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Combustion-resistance of silicon-based ceramics and composites at very high oxygen pressures

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The resistance of ceramic matrix composites to combust at high oxygen pressures is expected to provide information in developing oxygen-rich propulsion systems. In contrast to metals, silicon based ceramics, SiC, Si_3N_4 and SiC-composites, have prevalently covalent bonding characteristics and their promoted combustion characteristics were different. These materials dissociate at very high temperatures rather than going through discrete solid—liquid phase transformation (melting). The silicon based ceramics and composites burn heterogeneously at very high oxygen pressures and the critical threshold pressure at which no test specimen sustains combustion correlated with composition, the nature of the bonding and the solubility of oxygen. © *2004 Kluwer Academic Publishers*

1. Introduction

When condensed phase materials, liquids or solids, are projected into oxygen-enriched atmospheres, a combustible mixture is formed. If this mixture is ignited, a flame surrounds the condensed phase and the condensed phase burns. The understanding and controlled use of this thermophysical phenomena is called combustion and is of great interest to humankind for various applications in our everyday life, as well as for various technical processes-, such as energy conversion-, metallurgy-, and naturally, aeronautics and the aerospace industry. The ability of a material to coexist safely with both oxygen and potential sources of ignition at given temperatures and pressures is crucial for selection of materials in a broad range of proposed propulsion systems.

The majority of the structural components of aeronautics and aerospace systems are metallic alloys and numerous investigations have been dedicated to metals and metal alloys oxygen combustibility particularly for very high-pressure systems. Materials with metallic bonding characteristics act as a fuel by evaporating from the surface and diffusing to the flame front as the oxygen moves from the surroundings to the burning front. This description of condensed phase burning is most readily and usually applied to droplet burning and is called homogeneous burning via gas phase reactions. Glassman [1], in his pioneering work on vapor-phase combustion for metal droplets adequately explains several, but not all, experimental facts. Thermochemical predictions to elucidate the reaction paths and transition states for metals at high temperatures and pressures are not available. Further complications arise for multicomponent alloys it has been shown [1, 2] that combustibility is sensitive to minute compositional changes.

Ceramic matrix composites (CMC's) have markedly lower densities than metals and offer sufficient strength and acceptable toughness at high temperatures to make them ideal candidates for aerospace and aeronautic structural applications. In addition to these facts, the finding that the combustion characteristics of CMCs at very high oxygen pressures have not been previously studied prompted the concentration of this study on the solid phase burning characteristic of CMC's. Several factors influenced the choice of the particular CMCs for this study. First, the monolithic SiC, Si_3N_4 and SiC/SiC composites are potential candidates for advanced propulsion systems due to their ability to enhance performance and decrease weight. Second, preliminary oxygen compatibility results for SiC/SiC composites and monolithic Si_3N_4 have shown moderate and excellent oxidation resistance, respectively. Third, SiC/SiC composite and monolithic Si_3N_4 are currently the most mature structural materials within their class. Finally, both are readily available as commercial materials.

2. Experimental

The oxygen compatibility of ceramic materials and CMC's was characterized using the promoted combustion test fixtures located in the Materials Combustion Research Facility (MCRF) at NASA's Marshall Space Flight Center (MSFC), Fig. 1. This test was developed to determine the pressure thresholds for combustion of metallic materials. Generally, the pressure threshold of tested materials is defined as the maximum pressure at which no specimen sustains combustion for more than

