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STRENGTH DEGRADATION OF OXIDE/OXIDE AND SiC/SiC CERAMIC MATRIX COMPOSITES IN CMAS AND CMAS/SALT EXPOSURES

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ABATRACT

CMAS (Calcium-Magnesium-Aluminosilicate) has shown to induce some deleterious effects on yittria-stabilized-zirconia (YSZ) based thermal barrier coatings (TBCs) of hot section components of aeroengines. The effects were shown to be dependent on the types and operating conditions of engines/components. The work presented here explored how CMAS would affect ceramic matrix composites (CMCs) in terms of strength degradation. Four different, gas-turbine grade CMCs were utilized including two types of MI SiC/SiCs and other two types of oxides/oxides (N720/aluminisilicate and N720/alumina). Test specimens in a simple flexure configuration were CMAS-treated at 1200 °C in air under either isothermal or thermal cycling condition. The effects of CMAS were quantified via residual strengths of treated test specimens. Strength degradation with respect to as-received strengths ranged from 10 to 20 % depending on the types of CMCs. It was further observed that significant degradation of strength up to 90% occurred in an oxide/oxide CMC when sodium sulfate was added to CMAS.

[*Key words*: CMAS (calcium-magnesium-aluminosilicate); ceramic matrix composites (CMCs); SiC/SiC; N720/alumina; N720/aluminosilicate; oxide/oxide; strength degradation; mechanical testing] *

INTRODUCTION

It has been shown that yttria stabilized zirconia (YSZ) thermal barrier coatings (TBCs) used in aeroengines exhibited some deleterious effects when they were exposed to CMAS (calcium-magnesium-aluminosilicate) at elevated temperatures. CMAS, melted and molten at high temperatures (≥1150°C in air), infiltrated into open structure of TBC, resulting in premature failure of TBCs via chemical reactions and CTE (coefficient-of-thermal-expansion) mismatch between melt CMAS and TBCs. This CMAS effect on TBCs would be accelerated in areoengines since harsh operational conditions are expected to occur in the engines, ascribed to their significant mechanical and/or acoustical loading/vibrations, extensive rubbing between stationary and rotating components upon demanding maneuverability, and randomly changing thermal loading, etc.

The effects of CMAS on TBCs have been investigated in terms of thermo-chemical interactions [1,2], thermo-mechanical aspects [3,4], and radiative transmission phenomenon [5]. Recently, attempts have been made to explore CMAS interaction with environmental barrier coatings (EBCs) [6] and CMAS effect on thermal conductivity at elevated temperatures [7].

Ceramic matrix composites (CMCs) have been developed as one of most promising and viable material systems to date for hot-section components of current and future aeroengines. Extensive work on CMCs regarding processing, materials/constituents, net-shape manufacturing, cost-effectiveness, and mechanical, thermal, chemical and environmental (particularly for water vapor) aspects has been undertaken in the past several decades to address those issues. A new question still arises as to how CMCs would be affected by the attacks of CMAS at elevated temperatures. To the authors' best knowledge, no work seemed to have been done on this particular subject. The objective this work, as a consequence, is to determine the effects of CMAS on CMCs. Test specimens of four different CMCs were CMAS treated at 1200°C and their strength was determined to assess the severity of CMAS attacks. Two different thermal loading of isothermal and cyclic heating were used during CMAS

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Table 1. Continuous fiber-reinforced CMCs used in this work

Materials	Weave/Fibers	V_f^{**}	Manufacturer
MI SiC/SiC* [10-12]	2-D woven, Sylramic SiC	0.33	GEPSC‡
MI SiC/SiC* [10,11]	2-D woven, Hi-Nic SiC	0.39	GEPSC‡
N720/AS# [13,14]	2-D woven, N720	0.45	GE
N720/Al_2O_3 [14]	2-D woven, N720	0.45	ATK/COIC

Notes:
* All *in situ* BN fiber interface coated; MI: melt infiltration
\# AS: Aluminosilicate
** V_f: Fiber volume fraction
‡ Currently GE Ceramic Composite Products (CCP), Newark, DL
\- No fiber interface coating applied in the oxide/oxide CMCs of N720/AS and N720/Al_2O_3.

