Creep deformation of whisker-reinforced alumina

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Abstract

The creep behavior of alumina reinforced with SiC whiskers was studied under different loading geometries and test ambients. Deformed microstructures were examined and characterized to ascertain mechanisms of deformation and damage, and to understand better the causes of the measured creep response. The composites undergo creep by grain boundary sliding that is generally accommodated by diffusion, although high stresses and temperatures lead to increasing degrees of creep damage in the form of cavitation at interfaces and grain boundaries. Creep rates decrease with increasing whisker volume fraction as whiskers increasingly inhibit grain boundary sliding. In aerobic test atmospheres, the composites undergo a thermal oxidation reaction that generates glassy films at internal boundaries and carbon monoxide gas, both of which facilitate cavitational damage. Systematic study of the thermal oxidation reaction in the absence of stress shows that oxidation occurs at interfaces, generating silica glass and graphitic carbon via a "carbon-condensed" oxidation displacement reaction.

1. Introduction

Reinforcement of alumina with SiC whiskers results in substantial improvement in room-temperature fracture toughness and strength, as well as increased resistance to thermal shock and erosion [1-3]. Because of the inherent thermal and chemical stability of alumina and the benefits of whisker reinforcement, it is natural to consider the mechanical behavior of whisker composites at high temperatures. Creep resistance is often the most critical property governing the use of ceramics in high-temperature applications, and several recent studies have shown that whisker reinforcement leads to dramatic improvements in creep resistance [4-9]. Chokshi and Porter conducted flexural creep experiments on whisker-reinforced alumina at 1500 °C and reported a dramatic reduction in creep rates compared with monolithic alumina [4, 5]. They reported an increased stress dependence and proposed a dislocation-controlled creep mechanism in which most of the load was supported by the SiC whiskers. Xia and Langdon conducted creep experiments on similar composites with different volume fractions of reinforcements [6]. They found that the creep resistance improved with increasing volume fractions of whiskers, and also proposed a dislocation-controlled creep mechanism. These experiments were also conducted at relatively high temperatures (less than 1500 °C), and involved flexural loading. Flexural creep experiments at lower

temperatures (1200-1400 °C) were conducted by Lin and Becher and by Nutt *et al.* [7–9], and both groups concluded that the dominant creep mechanism was grain boundary sliding accommodated by diffusion. Improvements in creep resistance were attributed to the SiC whiskers, which inhibited grain boundary sliding [7–9], although the sliding was often facilitated by viscous flow of intergranular glass phase that originated from the oxidation of SiC exposed at the surface [9].

All of the aforementioned studies were performed in air and in flexure. Compressive creep experiments have been conducted recently in inert ambients and compared with parallel experiments conducted in air [10, 11]. These investigations were conducted at temperatures below 1500 °C, and yielded the conclusion that creep under these conditions occurred primarily by grain boundary sliding, inhibited by the SiC whiskers. Creep rates were similar but slightly lower in nonoxidizing test ambients, and the stress exponents were similar in both test ambients, although substantially lower than those reported for flexural creep. Interfacial phenomena were examined in detail in one investigation, and it was concluded that creep in oxidizing ambients resulted in accelerated creep damage by interface cavitation [9, 11]. The purpose of the present work is partly to review some of the recent work discussed above and to focus attention on the role of grain boundary and interface phenomena in high-temperature creep of whisker-reinforced alumina. In particular, thermal oxidation during creep is considered, focusing attention on interface films associated with the oxidation reaction and the role of these films in high-temperature plasticity and creep damage. The mechanisms of the reaction are examined at the microscopic level to provide a clearer understanding of the interfacial phenomena that transpire during creep deformation.

2. Experimental details

The material selected for most of the experiments described herein was a whisker-reinforced alumina (Greenleaf Corporation, WG-300). The material was produced by hot-pressing and contained approximately 33 vol.% SiC whiskers. Additional creep experiments were conducted on materials containing 0, 10, and 30 vol.% SiC whiskers (Advanced Composite Materials Corporation). Microstructural characterization of the as-fabricated WG-300 composites revealed whiskers that were approximately 0.5 μ m in diameter, with aspect ratios of 5-10, and matrix grains that were 1-2 μ m in diameter. The composites were remarkably glass free, with virtually no glass at triple grain junctions or at grain boundary-interface (GBI) junctions. Extremely thin (approximately 1 nm) glassy films were sometimes present at interfaces, and these were presumably silica rich, possibly a consequence of native oxide on the whiskers. However, grain boundaries were apparently glass free [11]. No intergranular pores or grain-boundary cavities were observed, implying that densification was virtually 100%.