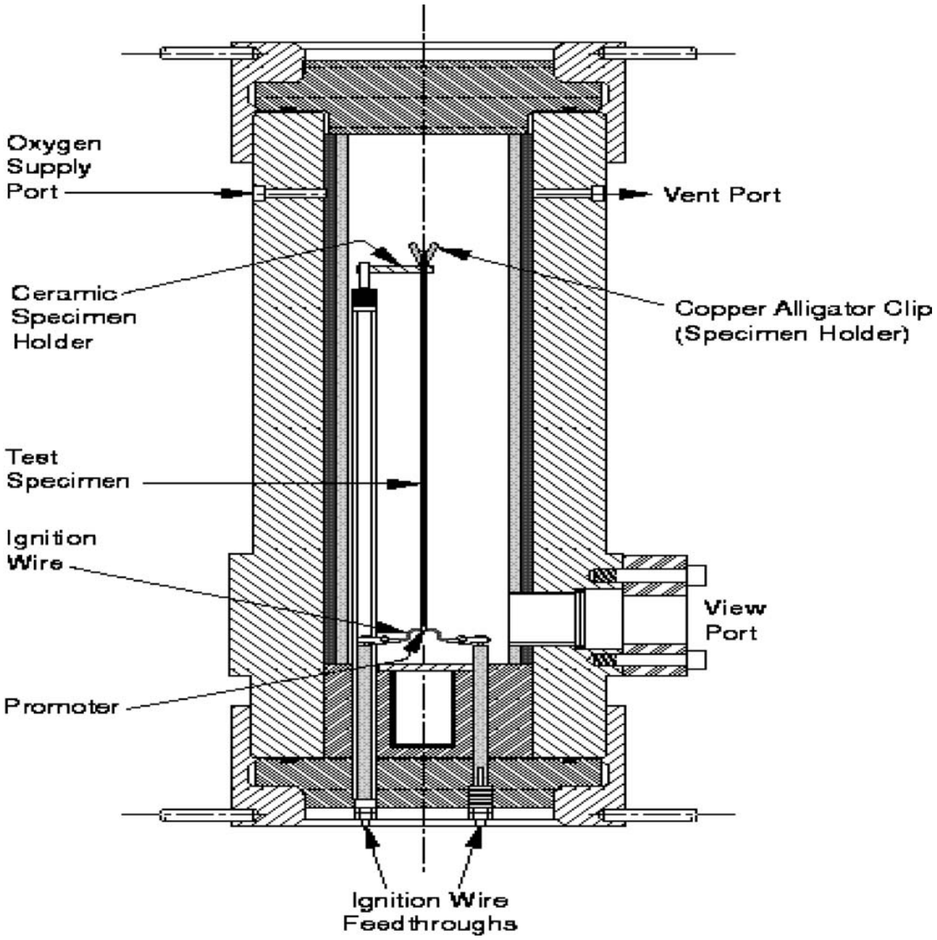


Figure 1 Promoted combustion test configuration. According to NASA Handbook 8601C [3] (now NASA-STD-6001), standard test specimens are to be prepared to 0.32 cm in diameter by 30 cm in length. As this program focused on combustion mechanisms rather than the relative ranking of tested materials, specimen preparation did not strictly adhere to these guidelines. The pressure range for this test system, as configured, is from 0 to 69 MPa (10,000 psi).

half its length. For this pressure to be recognized as the actual threshold, further testing at higher pressures must produce sustained combustion for greater than half the length of at least one specimen. The test apparatus used is a cylinder of 17-4 PH stainless steel, with a reinforcing collar around one end. This collar supports four sight ports by providing the extra thickness required to sustain chamber integrity at the elevated pressures routinely used in this test.

Testing is carried out by supporting a solid rod of a candidate material vertically from its top end inside the chamber. A metallic promoter is attached to the rod's lower end. A bare aluminum-palladium wire is wrapped around the promoter, and an electric current through this wire provides the energy (heat) necessary to ignite the promoter, which then ignites the rod. For this test series, a 0.2 gram slug of 6061-T6 aluminum was used as the promoter. Thus, the same amount of energy is made available to the rod in each test. All tests were videotaped.

Test specimens were prepared to a sample size of 16.5 cm long by either 3.17 mm diameter, or 3.17 mm wide by 3.17 mm thick where a circular cross section was not possible. In a standard Promoted Combustion Test, per NASA Handbook (NHB) 8060.1C, Test 17, (now NASA Standard 6001, Test 17), the standard sample size is 30.5 cm long by 3.17 mm diameter, and five samples are tested at each test pressure [3]. In this series of tests, each material was tested to failure at a predefined set of pressures from 1.72 to 41.4 MPa (250 to 6000 psi), with the initial pressure determined by past testing experience. For these materials, this pressure was 41.4 MPa (6000 psi). A failure was defined as a burn of at least 15 cm for one specimen at any given pressure. At the first failure, testing was continued at the next lower pressure. If no failure occurred in five tests at a given pressure, testing was halted, and that pressure defined as the self-extinguishment threshold pressure for that material. Likewise, the lowest pressure at which the ignited specimen was completely consumed was defined as the sustained combustion threshold pressure for that material. All samples were tested in 99.5% oxygen.