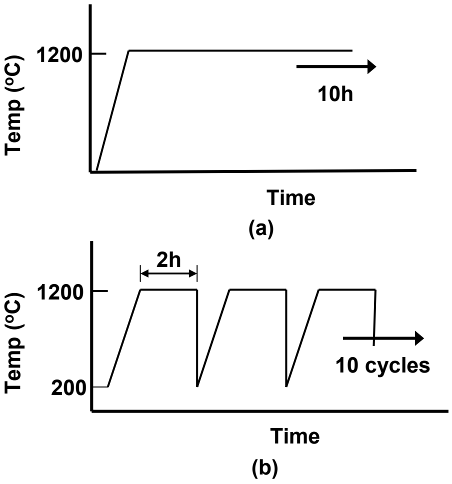

Figure 1. Thermal conditions applied in CMCAS exposure at 1200°C in air: (a) isothermal and (b) thermal cyclic conditions.

exposure. Also, the combined effects of CMAS and salt were determined. This work is considered preliminary since detailed chemical, thermal, or environmental interactions were not included in the study.

EXPERIMENTAL PROCEDURES

CMAS, or sand, is omnipresent and prevailing from the crust of the Earth. The CMAS used in this work was acquired from a proprietary source. A typical composition of CMAS has been modeled as $35CaO\text{-}10MgO\text{-}7Al_2O_3\text{-}48SiO_2$ in mol% [1]. But in reality, there has been variability in composition from source to source. Some mechanical properties such as hardness and fracture toughness of "melt" CMAS[†] that was melted at 1300°C in air and then solidified via slow cooling to room temperature were determined via indentation techniques [8,9].

Four different CMCs were used in this work including Hi-Nic MI SiC/SiC, Sylramic MI SiC/SiC, N720/aluminosilicate, and N720/alumina composites. Descriptions regarding these SiC/SiC and oxide/oxide CMCs can be found elsewhere [10-14] and here their brief architectural information is presented and shown in Table 1. CMC test specimens machined from their respective panels were all in a flexure configuration and were measured 12 mm in width and 50 mm in length. The thickness of test specimens was as-received thickness of typically 2 mm for the SiC/SiC CMCs and 2.7 mm for the oxide/oxide CMCs. A small amount of dry powdery CMAS of about 10 mg was placed in an area covering 10mm (longitudinal) by 6 mm (transverse) at the central region of each of CMC flexure test specimens. Test specimens with CMAS were then exposed to isothermal (10h) or thermal cycling (2h/10cycles) condition at 1200°C in air, as shown in Fig. 1. The severity of CMAS attack was quantified by conducting strength testing for the CMAS treated specimens to determine their residual strength. Testing was performed at ambient temperature with a four-point flexure fixture with 20 mm-inner and 40mm-outer spans using a displacement rate of 0.5 mm/min in an electromechanical test frame (Instron Model 8562). Each test specimen was oriented such that the CMAS-treated side was subjected to the prospective tensile stress in flexure. For a given CMC, a total of four test specimens were used at each thermal condition.

Additional testing was also conducted using a mixture (about 10 mg) of CMAS and salt (sodium sulfate, Na_2SO_4) in a 50 to 50 weight percent under the same thermal conditions applied to the CMAS treatments. Residual strength of CMAS/salt treated test specimens was also determined. The number of test specimens in CMAS/salt tests was four for a given CMC. The sodium sulfate has been considered as prevailing corrosion species formed from sodium chloride and sulfur oxides from fuel combustion in gas turbine engines [15]. SEM and EDS were used to characterize some involved interactions of environmental species with fibers and matrices for selected CMC test specimens.

[†] The "'melt" CMAS' represents a CMAS material that was obtained via melting some amount of dry (powdery) CMAS at 1300°C in air and then slowly cooling to ambient temperature to form a solid . This term "melt" CMAS was used throughout the text.