Creep experiments were conducted in both flexure and in compression, and in both aerobic and anaerobic test atmospheres. The methods and test apparatus have been described previously [10, 11], but they can be summarized as follows. Flexural creep tests were conducted at 1200 and 1300 °C in air. A four-point loading fixture with inner and outer spans of 19 and 38 nm was used to apply constant loads corresponding to applied stresses of 30-250 MPa. Applied stresses and resultant strains were determined using a method based on linear elastic beam theory, described by Hollenberg et al. [13]. Compressive creep experiments were conducted in an apparatus designed to apply constant stress in regulated ambients of circulated inert gas or air [13]. Creep experiments were conducted at 1200-1400 °C under applied stresses of 25-250 MPa using both oxidizing and non-oxidizing test ambients. In both types of experiments, the samples were held under constant applied stress (or load, for flexure) at a constant temperature until a constant creep rate was observed for at least 10 h. The stress (or temperature) was then changed, and the procedure was repeated. Strains were generally kept to low levels to avoid problems of non-uniform deformation inherent with large strains.

Test specimens were cooled under load and sectioned to prepare samples for transmission electron microscopy (TEM) examination. The approach taken in these investigations is to identify a peculiar aspect of the creep response, such as a change in stress exponent or a change in activation energy. The microstructural causes of the phenomenon were then investigated by preparing samples from both regimes and attempting to identify differences associated with each regime. Sections were taken from both the tensile and compressive sides of the bend bar, and perpendicular to the load train axis. Specimens were examined at 120 kV and in some cases at 200 kV in microscopes equipped with double-tilt holders.

3. Results and discussion

3.1. Creep response: flexure and compression

The flexural creep response of the composite is summarized in Fig. 1, a plot of secondary creep rates vs. applied stress for a range of stress levels at 1200 and 1300 °C [9]. The data sets for both temperatures are bilinear and exhibit a greater stress dependence above a critical stress level. Assuming power-law constitutive behavior, in which the strain rate is proportional to the applied stress raised to a power n $(\dot{\varepsilon} = A\sigma^n)$, the stress exponent n changes from approximately unity at low stress levels to about 5 above a critical stress. Arrhenius plots of secondary creep rates for applied stresses of 50 and 100 MPa yielded apparent activation energies for creep of approxi-



Fig. 1. Strain rate vs. stress relations for flexural creep of SiC-reinforced alumina composites: \blacktriangle 1200 °C; \circ 1300 °C. The stress exponents for low-and high-level stress regimes are n=1 and n=5 respectively.

mately 300 kJ mol⁻¹, independent of the applied stress [9].

A pronounced change in the stress dependence of the strain rate is generally interpreted as indicating a change in the creep deformation mechanism. Stress exponents of 1-2 are generally associated with a diffusional creep mechanism, although such generalizations are not always accurate for multiphase materials. Reports in the literature on creep of whiskerreinforced alumina indicate a fairly wide range of values for stress exponents, from approximately 1 to 7 [6, 7, 10]. Flexural creep experiments on whiskerreinforced alumina conducted in air at 1400-1600 °C yielded stress exponents of 4-6, and it was concluded that dislocation glide was the likely mechanism for creep [4, 5]. However, Lin and Becher performed flexural creep experiments on similar composites at 1200-1400 °C and reported a stress exponent of about 2 [7], concluding that grain boundary sliding (partly accommodated by diffusion) was the dominant deformation mechanism. Our TEM observations, presented below, support a grain boundary sliding mechanism accompanied by cavitation for the temperature range and stresses investigated.

Compressive creep experiments were conducted at 1200–1400 °C with applied stresses of 25–175 MPa [11]. The data conformed to a power-law constitutive relation also, as shown in Fig. 2(a). The stress dependence for each temperature corresponds to a stress exponent of n=3. Arrhenius plots of the data yielded two distinctly different activation energies, as shown in Fig. 2(b). Below 1270 °C, the apparent activation energy for creep was 270 kJ mol⁻¹, while at higher temperatures the activation energy was 655 kJ mol⁻¹. The data imply a thermally activated creep mechanism that becomes operative above 1270 °C.