The SiC/SiC composites (DuPont/Lanxide Corporation, Newark, DE) listed in Table II were produced using chemical vapor infiltration process of continuous SiC fiber preforms (two-dimensional weaving). The composite systems in Table II are divided into the following classes of materials: (i) Carbon or boron nitride (BN) coated Nicalon fiber (Nippon Carbon, Tokyo, Japan) in SiC matrix; (ii) Carbon or boron nitride (BN) coated Hi-Nicalon fiber in SiC matrix; "enhanced' SiC/SiC". The surface coatings for Dupont/Lanxide SiC/SiC composites were approximately 20 μm in thickness and had the same composition as the matrix phase. The composite Hi-NiC/SiNC (Dow Corning, Midland, MI) in Table III was produced by using the polymer impregnation pyrolysis route, and composite consists of a proprietary coated Hi-Nicalon fiber in an amorphous SiNC matrix. The melt infiltrated ceramic matrix composite was produced using Hi-Nicalon fibers and the processing conditions are available in the literature [4]. The fiber content of all composites was approximately 30 to 40 vol%.

The monolithic SiC was purchased from CERCOM, Inc., Vista California and produced using CERCOM's "pressure assisted densified" ("PAD") process. The supplier did not provide information about the chemical composition but indicated that grain boundary chemistry is altered to achieve a high density of 3.2 g/cm^3. The chemical vapor deposition (CVD) coupons of SiC were purchased from Morton International, Inc. (currently Rohm and Haas), Woburn, MA, and certified to a purity level as exceeding 99.9995%. The monolithic Si_3N_4 coupons trade name AS 800 were purchased from Allied Signal Corporation, Torrance, CA. The AS 800 was engineered using oxide dopant additions to optimize the high temperature mechanical properties.

3. Results and discussion

Table I lists the measured threshold pressures of selected metals and constituent elements of CMC's, including silicon, boron and carbon. As a first approach approximation, adiabatic flame temperature ($T_{ad,max}$) was calculated using computer program developed by Gordon and McBridge [5] for the stoichiometric concentration of metal dust for the reaction with air (at 25°C and 1 bar). The boundary conditions for the determined critical threshold pressure for promoted combustion P_c and $T_{ad,max}$, are not equivalent, but both P_c and $T_{ad,max}$ assess the combustion characteristics of the material. The calculated $T_{ad,max}$ values listed in Table I provide a measure of the exothermicities, from unreactive copper with $T_{ad,max} = 1510$ K to the highly reactive hafnium with $T_{ad,max} = 4120$ K. For tantalum and iron, the $T_{ad,max}$ values are lower than their boiling temperatures, T_b, and one could expect high resistance to ignition. However, the P_c values for tantalum and iron are very low (0.1 to 0.7 Pa), hence correlation between P_c and $T_{ad,max}$ is not satisfactory. The amount of energy released will be different depending on the reaction path, as has been demonstrated by Dreizin [6]. As will be discussed further with silicone-based ceramics, the amount of oxygen dissolved in the material has a profound effect on the combustion characteristics (heterogeneous or homogeneous) and the reaction rate. The dissolution enthalpy of oxygen would be less than that of stoichiometric oxidation enthalpy and could account for the poor correlation between the calculated adiabatic flame temperature $T_{ad,max}$ and critical threshold pressure P_c, evident in Table I.