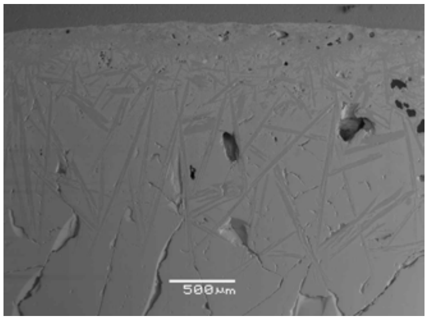

Figure 2. Overall view of CMAS melted at 1200°C in air for 10 h and then solidified.

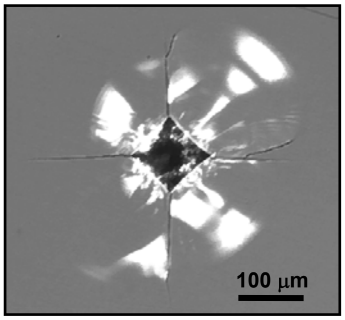

Figure 3. Vicker's indentation made on the melt CMAS with an indentation load of 9.8 N. Well developed cracks emanating from the impression corners are seen.

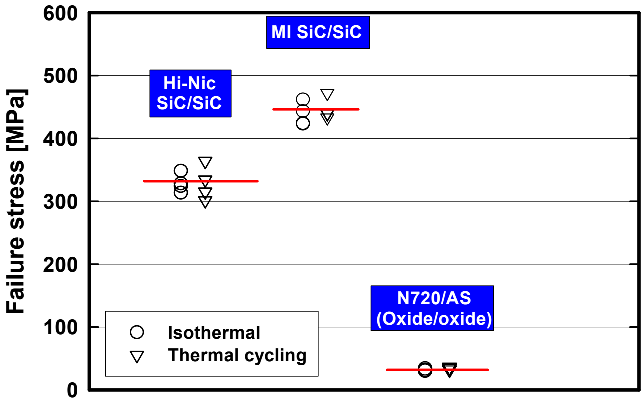

Figure 4. Residual strength responses of CMCs to CMAS treatments at 1200°C in air for both isothermal and thermal cycling conditions.

RESULTS AND DISCUSSION

Melt CMAS - Properties

The CMAS melted at 1300°C for 10h in air formed as a blackish thin glass deposit on an Al_2O_3 substrate, as seen from Fig. 2. The melt CMAS was found to possess its chemical composition of (30-40)CaO-(10-20)Al_2O_3-(50-60)SiO_2 in weight % with a little trace of Mg [16]. In this case, the sand is referred to as CAS (calcium aluminosilicate) rather than CMAS. Indentation response of the melt CMAS, which was determined via a Vicker's indentation at 9.8N, is shown in Fig. 3. Well developed Vicker's radial cracks with some formation of lateral cracks are evident, very reminiscent of those observed in many silicate glasses. Both crack and impression sizes were determined to estimate fracture toughness [8] and Vicker's hardness [9] of the melt CMAS with a total of eight indents. The hardness value was estimated as $H=5.90\pm0.34$ GPa, while fracture toughness[‡] was $K_c=0.67$ MPa$\sqrt{}$m. The coefficient of variation (COV) was *very small* with less than 10% in hardness, average crack size, and fracture toughness. Density was found to be about $\rho\approx2.7$ g/am^3, estimated with a piece cut form the melt CMAS.

The values of H, K_c, and ρ are surprisingly close to those of many glasses such as fused silica, soda-lime or borosilicate glasses, indicating that the melt CMAS is nothing more than one of typical silicate glasses in its response to hardness, fracture toughness, and density. This implies that other properties like elastic modulus, CTE, thermal conductivity/diffusivity, and heat transfer coefficients, etc, would not be significantly different from those of typical silicate glasses. However, those properties need to be characterized through pertinent test methodologies, as being used as input parameters particularly for delamination modeling [3,4].