While the measured stress dependence of the creep rates is only slightly different for flexure and compression (n = 5 vs. n = 3), the creep rates are much lower in compression than in bending for comparable stresses. This phenomenon is not uncommon in ceramic materials [14], and is possibly accentuated by the fact that in bending, stress is necessarily concentrated beneath the load pins, causing localized deformation that can lead to higher apparent strain rates.

The role of whisker reinforcements in inhibiting creep was explored by conducting experiments on composites containing different volume fractions of SiC whiskers. Because of the potential interactions with oxidizing atmospheres, creep experiments were conducted in circulated dry nitrogen on composites containing 0, 10 and 30 vol.% SiC. The results of flexural and compressive creep experiments with these materials are shown in Fig. 3. The stress exponent for compression was approximately 1.5 for monolithic alumina



Fig. 2. Compressive creep response of composites in air. (a) Strain rate vs. stress relations: \blacktriangle 1300 °C; \circ 1400 °C. (b) Arrhenius plot of minimum creep rate vs. inverse temperature (stress 150 MPa)[11].

and the 10% composite, and approximately 3.5 for the 30% composite. The stress exponents for flexure were about 1.5 for monolithic alumina, and 2–2.3 for the composites. This stress dependence is generally consistent with diffusional creep mechanisms [14]. Creep rates for flexure were reduced by factors of 4, 8 and 25 for the composites with 10%, 20%, and 30% SiC. In compression, the reduction in strain rate was even more dramatic, decreasing by a factor of 30 for composites with 10% SiC and by two orders of magnitude for composites with 30% SiC.

3.2. Creep deformation mechanisms

The flexural creep data showed two distinct regimes in which the stress dependence was markedly different, and in this section the microstructural differences resulting from creep under these conditions are examined. The most salient microstructural change associated with the n=1 regime was the development of glass pockets at grain boundary-interface (GBI)



Fig. 3. Creep behavior for composites with different whisker loadings. (a) Compressive creep, stress exponents range from 1.8 to 3.5 for the different materials. (b) Flexural creep, both compressive and flexural creep experiments were performed at 1300 °C with stresses of 10-300 MPa [8].

junctions (Fig. 4). The pockets were generally triangular in shape and were bounded by two alumina facets and a whisker flank. The appearance of numerous bubbles within the glass phase suggests the evolution of gas, most probably CO, a secondary reaction product of the oxidation of SiC, as discussed in a later section. Compositional analysis by X-ray spectroscopy revealed the presence of silicon, aluminum, and a small amount of calcium (Fig. 4(b)). From the compositional data, it was concluded that the glass was predominantly silica. It is interesting to note the presence of calcium, which is the dominant impurity constituent in the asgrown whiskers, as well as a strong glass former [15, 16]. The whiskers are undoubtedly the source of the calcium, since similar glass pockets that were some-



Fig. 4. (a) Accumulation of non-crystalline silica phase at a grain boundary-interface (GBI) junction after secondary creep at 50 MPa. (b) X-ray spectrum from triangular region shown in (a) showing silicon, aluminum, and calcium [11].

times observed at triple grain junctions showed no trace of calcium. The presence of calcium also helps explain the substantial concentration of aluminum in the glass. The equilibrium solubility of aluminum in silica is normally very low, but it is well established that trace amounts of impurities such as calcium can greatly increase the solubility limits of foreign species in silica [17].

Flexural creep at higher stress levels (for which n = 5) resulted in cavitation at GBI junctions, as shown in Fig. 5. The cavities were similar in shape to the glass-filled pockets shown in Fig. 4, and frequently appeared



Fig. 5. Cavitation at grain boundary-interface junction in composite after secondary creep at 1300 °C, stress 250 MPa.

to be lined with glass phase. Incipient cavities, consisting of glass pockets with small pores, were also observed at GBI junctions. A plausible sequence of events leading to cavitation is described in Fig. 6. [8]. Glass phase accumulates at GBI junctions during creep, where stress is concentrated. At low stresses, or perhaps during initial stages of creep at higher stresses, the glass allows the boundary to pull away from the interface, thus accommodating intergranular sliding. Under conditions of high stress, diffusion cannot keep up with the sliding, and pores initiate within the glass phase, which is undoubtedly softer than either the alumina matrix or the whisker reinforcements. The viscosity of silica glass in its pure form is about 10 P at 1300 °C, and is markedly reduced by the presence of impurities such as calcium [18]. Thus the viscous flow of localized glass phase constitutes an important creep deformation mechanism in the composite, facilitating intergranular and interfacial sliding as well as cavitation.