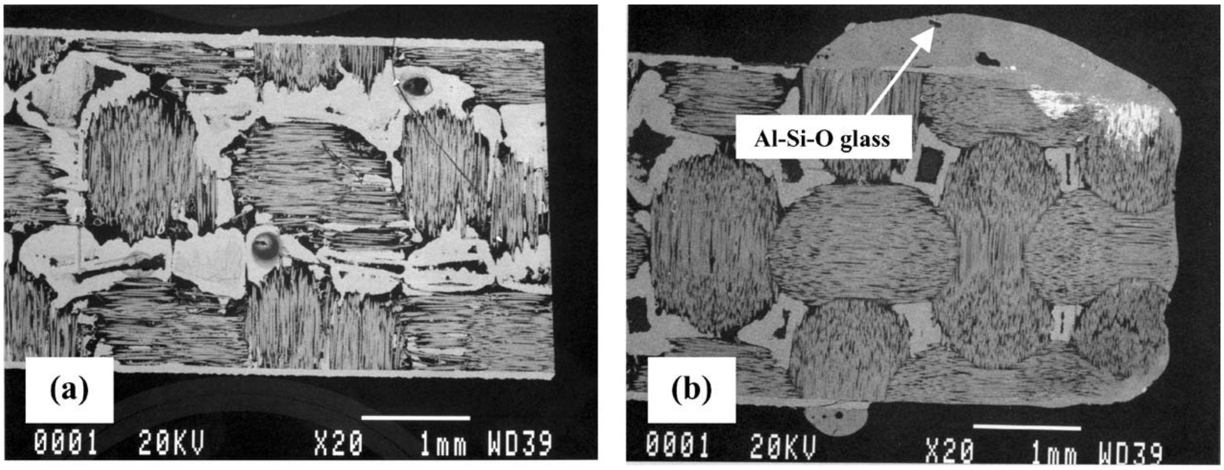
TABLE I Measured promoted combustion pressure, and calculated adiabatic flame temperature, $T_{ad,max}$ for selected metals. The calculated adiabatic flame temperature $T_{ad,max}$ is for the stoichiometric concentration of metal dust for the reaction with air [4]

Metal	Atomic mass	Boiling temperature (K)	$T_{ad,max}$ (K)	Promoted combustion pressure, P_c MPa (Psi)
Hafnium	178.48	4876	4120	Ambient
Magnesium	24.31	1363	3100	
Aluminum	26.98	2793	3550	0.1–0.7 (14–99)
Tantalum	180.95	5731	3290	
Iron	55.85	3135	2250	
Silicon	28.08	3540	2870	6.9–34.5 (1000–5000)
Boron	10.81	4275	2850	
Carbon	12.01	4100	2320	0.1–0.7 (14–99)
Copper	63.55	2836	1510	>69 (>10000)
Lead	207.20	2023	1660	

In contrast to metals, silicon based ceramics (SiC, Si_3N_4 and SiC-composites) have predominantly covalent bonding characteristics. These materials can dissociate at very high temperatures rather than going through a discrete solid–liquid phase transformation (melting). It is therefore expected that silicon-based ceramics will burn differently than metals. The fundamental question is if the amount of heat released during combustion of SiC is large enough to disassociate SiC into elemental Si and C. In order to understand the early stages of the combustion process a SiC/SiC (Dupont/Lanxide) composite was tested at low oxygen pressure and microstructural characterization was subsequently performed. The SiC/SiC composite did not ignite at 6.9 MPa; no sustainable combustion was observed in any of the ten specimens tested. After the promoted combustion test, the SiC/SiC composite was characterized by scanning electron microscopy (SEM). Fig. 2 shows the microstructure of the specimen surfaces at the degraded end (noted as 'burnt' end) and opposing 'unburnt' end is shown in Fig. 2. The reaction product of the igniter deposits as Al_2O_3 and/or reacts with the pre-oxidized specimen to form Al-Si-O glass. This is the equilibrium composition of the combustion products for the system under consideration, and is shown to adhere the specimen surface, Fig. 2. This Al-Si-O glass layer decreases rapidly as one moves away from the burnt end.

The burnt-end sections of specimens tested at different oxygen pressures have been further analyzed using backscattered images (BSE) and elemental X-ray maps. Beneath the silica layer, covering the entire outside surface of the specimen, is a layer of what appears to be silicon oxycarbide phase as determined by energy dispersive spectra (EDS). This finding is analogous to the dissolution of oxygen in the metals which was discussed above. The implications of this result are two-fold. First, when materials ignite, they produce a metastable silicon oxycarbide phase that persists during ignition, which transforms to stable phases at later stages of combustion. Second, an important complication that is encountered in these fast heterogeneous reactions is the influence of diffusion, and other transport processes, which often become rate controlling, masking the influence of chemical reaction rates [7, 8].

