glass-Ceramics Evans et al., (1987) have shown that bridging by intact fibers in the crack wake and fiber pull-out after failure contribute to additional toughness of fiber reinforced ceramics (Prewo and Brennan, 1980). The processes are strongly influenced by the sliding and debonding resistance of the interfacial region. In the present studies the interfaces are investigated in a laminated composite consisting of SiC (Nicalon) fibers in a lithium-alumina-silicate (LAS) glass ceramic matrix. The matrix shows systematic changes in sliding resistance upon heat treatment (Bischoff et al., 1988).

As produced specimens were annealed in air at 800°C for 2,4,8,16 and 100h, and for comparison, in helium at 800°C for 4h. TEM specimen preparation of as produced and annealed material was performed. Low magnification images in the as-processed state of the composite reveal that in many cases, circumferential cracks exist around the fibers (see Bischoff et al., 1988). Cracks extend around 1/2 to 2/3 of the circumference. When such cracks are not present, small crack-like flaws are usually evident at the interface. As shown in a TEM micrograph (Fig. 2), two distinct interfacial zones are apparent between

the fiber and the matrix. The zone adjacent to the fiber, which always exhibits a bright contrast, is amorphous. The dark, second layer, of thickness varying between 20 and 200nm, consists of small grains of about 20nm to 100nm in diameter. The circumferential cracks are found to always occur in the bright, inner layer, close to the interface with the dark layer (Fig. 2). Analysis by electron energy loss spectroscopy (EELS), established that the bright layer is amorphous C. Analysis of the dark layer by EELS and energy dispersive x-ray spectroscopy, indicates that the grains are primarily NbC, consistent with previous studies.

Heat treatment in air between 2 and 100 hours at 800°C resulted in a drastic change of the interfacial layers. A similar bright field image is obtained (Fig.3), but there are essential differences in their composition, compared to the as-produced state. Chemical analysis by the use of EELS revealed that the amorphous layer was SiO_2. The thickness of the SiO_2 layer increased with increasing annealing time (Bischoff et al., 1988). Circumferential separations again appeared. At times of up to 16 hours these separations occurred on the outside of the SiO_2 layer and the number density of fibers that exhibited separations remained essentially constant with annealing time. After 100 hours of annealing, the bond layer became sufficiently "strong" so that circumferential cracks, when present, often extended partially into the matrix.

The oxidation of the SiC fiber results in a SiO_2 layer (and fugitive CO_2). The volume of the SiO_2 layer is larger than that of the original SiC by ~1.8. This volume increase results in closure of the gap between the fiber and the LAS matrix caused by C removal. The SiO_2 layer thickness is spatially quite uniform and consistent with parabolic kinetics up to thicknesses of the order of the original C layer thickness (~150nm). At this stage, it is reasonable to suppose that the gap caused by C oxidation closes. Oxygen access to the interface must then be restricted such that the further thickening of the oxide occurs at a reduced rate. The drastic change in the mechanical properties of LAS/SiC composites caused by heat treatment in air can clearly be attributed to the replacement of the C layer by SiO_2. The principal effect of the change in the interfacial boundary layer coincides with a corresponding, abrupt increase in sliding resistance (friction coefficient), between the fiber and matrix. This conclusion implies that the optimum boundary layer, for improved or maintained high-temperature toughness of a composite, is a material which behaves essentially as a solid lubricant, either a layered structure or a soft metal thermodynamically stable and compatible with fiber and matrix materials.

CONCLUSIONS

Interfaces and interfacial boundary layers determine the mechanical properties of ceramics and ceramic composites. Boundary phases must be tailored so that the required mechanical and frictional properties can be obtained. The boundary layers must be thermodynamically stable at elevated temperatures so that degradation of the mechanical properties is reduced.
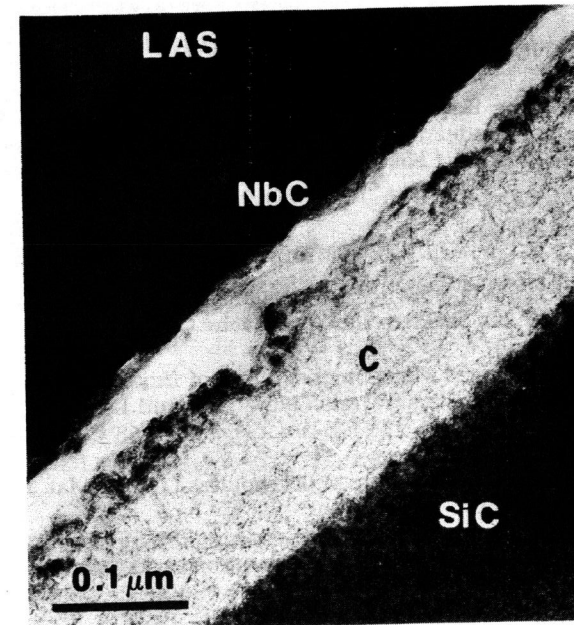