Residual Strength Responses

The results of strength testing for CMAS treated test specimens under both isothermal and thermal cycling conditions are presented in Fig. 4, where residual strength determined was compared between the two different thermal treatments. As seen from the figure, residual strength was irrespective of thermal condition, either isothermal or cyclic-thermal loading, even though they were completely different in thermal sequence and duration.

[‡] The value of elastic modulus in the K_c calculation was assumed to be E=70 GPa, which is common to many silicate glasses. The sensitivity of E in the K_c calculation [8] is insignificant.

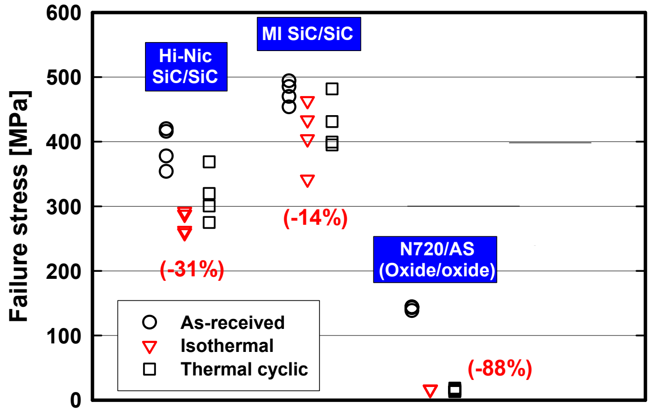

Figure 5. Residual strength responses of CMCs to CMAS/salt treatments at 1200°C in air for both isothermal and thermal cycling conditions. The as-received strength of each CMC is included for comparison. The numbers in parentheses indicate the amount of average strength degradation in isothermal condition with respect to average as-received strength for each material.

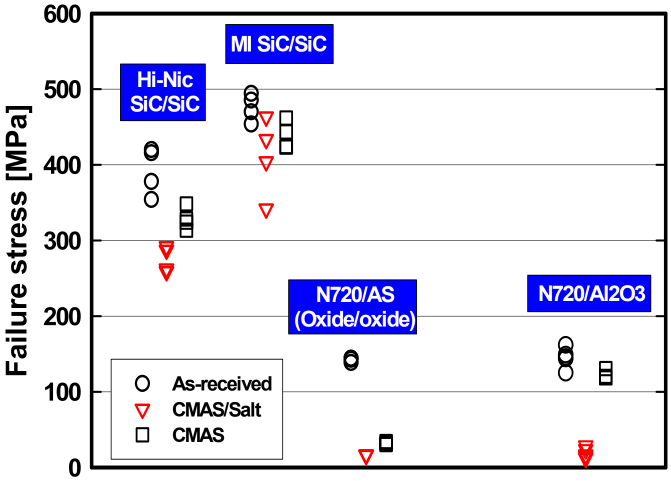

Figure 6. Residual strength responses of four different CMCs to CMAS and CMAS/salt treatments at 1200°C in air under isothermal condition. The as-received strength of each CMC is included for comparison.

Figure 5 compares residual strength for CMAS/salt treated test specimens between the two different thermal conditions. As in the CMAS case, the strength degradation in the combined CMAS/salt environment was not significantly dependent on the type of thermal conditions. It was originally postulated that the thermal cyclic condition would result in more damage than the isothermal counterpart through repeated CTE mismatch during thermal cycling between the melt CMAS (or CMAS/salt) and the fibers/matrices of the composites. However, this seems to be not the case. Accordingly, only the isothermal condition was utilized for a more recent CMC, which was an N720/alumina oxide/oxide CMC.

