Formation of Oxide Scales on Zirconium Diboride–Silicon Carbide Composites During Oxidation: Relation of Subscale Recession to Liquid Oxide Flow

Sigrun N. Karlsdottir†‡ and John W. Halloran

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48104

The formation of oxide scales on zirconium diboride (ZrB2)–silicon carbide (SiC) composites oxidized at high temperatures (>1500 °C) is studied. Subscale recession found in oxidized ZrB2 composites is proposed to form due to flow of boron oxide (boria) (B2O3), rich borosilicate liquid through convection cells that form upon oxidation of the composite at high temperatures. The flow of the B2O3-rich liquid to the surface, with the subsequent loss of B2O3 to evaporation, explains the formation of a glassy silica-rich layer on the surface commonly reported in the literature. Also the outward flow of the liquid creates a localized inward path for oxygen due to lower viscosity that allows faster oxidation under the convection cells which creates the subscale recession. Optical and electron micrographs of a ZrB2–15 vol% SiC composite oxidized at 1550 °C are presented as evidence of flowing liquids. Micrographs of oxide scale deformations are also presented, which are proposed to be related to the formation of oxide scale features called convection cells. The subscale recession and oxide scale deformations of ZrB2–15 vol% SiC composites oxidized for 3 and 4 h at 1550 °C were studied with microstructure and chemical composition analysis.

I. Introduction

The zirconium diboride (ZrB2)–silicon carbide (SiC) and HfB2–SiC composites oxidize to form a complex multilayer oxide scale at temperatures between 1400° and 1700 °C.1–3 Often the oxide scale features a silica (SiO2)-rich outer layer, which lies over a subscale of crystalline zirconia (ZrO2), often with a columnar microstructure with SiO2 between the ZrO2 grains. Deposition of SiC from the virgin material under the ZrO2 scale has also been observed and reported.4,5 While frequently observed, the mechanisms that form this complex scale are not understood in detail.6,7 The interpretation of this complex oxide scale presents several puzzles. ZrO2 appears often as a columnar subscale and as a noncolumnar phase in the SiO2 layer. Deposition of SiC underneath the ZrO2 scale suggests formation of SiO2 liquid or SiO vapor under the ZrO2, but most of the SiO2 is found over the ZrO2. The SiO liquid can dissolve with boron oxide (boria) (B2O3) liquid (formed upon oxidation of ZrB2) forming a borosilicate surface layer (B2O3–SiO2). B2O3 is, however, largely absent, due to evaporation at higher temperatures. B2O3 has a vapor pressure of 233 Pa at 1500 °C, whereas SiO2 has a vapor pressure of 3 × 10−4 Pa.5 How can these oxide scale features be interpreted?

Recently, Karlsdottir et al.9 proposed that liquid flow of B2O3–SiO2–ZrO2 (BSZ) liquids plays an important role in the formation of these scales, based on distinctive microstructural features observed on the external oxide surface and in cross section. These features are called convection cells. Figure 1 shows an example of these convection cells. The image shows a backscattering electron (BSE) image of a surface of a ZrB2–15 vol% SiC specimen oxidized at 1600 °C for 30 min. The surface of the oxidized specimen is covered with convection cells forming a pattern. The convection cells have ZrO2 islands (white area) located in larger SiO2-rich “lakes” (gray area) with B2O3-rich patterns (dark contrast) surrounding the islands. The area around the convection cells consists of a SiO2-rich glass (gray region) with small micrometer-sized ZrO2 dispersoids (white dots). The B2O3 flower-like patterns are visible in BSE images, but in stronger contrast when imaged by cathodoluminescence (CL). The ZrO2 islands have been proposed previously9 to have formed by precipitation during the evaporation of B2O3 from a BSZ liquid that rises through an outer SiO2-rich borosilicate layer and flows laterally by viscous fingering forming the B2O3-rich regions around the ZrO2 islands.9,10 The driving force is proposed to be the large volume increase upon oxidation of the bulk material due to the formation of solid ZrO2(s) and BSZ liquid.2 Figure 2 is a schematic of these convection cells and their formation.

These convection cell features had not been discussed by others before, but close examination of cross-sectional micrographs in the literature suggest that the features might have been observed, but have not be interpreted. In this paper the interpretation of oxide scale features of diboride–SiC composites will be discussed. Optical and electron micrographs will be presented as evidence of flowing liquids. Oxide scale deformation related to the formation of convection cell will also be presented and discussed. Finally, subscale recession found in oxide scales formed during oxidation of boride–SiC-based material are discussed in connection to convection cell features.