The heterogeneous reaction of metal and oxygen (and possibly of volatile oxide species) may take place at the surface of the growing oxide particles, which is in competition with the homogeneous gas phase reactions



"unburnt end"   "burnt end"

Figure 2 Heterogeneous surface phase reaction of CVI-SiC/SiC composite from DuPont/Lanxide following promoted combustion test at 6.9 MPa (1000 psi). No alteration or oxidation observed at the unburnt end (a). The burnt end contains the reaction product of Al-Si-O glass (b).

followed by condensation. Specifically, it is suggested that silicon metal plays a compelling part in the promoted combustion characteristics of SiC. This suggestion is based on the EDS spectra taken on several monolithic SiC and SiC/SiC composite specimens, which revealed elemental silicon at or near the specimen surface where initial burning takes place. Therefore it is inferred that dissociation and disintegration occurs before burning takes place. The SiC/SiC composite burns predominantly in conjunction with decomposition by heterogeneous reactions, since both fuel (SiC/SiC composite), and the reaction products adhering to the specimen surface, were identified in the condensed state. We extended our post combustion test microstructural characterization to samples tested at pressures ranging from 6.9 to 41.4 MPa. Fig. 3 shows the representative micrographs of SiC/SiC composites subsequent to promoted combustion test at 17.2 and