A summary of residual strength of four different CMCs subjected to both CMAS and CMAS/salt treatments is depicted in Fig. 6, where residual strength was compared between CMAS and CMAS/slat treatments under isothermal condition. As-received strength was included for each of CMCs for comparison. The amount of degradation of average strength with respect to average as-received strength for Hi-Nic SiC/SiC was about 20 and 31 %, respectively, in CMAS and CMAS/salt treatments. For Sylramic SiC/SiC, the respective strength degradation amounted to 8 and 14%; for N720/aluminosilicate it was 88 and 80%; for N720/alumina it was 16 and 87 %. Hence, strength degradation was greater in CMAS/salt than in CMAS only environment, regardless of the type of CMCs used. It was found later that the N720/aluminosilcate oxide/oxide was a seemingly incapable material as a load-carrying structural member at 1200°C because of appreciable degradation in its matrices occurring even with no CMAS or CAMS/salt exposure at 1200°C. The resulting strength of N720/aluminosilicate after simple heat treatment at 1200°C in air for 10 h was around 40 MPa, with an about 70% strength degradation. By contrast, other CMCs such as MI SiC/SiCs and N720/alumina showed no to negligible strength degradation under the same heat-treatment.

Of particular interest is the N720/alumina oxide/oxide CMC where appreciable strength degradation up to 87% took place in CMAS/salt treatment. By contrast, the strength degradation in CMAS treatment was about 16%, much less than that in CMAS/salt treatment. Figure 7 shows SEM images of an N720/alumina test specimen subjected to CMAS treatment. CMAS infiltration into the material was evident but it was confined only to the upper region of the sample, as also shown in the EDS analysis. Some evidences of reactions occurring in both matrices and fibers are observed from the upper region; whereas, little or no sign of interactions is seen from the middle or lower region. The reaction confined to the upper shallow region would have been responsible for the strength degradation of about 16%.

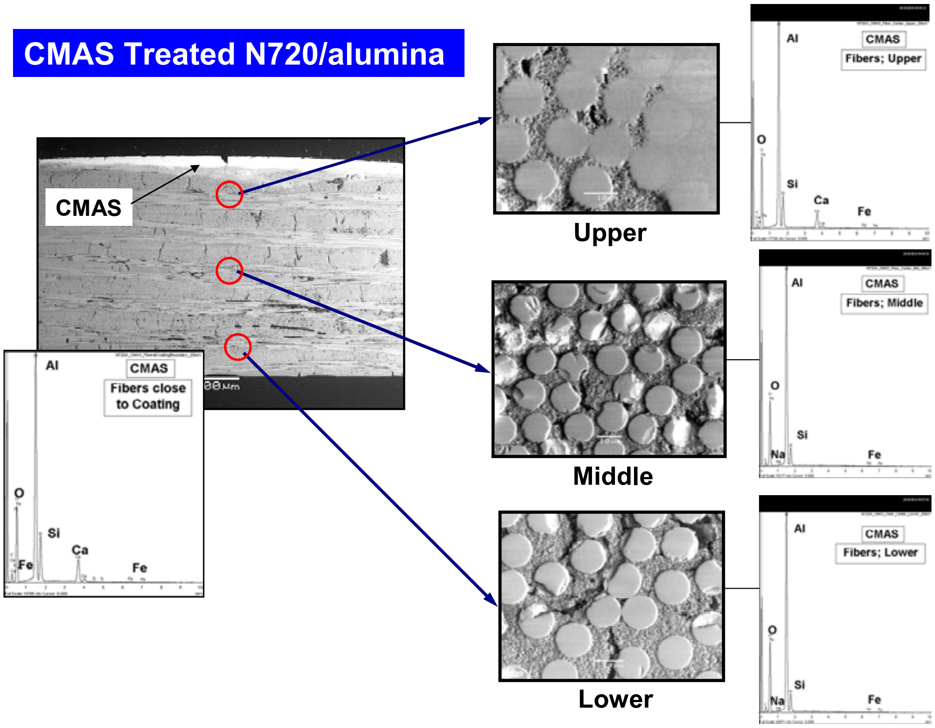

Figure 7. Microstructure and EDS in different locations of an N720/alumina oxide/oxide CMC treated in CMAS at 1200°C in isothermal condition.