II. Experimental Procedure: Materials and Methods

ZrB2–15 vol% SiC composite materials were fabricated at Institute of Science and Technology for Ceramics, National Research Council (CNR-ISTEC) in Faenza, Italy, using methods presented elsewhere.11 Before testing, ca. 200 µm was removed from surface by diamond grinding (Omni Brade, TBW Industries, Furlong, PA). This was to remove any heat-affected zone that could have formed during wire electrical discharge machining (w-EDM) (Ann Arbor Machine Model 1S15, Ann Arbor, MI), which was used to cut the bulk material into thin sheets. The thin sheets of the ZrB2–15 vol% SiC material were then cut with a diamond saw (Isomet® 1000 diamond precision saw, Buehler, Lake Bluff, IL) into small rectangular coupons with total surface area on average of ca. 1 cm². They were oxidized at high temperatures in ambient air at temperatures between 1550° and 1600 °C for different times ranging from 4 to 4 h. The tests were performed either in a high-temperature box furnace (SentryTech Corporation, Berea, OH) or in a tube-furnace (Lindberg, Watertown, WI). The heating rate used was 13°C/min with free cooling or with 13°C/min cooling rate. In the
The specimens were supported by the same material (ZrB$_2$–SiC) that was placed on an Al$_2$O$_3$ support in an Al$_2$O$_3$ crucible.

Chemical composition and microstructural analysis were done on the surfaces and cross sections of the oxidized specimens using bright field optical microscopy of the as-oxidized surface, scanning electron microscopy, BSE microscopy, and electron microprobe analyzer (EMPA). A Cameca SX100 was used for EMPA, using well-characterized mineral standards for quantitative analysis of boron (B), oxygen (O), zirconium (Zr), and silicon (Si), and for imaging in the BSE and CL modes. The EMPA standards and technique that were used are described in more detail elsewhere. The cross sections of the oxidized specimens were prepared for microstructural analysis by nonaqueous polishing procedures down to 1 µm finish. Specimens were coated with carbon before microstructural and elemental analysis.

III. Interpretation of Oxide Scale

Examination of the surface of the oxidized samples provides clear evidence of liquid flow. Figure 3(a) is an optical micrograph of the surface after oxidation for 4 h at 1550°C. Optical metallograph image in reflected light shows what appears to be "islands" of ZrO$_2$ in a film of borosilicate glass. These islands are assemblies of ZrO$_2$ grains emerging from the once-liquid glassy surface. The darker regions of the glass are rich in SiO$_2$, and are dark because of the relative transparency scatters little of the incident light. Very small dispersed ZrO$_2$ particles barely visible are on the surface of the SiO$_2$. The cloudy features are subsurface B$_2$O$_3$-rich borosilicate. These borosilicate regions are turbid because of liquid–liquid phase separation in the glass during cooling. The appearance of the turbid and clear regions of the glass is suggestive of liquids flowing from the neighborhood of the ZrO$_2$ island. Figure 3(b) is a BSE image of the same field of view as Fig. 3(a). In BSE imaging, the ZrO$_2$ islands appear in bright contrast. The SiO$_2$-rich glassy regions appear in light gray contrast, and the B$_2$O$_3$-rich regions in darker contrast. The small dispersed ZrO$_2$ particles on the SiO$_2$ are highly visible. The arrangement of these small ZrO$_2$ dispersoids is hard to understand without presuming that they were arranged by flowing liquids. We present these images as evidence in support of the hypothesis of convective flow, as illustrated in the schematic of Fig. 2.

Now let us direct our attention to cross section of the oxide scales. Figures 4(a)–(c) show BSE images of a cross section of a ZrB$_2$–15 vol% SiC specimen oxidized at 1550°C for 3 h in a tube-furnace in ambient air, with a heating rate of 13°C/min and free cooling. The images show significant deformations of the oxide scale. The SiO$_2$ outer scale appears in the BSE image in darker contrast, while the ZrO$_2$ subscale is in brighter contrast. The contrast between ZrO$_2$ and ZrB$_2$ is slight in this image. The higher magnifications, Figs. 4(b) and (c), show that the ZrO$_2$ scale is deformed; it appears to be lifted up, like a blister. Inside the "blister" is a glassy phase shown by EMPA maps and analysis to be rich in B$_2$O$_3$, SiO$_2$, and with some ZrO$_2$.