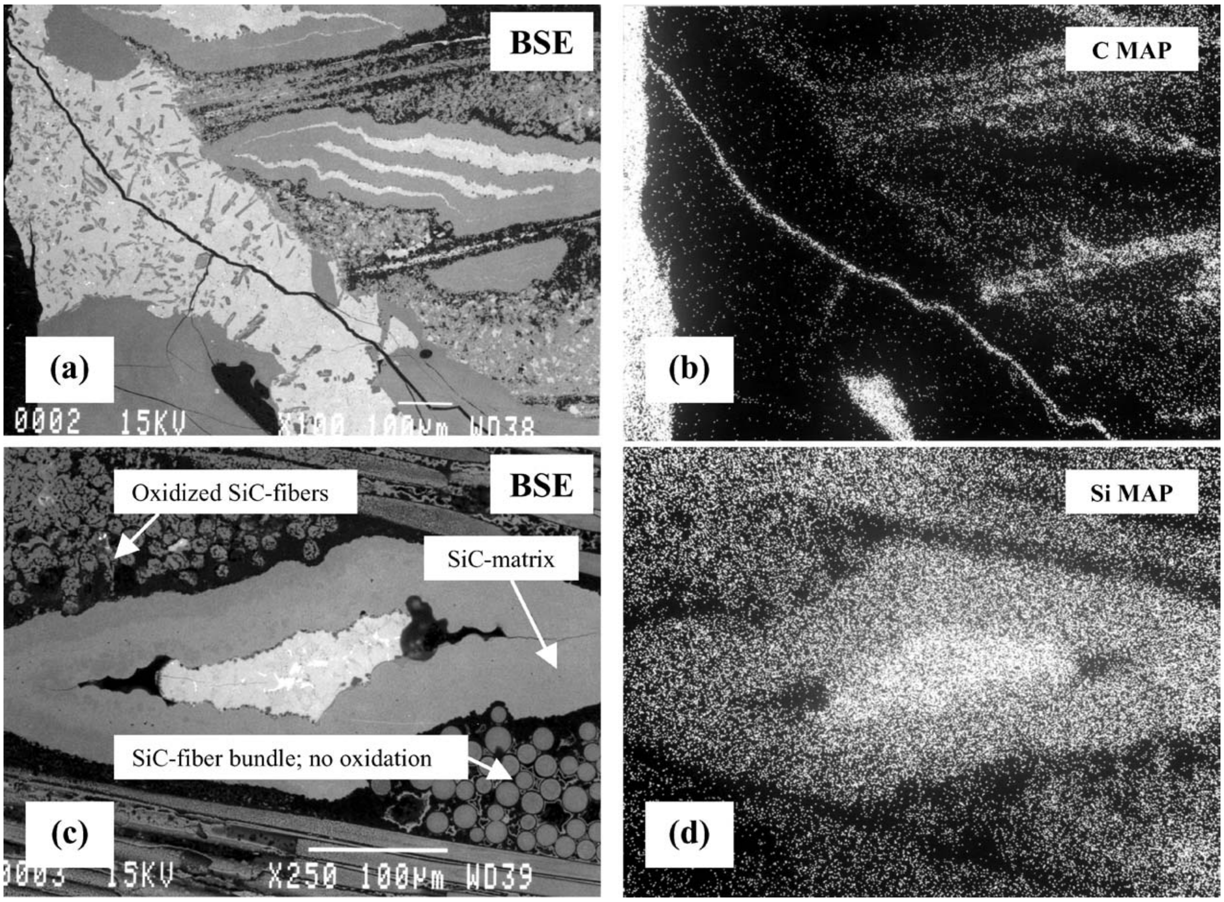


Figure 3 (a) BSE image of CVI-SiC/SiC composite subsequent to the promoted combustion test at 17.2 MPa (2500 psi). (b) Elemental X-ray map image of carbon determined by EDS for CVI-SiC/SiC composite tested at 17.2 MPa (b). (c) BSE image of CVI-SiC/SiC composite subsequent to the promoted combustion test at 20.7 MPa (3000 psi). (d) Elemental X-ray map image of silicon determined by EDS for CVI-SiC/SiC composite tested at 20.7 MPa.

TABLE II Burn lengths of CVI-SiC/SiC composite subsequent to promoted combustion test at different oxygen gas pressures. Each data represents different sample

Materials			Burn lengths in cm at oxygen gas pressure		
Composite: Fiber (Producer)	Fiber matrix interface	Surface coating	10.35 MPa	13.8 MPa	20.7 MPa
SiC/SiC:	Carbon	N/A	0.3	2.0	16.5
Nicalon fiber			0.5	3.0	
(DuPont/Lanxide)			0.5	3.6	
			0.7	3.6	
			0.8	3.8	
				4.1	
				4.8	
				5.1	
				5.3	
				5.6	
Enhanced SiC/SiC:	Carbon	SiC		2.8	16.5
Hi-Nicalon fiber				3.0	
(DuPont/Lanxide)				3.8	
				4.6	
				5.8	
SiC/SiC:	Boron nitride	N/A		2.0	16.5
Nicalon fiber				3.8	
(DuPont/Lanxide)				4.0	
				4.3	
				5.1	
Enhanced SiC/SiC:	Boron nitride	SiC		1.5	
Hi-Nicalon fiber				1.8	
(DuPont/Lanxide)				2.3	
				3.8	
				4.5	

20.7 MPa. The microstructural characteristics of SiC/SiC composites combustion tested at higher pressures were similar to Fig. 3 and therefore will not be repeated here.

Promoted combustion tests of the SiC/SiC (Dupont/Lanxide) ceramic matrix composite at elevated pressures revealed that the material has limited resistance to ignition at higher pressures, Table II. At 13.8 MPa (2000 psi) and 17.2 MPa (2500 psi) the porous SiC/SiC composites with carbon rich interface layers are ample fuel for combustion ($\sim$30% burns). Substantial disintegration and fracture occurred, as observed via analyses of video images, presumably due to differential thermal mismatch between the reaction product (Si, SiO_2) and the composite. Metallographic examination of the burnt end of the sample, shown in Fig. 3, indicates that the reaction product did not stay on the surface of the composite and was therefore unable to protect it from further combustion. At higher pressures of 20.7 MPa (3000 psi) and 41.4 MPa (6000 psi), 86 and 100% of the length of composite burned respectively.

Table II shows that burn lengths of SiC/SiC composite at 13.8 MPa (2000 psi) with and without a protective coating were the same (within the experimental error). The burn lengths of composites with different chemistries at the fiber matrix interfaces were the same when tested at 13.8 MPa. Thus, within the experimental error, a carbon or boron nitride (BN) interface does not change the burn characteristics of the CVI SiC/SiC composite. Since these materials dissociate prior to burning, some insight about their combustion characteristic can be obtained by comparing the elemental reaction exothermicities of silicon, carbon, and boron, and their vapor pressures at their respective flame temperatures. Using a computer program developed by Gordon and McBridge [5] the adiabatic flame temperatures of Si, B, and C exposed to air are 2870, 2850 and 2320 K, respectively (Table I). The reactivity of Si and B is similar, whereas C is slightly less reactive than the two. Hertzberg *et al.* [9] studied combustion properties of Si, C and B dusts and revealed that elemental Si burns homogeneously whereas C burns heterogeneously. It is therefore anticipated that CVI SiC/SiC composite has simultaneous reaction mechanisms competing against each other, and that the disintegration rates increase the reaction rates. The initiation of the combustion should be related to the bonding strength of Si and C and therefore the stoichiometry of the composite. The CVI SiC composite is C rich, thus the observed heterogeneous burning characteristic is in agreement with Herztberg *et al.*'s work on elemental dust. Table II also contains the testing results of SiC/SiC composite with a BN interface. The replacement of carbon with BN somewhat improves the oxidation resistance of the composite in air [10, 11], although a boron oxide coating, which initially was expected to develop during the ignition phase, was apparently removed through vaporization. Although it was anticipated that the coated SiC/SiC would be more resistant to ignition than the non-coated, the threshold ignition pressure and burn lengths are similar. The currently available test configuration (NASA-STD-6001, Test 17) does not provide adequate means for explanation of this finding.