The marked change in the stress exponent that occurs above a critical stress level appears to be associated with an increase in the cavitational component of creep strain. As indicated in Fig. 6 and supported by extensive microscopy observations, cavitation is preceded by accumulation of glass phase at GBI junctions. The formation of glass films may involve multiple sources. Silica glass is generated at the specimen surface as a product of the thermal oxidation of SiC [5, 9, 11, 19]. Under stress, the glass formed at the surface may not remain there, and may penetrate along



Fig. 6. Schematic illustration of the process of glass-phase-facilitated cavitation at GBI junctions.

interfaces and grain boundaries, effectively lubricating sliding processes. Supporting this contention are observations of glass films extending along interfaces near pockets of glass phase at GBI junctions, as shown in Fig. 7. The thin film of glass that extends along the interface supports the view that glass flows toward GBI junctions along interfaces during creep. A second possibility involves the redistribution of pre-existing glass phase. SiC often generates a thin native oxide layer of silica, and it is probable that such oxide layers are commonly present on SiC whiskers in the as-grown condition. Figure 7(b) shows a non-crystalline film at a whisker-matrix interface prior to creep deformation. The film is extremely thin, approximately 1 nm or less. However, as shown in Fig. 7(a), such films may very well redistribute under stress and migrate to GBI junctions. The added presence of calcium supplied by outdiffusion from the SiC whiskers may also increase the solubility of alumina in the glass phase, supplying additional glass phase.

The reduction in creep rate with increasing reinforcement volume fraction results directly from the presence of the SiC reinforcements, which do not undergo creep under these conditions [14]. The whiskers inhibit the sliding of alumina matrix grains, which would otherwise be the dominant mode of creep deformation at these temperatures and stresses [20]. In compression, the effects of the whiskers on creep resistance are more pronounced than in flexure because of the efficient load transfer between whiskers across points of contact and/or points of close proximity. Most of the compressive load is carried by the whiskers, which interlock to form a skeletal substructure that resists compressive loads [8]. This is particularly true for the composite with 30% SiC, where average interfiber distances are smallest. The notion of constrained matrix flow between rigid reinforcements has been explored by computational methods for both metal- and ceramic-matrix composites [8, 21]. As interfiber distances decrease, the crosssectional area for matrix flow decreases, resulting in large hydrostatic compressive stresses that inhibit local creep deformation. The degree of such constraint hardening is expected to be more significant in compressive loading situations than in tensile deformation



Fig. 7. (a) Accumulation of silica glass at GBI junction after flexural creep at 1300 °C and 150 MPa. The arrow indicates a glassy film along the fiber-matrix interface. (b) Non-crystalline interfacial film at fiber-matrix interface prior to creep deformation. Planar defects in the whisker give rise to the chevron appearance of the lattice fringes [15].

[8], and experiments are currently underway to test this hypothesis.

The absence of intragranular dislocations in specimens after creep under any of the conditions selected supports a creep deformation mechanism other than dislocation movement. Furthermore, corrugated grain boundaries were often observed in the alumina matrix, and these features are also commonly observed in monolithic alumina that has undergone diffusional creep [20]. These observations support the conclusion that diffusional creep and/or grain boundary sliding are the most likely deformation mechanisms, and because of the extremely fine grain size of the material, the dominant diffusion path is likely to be along grain boundaries. In addition, glassy films play an important role in the creep deformation, facilitating interface sliding and cavitation at GBI junctions. The effect of the glass phase appears to be most important at high temperatures and stress levels, where boundary sliding becomes increasingly unaccommodated.