Figures 5(a)–(e) show a BSE image of one of the deformations shown in Fig. 4(a) and the corresponding EMPA maps of this area, showing the distribution of B, Si, O, and Zr. The distinction between the ZrO$_2$ in the primary scale and the ZrB$_2$ substrate can be made by comparing the zirconium image Fig. 5(c) with the boron image Fig. 5(e) and the oxygen image Fig. 5(f). Clearly the ZrB$_2$ substrate and the ZrO$_2$ primary scale are being separated by a liquid rich in O, Si, and B, with significant distortion of the ZrO$_2$ primary scale. Figure 6 shows the corresponding line analysis from these elemental maps, indicating that the glass inside the "blister" is rich in B$_2$O$_3$, and SiO$_2$, and has some ZrO$_2$. Based on a calculated ternary phase diagram of a ZrO$_2$–SiO$_2$–B$_2$O$_3$ system, an isothermal section at 1500°C, published previously by Karlsdottir et al., it is presumed that this material is the glass formed by cooling of a BSZ liquid in equilibrium with ZrO$_2$ in this area. The driving force for these deformations is likely the very large volume increase upon oxidation of the bulk material due to the formation of condensed oxides, solid ZrO$_2$ and BSZ liquid, where the oxide products occupy a volume 3.2 times as great as the ZrB$_2$–SiC substrate. From the microstructural and chemical compositional analysis of the blisters (deformations) we propose that the BSZ liquid forms at the reaction interface, i.e. between a "primary" oxide scale (a thin outer SiO$_2$-rich borosilicate layer and an underlying porous ZrO$_2$) and the unreacted bulk material. Here it is hypothesized that the blisters
form because of the large volume increase, induced by the formation of the oxides during oxidation. The large volume increase of the formed oxides induces pressure and stresses when the oxide scale grows leading to a rupture in the “primary” oxide scale. Our hypothesis is that the BSZ liquid at the reaction interface is then squeezed up to the surface where it starts flowing, forming the convection cells and their features.

Figure 4(d) shows a secondary electron image of a polished cross section of a convection cell on an oxidized ZrB$_2$–SiC sample. The sample was oxidized for 4 h at 1550°C in a tube-furnace in ambient air, with a heating rate of 13°C/min and free cooling. The image shows the SiO$_2$-rich external scale, in dark gray contrast, covering a ZrO$_2$ subscale (primary ZrO$_2$) in light gray contrast, and B$_2$O$_3$-rich regions in dark gray contrast. The small dispersed ZrO$_2$ particles on the SiO$_2$ appear in bright contrast.

Fig. 3. Surface of an oxide scale on ZrB$_2$–15 vol% SiC composite after oxidation for 4 h at 1550°C. (a) Optical image in reflected light, showing “islands” of ZrO$_2$ in a film of borosilicate glass. The darker regions of the glass are rich in SiO$_2$, which are dark because of transparency, with small dispersed ZrO$_2$ particles barely visible. The cloudy regions are B$_2$O$_3$-rich borosilicate, turbid because of liquid–liquid phase separation in the glass during cooling. (b) Backscattered electron image of the same region, where ZrO$_2$ islands appear in bright contrast, SiO$_2$-rich glassy regions in light gray contrast, and B$_2$O$_3$-rich regions in dark gray contrast. The small dispersed ZrO$_2$ particles on the SiO$_2$ appear in bright contrast.

Fig. 4. (a)–(c) Backscattered electron images of cross sections of ZrB$_2$–15 vol% SiC composite oxidized for 3 h, showing the built up of the BSZ liquid between the “primary” oxide scale (SiO$_2$-rich top layer and an under laying ZrO$_2$) and the bulk material (ZrB$_2$–SiC). (d) Scanning electron microscopic image of a cross section of a convection cell on ZrB$_2$–SiC oxidized at 1550°C for 4 h, showing the inner structure of a convection cell.
Fig. 5. (a) Backscattered electron (BSE) image of a deformation with glass inside located in the cross section of the ZrB$_2$–15%SiC composite oxidized at 1550°C for 3 h; (b)–(e) the same area as in (a) imaged by electron microprobe analysis in oxygen Ka X-rays (b), zirconium La X-rays (c), silicon Ka X-rays (d), and boron Ka X-rays (e). The scale bars on the elemental maps represent the intensity of the corresponding element. The elemental maps (b)–(e) indicate SiO$_2$-rich surface layer and underlying ZrO$_2$ layer as well as the composition of the BSZ glass inside the deformation.