The results in Table II also summarize findings about the effect of oxidation-resistant surface coatings. The coating reduces the penetration of the oxygen to the interior of the specimen, and was therefore expected to reduce the effective area for the oxygen flux. The effect of this coating as a barrier to ignition and therefore combustion was, however, marginal and was reflected rather in reduced burn lengths than in ignition-resistance. The oxidation-resistant coating of the enhanced SiC/SiC composite did not stop the ignition at 13.8 MPa (2000 psi) and the material burned 5.8 cm. A sufficient number of tests at 13.8 MPa (2000 psi) listed in Table II suggest that this coating is ineffective in increasing the material's ignition and combustion resistance. There are, however, several complicating factors that need to be addressed before one can confidently deduce the effectiveness of the burn resistant coatings utilizing promoted combustion testing. The promoted combustion test is not well suited to evaluate the behavior of a burn-resistant coating on a less burn-resistant substrate. It is hypothesized that when ignited, the aluminum promoter (Fig. 1) locally melts off the coating or initiates local fracture of coating due to thermal stresses, and the interior of the specimen, once exposed, will then burn as the uncoated material. It is suggested then the promoted combustion test is a severe damage tolerance evaluation, effectively simulating behavior under conditions of significant coating loss. As such, it provides limited

TABLE III Burn lengths of MI-SiC/SiC and Hi-NiC/SiNC composite subsequent to promoted combustion test at different oxygen gas pressures. Each data represents different sample

	Burn lengths in cm at oxygen gas pressure					
Materials (producer)	6.9 MPa	10.35 MPa	13.8 MPa	17.25 MPa	20.7 MPa	41.4 MPa
MI-SiC/SiC	0.5	0.76	16.51	16.51	16.51	16.51
(NASA GRC)		2.75	16.51			
			16.51			
Hi-NiC/SiNC			1.0	1.3	1.5	
(Dow-Sylramic)			1.0	1.3	1.5	
			1.0	1.5	2.3	
				1.8	3.8	
				1.8	3.8	
				2.0	4.0	
				2.3	4.3	
				2.5	5.3	
				2.8	5.3	
				2.8	5.3	

information to evaluate the inherent protectiveness of coating materials.

Table III summarizes the promoted combustion test results of two compositionally different SiC/SiC composites, melt infiltrated SiC/SiC (MI-SiC/SiC) composite and a SiC/SiNC composite (Dow–Sylramic). The MI-SiC/SiC composite was made at NASA GRC by infiltration of SiC fiber mats with a silicon and C mixture. The MI-SiC/SiC composite has high density, but also contains approximately 10% by weight of unreacted free silicon in the matrix after processing. The promoted combustion characteristics of MI-SiC/SiC, especially when compared with the CVI SiC/SiC composites listed in Table II, clearly indicate poor combustion resistance in an oxygen-rich environment. At 13.8 MPa (2000 psi), the MI-SiC/SiC burns completely, whereas the CVI-SiC/SiC composite shown in Table II does not sustain combustion. In conjunction with the previous discussion, one can suggest that the MI-SiC/SiC composite will burn primarily homogeneously rather than heterogeneously, as the CVI-SiC/SiC composites. In contrast to MI-SiC/SiC composite, the SiC/SiNC composite (Table III) is very resistant to ignition and burning. It should be noted that the SiC/SiNC composite has no free silicon and has a substantial amount of nitrogen substituted in the SiC lattice. It has different chemistry and bonding characteristics than the SiC/SiC composites listed in Table II, and these modifications markedly improves combustion resistance of this composite.