3.3. Atmospheric effects on creep

Most of the experimental investigations of creep to date have involved aerobic test ambients, and all of these, to greater or lesser extent, have necessarily involved thermal oxidation of SiC also. One of the primary reaction products is silica glass, and because of the important effects of glass phase on creep response and damage mechanisms, as demonstrated in the previous section, it is of scientific interest to establish the effect of the oxidation reaction on creep response. To address this issue, compressive creep experiments have been conducted in circulated dry nitrogen and in circulated air with the goal of determining quantitatively the effect of the oxidizing ambient. Figure 8 shows a comparison of creep rates in air and in an inert ambient, for temperatures of 1300 and 1400 °C. The stress dependence is virtually identical for both cases $(n \approx 3.5)$, although the strain rates in air are greater than those in nitrogen by factors of 3 and 5 for 1300 and 1400 °C respectively. For both ambients, there was an abrupt change in the apparent activation energy for creep at 1280 °C, as shown in Arrhenius plots in Fig. 8(b). This change was possibly related to an increase in the cavitational component of the creep strain. Measurements of specimen density after creep deformation revealed that the cavitational component of the total strain was about 10% at 1200, and about 30% at 1300 °C [11].

Examination of the crept microstructures was undertaken with the goal of determining differences associated with the test atmospheres, particularly with regard to the amounts of glass phase at interfaces and grain boundaries, and the extent of creep damage at these sites. Specimens crept in air showed many of the same microstructural features noted in the previous section, including glass-lined cavities at GBI junctions and triple grain junctions. The frequency with which cavities were observed was somewhat surprising given that the loading was compressive. However, the cavities were generally located at stress concentration sites (particularly GBI junctions), where the deformation is undoubtedly non-homogeneous because of the dissimilar mechanical properties of the constituents. An example of a typical cavity at a GBI junction is shown in Fig. 9(a). Glass phase ligaments extend across the void where the grain boundary has pulled away from the interface. Accumulation of glass undoubtedly preceded and facilitated the nucleation of the void, and the glass is apparently associated with oxidation of SiC exposed at the specimen surface, and perhaps beneath the surface as well. Additional cavities were often observed at sites where whiskers were in close proximity or in mutual contact (Fig. 9(b)). At such sites, matrix flow is severely constrained by the whiskers, thus inhibiting local creep deformation. However, the

O 1400°C

1300°C

Steady State Strain Rate (1/s) 10 1200°C AIR INERT 10 10 * 10^{2} 10 Applied Stress (MPa) (a) 10 log Strain Rate (1/sec) 655kJ/mo 10 10 Stress: 150 MPe 10 6.3 6.5 6.7 6.1 6.9 10⁴/T (1/K) (b)

Fig. 8. (a) Steady state strain rates vs. applied stress for creep experiments performed in nitrogen and in air at 1200-1400 °C. The data conform to power-law-type constitutive relations. (b) Arrhenius plots showing an increase in activation energy for creep at a threshold temperature of about 1280 °C.

presence of glass at such sites (due to thermal oxidation), undoubtedly accommodates the stress concentration and facilitates decohesion and cavitation, as shown in Fig. 9(b) [22]. The contributions of thermal oxidation and resulting glass phase to the creep deformation can be better understood by comparison with creep experiments conducted in the absence of air.

Creep in a dry nitrogen atmosphere resulted in less cavitation with less residual glass phase at interfaces and grain boundaries compared with creep in an oxidizing ambient. Cavities were observed, but with much less associated glass phase. Cavities often appeared to be lined with a thin glassy film, but approximately one third of the voids appeared to be glass

Fig. 9. Microstructural damage from compressive creep at 1300-1400 °C in air. (a) Cavitation within glass phase accumulated at GBI junction after creep at 1400 °C. (b) Glass-lined cavity between two SiC whiskers in close proximity.

100 nm



free. Distinguishing between glass-lined and glass-free cavities in TEM specimens is generally difficult for several reasons. First, glass phase tends to be etched faster by ion milling than crystalline ceramics, and consequently residual glass phase often disappears during sample thinning. Secondly, it has been shown that glass phase, particularly grain boundary films, can redistribute during cooling, even under applied loads. And perhaps more importantly, amorphous material is often sputtered into cavities during ion milling, creating the false appearance of a glassy lining. Thus, interpretation of such observations requires extreme care and discretion. However, it is clear from the above observations that there is substantially more glassy phase present in composites after creep in air relative to those crept in nitrogen, all other factors being equal, including time, temperature, and stress. Thus, most of the glass phase observed in the former samples must come from the oxidation of SiC whiskers. Similarly, most of the glassy films observed in the latter samples must come from residual glass films present in the as-fabricated material, or possibly from limited dissolution of alumina and/or SiC during creep.