Fig. 6. (a) Backscattered electron image of a cross section of a cell on surface of a ZrB$_2$–15 vol% SiC composite oxidized at 1550°C for 3 h. The white line through the “blister” (deformation) indicates where the EPMA line analyses were done; the letter A indicates the start of the line scan and B the end (b) graphs of the recorded intensity ([Cps] counts per second) versus distance (µm) of the line scan.
the ZrO$_2$ “island”, suggesting this to be the glass of the B$_2$O$_3$-rich BSZ liquid. Note that the interface between the “primary” ZrO$_2$ subscale and the unoxidized ZrB$_2$–SiC substrate extends about 100 m beneath the surface under the ZrO$_2$ “island” (the center of the convection cell) but only about 50 m away from the center of the convection cell. Apparently this increased subscale recession of the ZrB$_2$–SiC substrate denotes faster oxidation at this location.

When interpreting the cross-sectional images of the deformations shown in Fig. 4, one needs to consider that because the location of the plane of polish is not known, it is hard to infer if the features seen differ because of their location, or if they differ because they have not developed (immature or “before eruption”) or have stopped operating (“extinct”). Figure 7 is an illustration of a convection cell intersected by several planes of cross section for polish. Line “a” in Fig. 7 intersects the center of a BSZ liquid pipe. This can create an image similar to Fig. 4(d). If the plane of polish intersects the side of a convection cell (through a ZrO$_2$ “island” filled with liquid), i.e. line “b”, it could create an image similar to Fig. 4(c), while a plane of polish more remote from the pipe (line “c”) could create an image similar to Fig. 4(b).

IV. Comparison with Literature

Microstructural features closely resembling the convection cells have been reported earlier in the literature but not interpreted as of significance. Figure 8 compares previously published images of specimens oxidized at CNR-ISTEC by Monteverde$^{12}$ with a specimen oxidized at University of Michigan (UM). Cross sections of HfB$_2$–SiC–HfN and ZrB$_2$–HfB$_2$–SiC–HfN composites oxidized at 1450°C for 20 h by Monteverde$^{12}$ at CNR-ISTEC are shown in Figs. 8(a) and (b). The images show vertical ZrO$_2$ features on top of an enhanced oxidation zone (increased thickness of ZrO$_2$ layer). Figure 8(c) shows a ZrB$_2$–15 vol% SiC composite fabricated at CNR-ISTEC and oxidized at 1500°C for 2 h at UM. The cross sections shown in Figs. 8(a) and (b) closely resemble the cross section of the convection cell shown in Fig. 8(c). Note the similarity in the morphology of the vertical ZrO$_2$ feature of the specimen oxidized at CNR-ISTEC to the morphology of the ZrO$_2$ “island” of the specimen oxidized at UM (indicated by a arrow in Fig. 8). Also, all three specimens shown in Fig. 8 have thicker ZrO$_2$ layer (enhanced oxidation zone) under the vertical ZrO$_2$ features. The similarity of these images indicate that the convection cells are seen in other boride–SiC materials such as these Hf(Zr)B$_2$–SiC–HfN composites, which have a different relative amount of in Hf(Zr)O$_2$, SiO$_2$, and B$_2$O$_3$ after oxidation.

Figure 9(a) shows similar features for a ZrB$_2$–30 vol% SiC composite oxidized for 30 min at 1400°C by Rezaie et al.$^{13}$ at the University of Missouri-Rolla (UMR) previously reported in the literature. Figure 9(b) shows a cross section of a ZrB$_2$–15 vol% SiC composite (fabricated at CNR-ISTEC) oxidized at 1550°C for 1 h at UM. The cross sections have very similar microstructural features: enhanced oxidation zone (thicker ZrO$_2$ layer) under a vertical ZrO$_2$ feature. This indicates that convection cells were formed on the ZrB$_2$–30 vol% SiC composite during oxidation.

**Fig. 7.** Schematic showing different planes of cross sections possible through a convection cell, showing the inner structure of the cell.