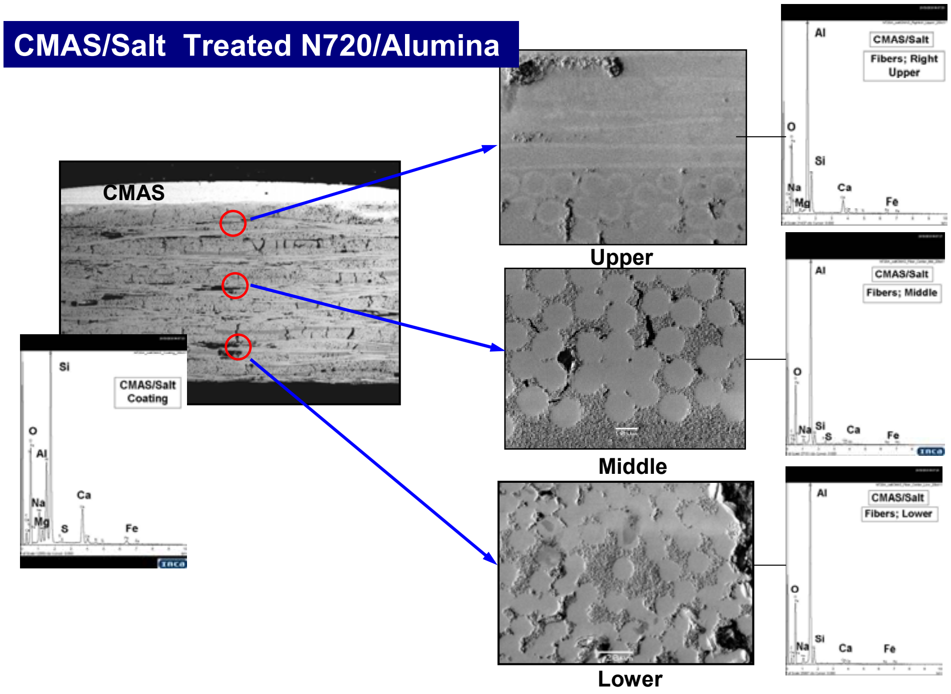

Figure 8. Traces of locations for microstructure and EDS of an N720/alumina oxide/oxide CMC treated in CMAS/salt at 1200°C in isothermal condition.