One of the salient features of all of the deformed microstructures regardless of testing ambient was the development of grain boundary facets. These often occurred on alternating crystallographic planes, resulting in corrugated configurations, as shown in Fig. 10(a). Corrugated grain boundaries are generally associated with diffusional creep [20]. In addition, corrugated grain boundaries in specimens crept at 1400 °C showed signs of subsequent cavitation, as shown in Fig. 10(b). It is proposed that this mode of cavitation is linked to a shearing or sliding of the grain boundary, as described by the schematic diagram in Fig. 10(c). At lower temperatures and stresses, grain boundary sliding is strongly inhibited by the presence of the reinforcing whiskers.

3.4. Thermal oxidation of composites: mechanisms and kinetics

The foregoing discussion illustrates how thermal oxidation and associated interface phenomena play an integral role in the high-temperature plasticity of whisker-reinforced alumina composites. By far the most common reinforcing phases used in various ceramic composites are carbides, and all are potentially susceptible to oxidation at high temperatures. The reaction mechanism involved can be described in terms of the evolution of phases within the reaction layer, both microscopically and macroscopically. Several studies of this reaction have been performed in similar composite systems, all using somewhat different approaches [19, 23–26]. Of greatest relevance to the present topic is the evolution of phases at the microscopic level, and



Fig. 10. Evidence supporting grain boundary diffusional creep. (a) Corrugated matrix grain boundary after flexural creep at 1300 °C, 150 MPa. (b) Cavitation at corrugated grain boundary after compressive creep at 1400 °C in nitrogen. (c) Schematic diagram for proposed sequence of events portrayed in (a) and (b) [11].

thus an overview of the salient results of these studies (as pertains to creep) is presented in this section.

observation of thermal The oxidation of alumina-SiC composites was first reported by Porter and Chokshi [5]. Specimens exposed to high temperatures (about 1500 °C) in air for extended periods of time showed discoloration, and polished cross-sections revealed a sometimes porous scale, as shown in Fig. 11. The thickness of the oxide scale increased with time and followed parabolic reaction kinetics. Their creep experiments were conducted at 1500 °C, where silica produced by the oxidation of silicon carbide subsequently reacted with the alumina matrix to form mullite. Luthra and Park performed a systematic study of the oxidation kinetics and reaction products, which included alumina, mullite, and aluminosilicate liquid, and gas bubbles [23]. The bubbles were attributed to the evolution of carbon monoxide, and it was concluded that the reaction rates were controlled by gaseous diffusion of oxygen (inward) and carbon monoxide (outward). It was further predicted that oxygen permeabilities of the three reaction product phases should be of the same order of magnitude.

Lin et al. examined the microstructural mechanisms of the reaction in detail using TEM [19]. Their approach was to observe the reaction products at different depths beneath the surface to understand better the various stages of the reaction and the distribution of products. At the reaction front, *i.e.* at the boundary between the reacted and unreacted material (see Fig. 11), SiC whiskers were partially reacted. The thickness of this reaction front was generally a small fraction (less than 10%) of the total scale thickness, suggesting that oxygen permeability through the scale (mullite plus aluminosilicate glass) was comparable with or faster than the permeability through alumina. Figure 12(a)shows a whisker in the vicinity of the reaction front in a composite oxidized at 1500 °C. The whisker has been partially consumed by the oxidation reaction, forming aluminosilicate glass and graphitic carbon, which is not



Fig. 11. Cross-sectional view of reaction scale formed after 60 h at 1500 °C in 10 vol.% composite (left) and 30 vol.% composite (right) [19].

in contrast in the image. The silica glass has not yet reacted with alumina to form mullite in this region, although there is substantial evidence of glass phase penetration along alumina grain boundaries in the vicinity.