**Fig. 8.** Scanning electron microscopic images of the cross sections of diboride/silicon carbide composites. (a) HfB$_2$–SiC–HfN and (b) ZrB$_2$–HfB$_2$–SiC–HfN composites oxidized at 1450°C for 20 h by Monteverde$^{12}$; (c) a ZrB$_2$–15%SiC composite oxidized at 1550°C for 2 h.

**Fig. 9.** Cross sections of ZrB$_2$–SiC composites. (a) ZrB$_2$–15%SiC oxidized at 1550°C for 1 h and (b) ZrB$_2$–30 vol% SiC oxidized at 1400°C for 30 min by Rezaie et al.$^{13}$
oxidation. Figure 10(a) shows a micrograph of the surface of the ZrB₂–SiC specimen oxidized for 1 h at 1550°C at UM. The image shows how the convection cells are spread over the surface, forming a pattern with small micrometer-sized ZrO₂ particles located between the boundaries of the cells. Figure 10(b) shows the flow pattern of the ZrO₂ particles in more detail. No micrographs of the surfaces of the specimens oxidized at CNR-ISTEC or UMR were reported, thus comparison of these surfaces to the UM specimens could not be done.

The features shown in previously published micrographs from CNR-ISTEC and UMR are suggested here to be in fact convection cells. These findings indicate that the convection cells do exist for other oxidized boride–SiC materials but have not been brought to attention in the literature or interpreted as of significance for the oxidation behavior of these materials.

V. Subscale Recession: Enhanced Oxidation Regions

Now let us direct our attention to the local regions of enhanced oxidation shown in Figs. 4(d), 8 and 9. These are the areas with more diboride recession (deeper) and thicker scales (thicker ZrO₂ layer) under the convection cell features. Why do these form? Our hypothesis is based on inward diffusion of oxygen. Let us assume that the rate of diboride oxidation is limited by inward oxygen transport as has been reported previously in the UHTC literature. Areas of greater recession demand greater inward oxygen diffusion to leave a thicker scale. The driving force is similar; hence, the oxygen diffusivity must be locally higher. Here we can invoke the Stokes–Einstein relation between diffusivity and viscosity, derived from studies of the Brownian motion of a solid sphere suspended in a fluid, where the particle’s diffusivity is inversely proportional to the fluid viscosity, i.e. \( D \sim 1/\eta \), more specifically:

\[
D = \frac{k_B T}{6\pi \eta r}
\]

where \( D \) is the diffusion coefficient, \( k_B \) the Boltzmann constant, \( r \) is the radius of the slowest particle moving through the fluid (the hydrodynamic radius), and \( T \) the absolute temperature. Another similar equation based on the theory of absolute reaction rates by Eyring is sometimes preferred for silicate glasses to relate melt viscosities to the diffusion coefficients of oxygen in molten silicates:

\[
D = \frac{k_B T}{\lambda \eta}
\]

where \( \lambda \) is the mean jump distance of the diffusing particle (O²⁻).

In the SiO₂-rich scale, the viscosity at oxidation temperatures of 1500°C is on the order of \( 10^{11} \) Poise (\( 10^{10} \) Pa·s). With the presumed composition of BSZ liquid,¹⁰ we have estimated based on limited data in the literature that the viscosity will be about \( 10^9 \) Poise (\( 10^8 \) Pa·s); this is a large viscosity difference, by about factor of \( 10^7 \). This implies that in the local regions of the BSZ liquid pipes, the diffusivity for inward diffusion of oxygen must be larger by a similar factor, about \( 10^7 \) times faster oxygen transport than in the SiO₂ scale remote from the pipe. When the convection cell forms (the deformation erupts) outward flow of material of low viscosity (BSZ liquid) occurs and a localized inward path for oxygen will be created. A synergy between oxygen transport in and liquid transport out occurs. Thus we expect a complex coupling of these phenomena.

Oxygen can diffuse through amorphous SiO₂ via two mechanisms: (1) so-called network oxygen ions can diffuse through the SiO₄ tetrahedral network and (2) interstitial (nominally molecular) oxygen can diffuse through the free volume of the silicate structure.¹¹ For the network oxygen ion diffusion the Eyring equation can be used to estimate the oxygen diffusion coefficient by using \( \lambda \) as the mean jump distance of the diffusing particle (O²⁻) with the Eyring equation:

\[
D = \frac{k_B T}{\lambda \eta}
\]

The diffusion coefficient of interstitial oxygen diffusion (molecular) can be estimated by using the Stokes–Einstein relation with \( \eta \) (hydrodynamic radius) substituted by the O₂ bond length (1.21 Å).²² The two mechanisms can operate simultaneously and most likely have different temperature dependencies. Thus oxidation at different temperatures could be governed by either mechanism. The question of whether oxygen diffuses through SiO₂ as a molecule or ionically or perhaps both remains unclear, which has led to a broad range of reported diffusion coefficients.