Fig 2.   Bright-field micrograph of an interface between the SiC fiber and glass matrix in as-produced fiber- reinforced composite.
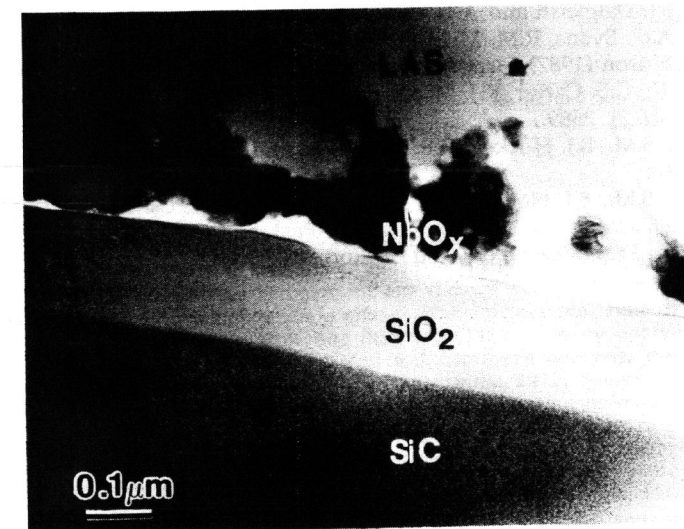

Fig 3.   TEM bright field images of interfacial layers after annealing in air for 16 hours at 800°C.

ACKNOWLEDGEMENT

REFERENCES

Becher, P.F. and G.C. Wei (1984), *J. Am. Ceram. Soc.* 67 C-267.

Bischoff, E. M. Rühle, O. Sbaizero and A.G. Evans (1988), *J. Am. Ceram. Soc.*, in press.

Bonnell, D. (1987). *Ceramic Microstructure: Role of Interfaces*, (J.A. Pask and A.G. Evans, edts.), Plenum Press, New York and London, p.877.

Chokshi, A.H. and J.R. Porter (1985), *J. Am. Ceram. Soc.* 68 C-144.

Clarke, D.R.(1979), *Ultramicroscopy* 4 33

Evans, A.G., M. Rühle, B.J. Dalgleish, M.D. Thouless (1987), Mat. Res. Soc. Symp. Proc. 78 259.

Joy, D.C., A.D. Romig Jr. and J.I. Goldstein (edts.) (1986), *Principles of Analytical Electron Microscopy*, Plenum Press, New York and London .

Lipetzky, P. , S.R. Nutt and P.F. Becher (1988), Proc. Mat. Res. Soc. Sym., Reno , in press.

Pask, J.A. and A.G. Evans (edts) (1987), *Ceramic Microstructure: Role of Interfaces*, Plenum Press, New York and London.

Prewo, K.M. and J.J. Brennan (1980), *J. Matr. Sci.* 15 , 463.

Rühle, M., B.J. Dalgleish and A.G. Evans (1987), Scripta Met. 21, 681.

Rühle, M., A.G. Evans, R.M. McMeeking, P.G. Charalambides and J.W. Hutchinson (1987), *Acta Metall.* 35 , 2701.

Simpson, Y.K., C.B. Carter, K.J. Morrissey, P. Angelini, and J. Bentley (1986), *J. Mat. Sci.* 21 2689.

Wiederhorn, S.M., B.J. Hockey, R.F. Krause, Jr. and K. Jakus (1986), *J. Mater. Sci.* 21, 810.

Wiederhorn, S.M., B.J. Hockey and R.F. Krause Jr.(1988), *Ceramic Microstructure: Role of Interfaces* (J.A. Pask and A.G. Evans, edts.), Plenum Press, New York and London, p.795.