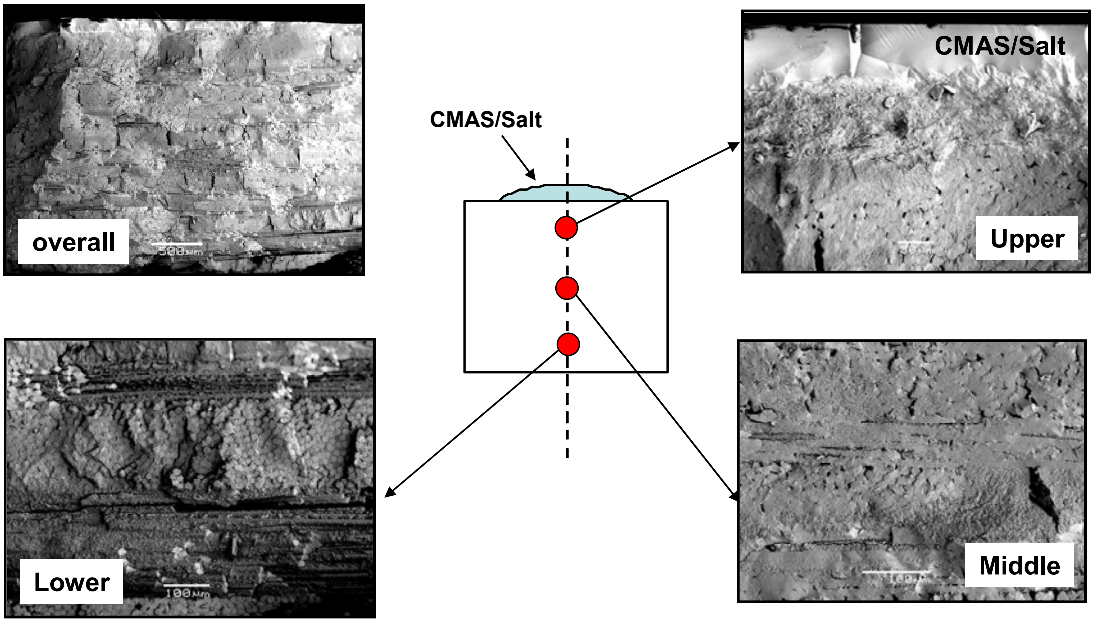

Figure 9. Fracture surface of an N720/alumina oxide/oxide CMC treated in CMAS/salt at 1200°C in isothermal condition. Brittle failure is characterized with no presence of fiber pull-outs.

However, the situation for CMAS/salt treatment was quite distinctive, as shown in Fig. 8. First of all, the degree of infiltration of CMAS/salt into the N720/alumina composite was so extensive that it nearly reached the bottom of the test sample, as seen from the EDS in the figure. Resulting reactions of CMAS/salt with the fibers and matrices were severe, causing the composite almost to lose its integrity of material constituents. In particular, the fibers in the upper region seemed to be "eaten away," leaving a white external layer on each of fibers. More detailed characterization will be sought out to identify possible interaction mechanisms.

Fracture surfaces and their related EDS of an oxide/oxide test specimen under CMAS/salt environment are also presented in Fig. 9. The specimen broke into two pieces in a very brittle manner during strength testing. The corresponding fracture strength was about 19 MPa! Note that the as-received strength of the composite was 145 MPa. The fracture surface was *flat* and exhibited an almost complete absence of fiber pull-outs, indicative of severe damage of the CMC both in fibers and matrices. As seen from the figure, the damage was significant in the upper region that even fibers were not readily observed. The significant open channels/structure of the oxide/oxide CMC with prevailing pores, cavities, and/or micro or macrocracks might have accelerated infiltration/interaction of the environmental species into/with the CMC. It should be noted that the porosity of the oxide/oxide CMC was about 25 %, which was intended in this type of oxide/oxide to enhance damage tolerance. The material needs to be improved against CMAS/salt attack via proper modifications of matrices, fibers, or architecture. Applications of interface coatings, or external protective coatings could be an alternative. This type of oxide/oxide composite has been shown to be better protected by means of an interface coating such as monazite [17] or by other external coating like FGI (Friable Graded Insulation) [18].

There has been an enormous amount of work on hot corrosion in SiC-based monolithic ceramics with detailed exploration of governing mechanisms [e.g., 19-21]. In comparison, the work presented here is preliminary in view of its scope and contents. A wide range of temperature and time is required to generalize the overall behavior of CMCs with response to CMAS and CMAS/salt attacks. In addition, thermo-chemical interactions of CMAS-treated CMCs with environmental species are required to be characterized in more detail, which will allow one to explore governing mechanisms. Finally, long-term exposure to the related environments in conjunction with other combined interactions with slow crack growth, fatigue, creep, water vapor, and/or FOD (foreign object damage) [12,13] is also to be explored to ensure overall reliability and durability of aeroengine-grade CMC material systems.

CONCLUSIONS

1. The Melt CMAS exhibited a similarity in hardness, fracture toughness, and density to many conventional silicate glasses such as soda-lime, borosilicate, and fused silica.
2. The difference in strength degradation in either CMAS or CMAS/salt was insignificant between isothermal and thermal cyclic conditions at 1200°C in air.
3. The degree of strength degradation, in general, was greater in CMAS/salt than in CMAS. Particularly, the degradation was appreciable for an N720/alumina oxide/oxide CMC in CMAS/salt, resulting in an 87 % degradation of strength with respect to its as-received strength. In this case, severe damage in both fibers and matrices occurred in the oxide/oxide CMC with almost no fiber pull-outs from its fracture surface, characterized as a complete brittle failure in its mode of fracture.

Acknowledgements

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