Fig. 11 shows the calculated diffusion coefficient of oxygen in a borosilicate melt versus the viscosity, calculated with the Stokes–Einstein relation and the Eyring equation. For the Stokes–Einstein relation the following parameter were used: \( T = 1550 \)°C, and \( \eta = 1.21 \) nm (where the O₂ bond length is used for the hydrodynamic radius of O₂²⁻) and viscosity values are estimated by relationship extrapolated from data by Jabra and colleagues. The same viscosity values were used for the Eyring equation as well as \( T = 1550 \)°C, and \( \eta = 0.159 \) nm, which is the Si–O distance in SiO₂ glass.¹⁹ The diffusion coefficients...
calculated by the two equations differ on the order of about one magnitude. The difference is not large compared with the wide range of values reported in the literature; also these values are comparable to measured and calculated values reported previously.

Figure 12 shows the diffusion coefficient of oxygen in a borosilicate melt versus mol% of SiO2 estimated by using the Stokes–Einstein relation with $T = 1550^\circ\text{C}$, $r = 0.121$ nm, and viscosity values estimated from data by Jabra and colleagues. Figure 12 shows how the measured oxygen diffusion constant decreases with an increase in SiO2 mol% in a B2O3–SiO2 melt. This is indicated by the low diffusion coefficient of oxygen for a pure SiO2 melt (100 mol% SiO2 $D = 1.1 \times 10^{-21}$ m$^2$/s) compared with a B2O3-rich melt (79 mol% B2O3–21 mol% SiO2 $D = 1.7 \times 10^{-14}$ m$^2$/s), which is 10$^7$ times larger, as estimated from the large viscosity difference mentioned above. The calculated diffusion coefficients of oxygen in borosilicate melts (Fig. 12) is smaller than the diffusion coefficient of oxygen in ZrO2 ($D = 1.1 \times 10^{-19}$ m$^2$/s) compared with a B2O3-rich melt (79 mol% B2O3–21 mol% SiO2 $D = 1.7 \times 10^{-14}$ m$^2$/s). This is larger by a factor of 10$^7$.

The local enhanced oxidation regions under the convection cells makes the oxidation of diboride–SiC composites at these temperatures a nonuniform process at a macroscopic scale. Observations of apparently uniform oxidation behavior reported in the literature could result from the fine scale of the local events. Just like an intergranular corrosion may be quite homogenous on the macroscopic scale, it is not localized on a microscopic scale. Perhaps in the early state of the oxidation uniform oxygen diffusion generates a pool of BSZ liquid. When the volume of the liquid and the pressure (by Pillings–Bedworth ratio) reaches a critical amount, it erupts. While it is erupting, oxygen can diffuse in by the same path; hence, it oxidizes faster under a cell creating the enhanced oxidation zone.

### VI. Summary

Oxide scale features previously published in the literature on ZrB2–SiC and HfB2–SiC composites are suggested here to be in fact the proposed convection cells reported for the first time by the authors. These features are of great significance contributing to the formation of complex oxide scales of these materials. The flow of a B2O3-rich BSZ liquid to the surface, with the subsequent loss of B2O3 to evaporation, explains the formation of a glazy SiO2-rich layer on the surface commonly reported in the literature. Also the outward flow of the BSZ liquid creates a localized inward flow for oxygen due to lower viscosity that allows faster oxidation under the convection cell. The formation of a convection cell (eruption of the “primary” scale) creates a leak in the SiO2 barrier, but the BSZ liquid eventually replenishes the SiO2 scale, patching the leak creating a positive feedback.

### References

20. F. Monteverde, Gregory Hilmas, and William Farhenholtz for providing samples and valuable discussions.

**Acknowledgments**

We thank Dr. David Shiffer of the Office of Naval Research for supporting the research under contract N00014-02-1-0034 and Drs. Alida Bellosi, Frederick Monteverde, Gregory Hilmas, and William Farhenholtz for providing samples and valuable discussions.