During the early stages of oxidation, graphitic carbon is formed concurrently with silica glass. Figure 12(b) shows a high-resolution image of a partly oxidized whisker that is separated from the alumina



Fig. 12. Initial stages of thermal oxidation reaction in composite exposed to air at 1500 °C. (a) Partially consumed SiC whisker surrounded by aluminosilicate glass (light regions, arrow) and graphitic carbon (nearest interface). (b) Initial stage of thermal oxidation reaction at SiC interface showing graphitic carbon (C) and silicate glass (G).

matrix by an interlayer that consists of silica glass and partly crystalline graphitic carbon. The undulating lattice fringes correspond to the 3.4 Å basal planes of graphite, and the light contrast of the surrounding phase is typical of silica glass. The results presented in Fig. 12(b) are consistent with formation of carbon-rich and silicon-rich reaction layers via solid state oxidation of the silicon carbide whisker according to the reaction

$$\operatorname{SiC} + \operatorname{O}_2 \to \operatorname{SiO}_2 + \operatorname{C} \tag{1}$$

which later becomes

 $3Al_2O_3 + 2SiC + 3O_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2CO \qquad (2)$

This "carbon-condensed" oxidation equilibria represented by eqn. (1) has the lowest standard-state Gibbs free energy of any of the silicon carbide oxidation reactions up to approximately 1500 °C, and it is thus the most thermodynamically favored [24]. During the early stages of the oxidation reaction, the local oxygen fugacity near the whisker exceeds the stability of SiC, producing a layer of graphite as well as a silica-rich glass. The position of the graphite layer and silica layers relative to the SiC is not consistent. There is general agreement that the reaction in this stage is ratelimited by diffusion of oxygen through the reaction scale (macroscopically) and through the silica layer (microscopically), although it is also possible that escape of CO is a concurrent rate-limiting process [5, 19, 23]. Although this is the first reaction to occur, as confirmed by microscopic observations, the reaction products are not stable and undergo further reaction to form mullite and CO. As silica is formed from oxidation of SiC, there should be an approximately 100% volume expansion, resulting in large internal stresses. However, the liquid subsequently reacts with alumina to form mullite, and as mullite is formed much of the remaining liquid is squeezed out, resulting in a liquidrich top surface that overlies a solid-rich subsurface in the reaction scale. This is in fact the case, as noted in previous reports [19, 23].

The primary significance of the oxidation reaction with regard to high-temperature plasticity is that the silica glass does not remain at the whiskers where it is formed, and penetrates instead along interfaces and grain boundaries, lubricating sliding displacements at grain boundaries and interfaces. In the presence of applied stress, the glass phase apparently flows to sites of stress concentration, particularly GBI junctions, thus partially accommodating the stress and facilitating flow. However, the glass has little mechanical strength and thus renders the composite susceptible to damage processes that ultimately limit lifetime and lead to failure. Even at room temperature, the reaction scale has a detrimental effect, reducing the threshold load for crack initiation under cyclic compressive loads [19].

4. Summary

Flexural and compressive creep of whisker-reinforced alumina occurs by diffusional creep and grain boundary sliding. At low stresses and temperatures, the sliding is accommodated by diffusion and facilitated by the viscous flow of intergranular silica glass generated by the oxidation of SiC. At higher stresses, cavitation occurs frequently within glass pockets at GBI junctions, accounting for a substantial component of the total creep strain. In the absence of oxygen, less intergranular glass phase is present, and consequently cavitation and sliding is more difficult. Strain rates are lower, although the stress dependence is generally unchanged, and the creep deformation mechanisms are apparently the same also. A change in the apparent activation energy for creep was consistently observed above a critical temperature (about 1280 °C), and while this may be related to an increase in creep damage, the reason is not well understood at present.

Environmental effects are critical to the hightemperature mechanical behavior of carbide-reinforced ceramics. Thermal oxidation reactions such as those described in the present work have deleterious effects on creep behavior which are irreversible. Interface properties are compromised by the glass phase generated from the oxidation reaction, and this leads to accelerated sliding and cavitation. Significant improvements in creep resistance might be realized by controlling the properties of the glass phase through additives that would reduce glass viscosity or enhance crystallization, or by the use of protective coatings. A more challenging but perhaps equally attractive approach involves the development of oxidation-resistant reinforcements such as oxides, nitrides, or silicides.

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