It is also expected that in combustion of silicon carbide and its composites, the heat transport processes exert at least a partially controlling influence. During ignition the specimen is raised to such a temperature that self-heating resulting from the exothermic reaction exceeds the rate at which heat can be dissipated by conduction and radiation. The time required for ignition of the solid, or the amount of material consumed at a given time, is governed not only by the energy input from igniter and "ignition temperature" of the SiC but also by thermal conduction through the system. The thermal conductivities of monolithic SiC, CVI-SiC/SiC composite, and MI-SiC/SiC composite at room temperature are 300, 30, and 40 W/m-K, respectively. Despite these differences in thermal conductivities at room temperature, their thermal conductivities are approximately the same at elevated temperatures (∼30–40 W/m-K) [13]. At elevated temperatures, the thermal conductivity differences of monolithic SiC, SiC/SiC composite and MI-SiC/SiC are not substantial enough, from the combustion point of view: all can be characterized as poor conductors. The comparable value for the thermal diffusivity of these materials implies that the energy balance for ignition, and more importantly for combustion, is determined essentially by the rate constants and heat release of the particular exothermic reaction leading to combustion; i.e., it is basically a chemical property of the solid SiC. For this reason, these findings show the strong need to better define the term "ignition temperature," which traditionally has been used to describe this property. The numerical value of ignition temperature will depend upon the boundary condition of the experiment [12] and, therefore, future research should focus answering that challenge. If a set of experiments can be designed with well-defined boundary conditions, a mathematical solution of the heat-conduction equation [1, 2 and 11] might lead to a more accurate prediction of the data and possibly estimation of the ignition temperature.

The summary of results on SiC/SiC composites described so far suggests that the most significant factor for burn-resistance is the chemistry of the ceramics. This result is confirmed by the study of monolithic SiC. The promoted combustion test results shown in Table IV suggest that SiC produced by chemical

TABLE IV Burn lengths of monolithic SiC produced by Cercom and Morton International using hot pressing and chemical vapor deposition techniques respectively. Si_3N_4 has been purchased from Allied Signal and was produced conventional sintering technique. Each data represents different sample

	Burn lengths in cm at oxygen gas pressure					
Materials (producer)	13.8 MPa	15.9 MPa	17.25 MPa	20.7 MPa	24.1 MPa	41.4 MPa
Monolithic SiC	0.7	0.7	16.51	16.51		
(Cercom)	1.2	1.8				
	1.2	3.6				
	1.2	7.1				
	1.5					
	1.5					
	1.5					
	1.8					
	4.1					
Monolithic CVD SiC			2.8	0.5	2.8	16.51
(Morton International)			3.3	2.0	3.3	
			3.6	2.3	3.6	
			4.6	2.5	4.6	
			11.4	2.5	11.4	
				2.8		
				2.8		
				3.0		
				3.0		
				3.0		
Monolithic Si_3N_4						1.0
(Allied Signal AS 800)						1.2
						1.2
						1.2
						1.5

vapor deposition with a Si:C ratio closer to 1:1 has markedly higher resistance to ignition than sintered SiC. The importance of chemical bonding characteristics is substantiated with the promoted combustion test results of Si_3N_4. In contrast to silicon carbide, silicon nitride (Si_3N_4: AS800-Allied Signal) showed excellent resistance to ignition. At 41.4 MPa (6000 psi) sustained combustion did not occur and burn lengths were approximately 0.5 cm or less. All attempts to ignite silicon nitride at even the highest available test pressure were unsuccessful. Si_3N_4 shows distinct heterogeneous combustion characteristics similar to SiC (as observed by microstructural analysis of the ignition end of the sample), but the nature of the Si-N bonding of Si_3N_4 is very different than SiC. Si_3N_4 has a larger amount of ionic bonding and a substantial amount of oxygen solution from the oxide sintering aides. In addition, Si_3N_4 contains homogeneously-distributed oxide additions as sintering aids that change the ionization potential dramatically. The system should be considered as Si-O-N, rather than an exact Si_3N_4 composition, which then, in light of previous discussion, explains the resistance to ignition at very high pressures.

4. Conclusions

The use of silicon-based ceramic materials in high-pressure oxygen-rich space propulsion systems is dependent upon the material's ignition and/or combustion resistance at the highest oxygen pressures. These tests results represent progress in the potential use of silicon-based structural ceramics in very high oxygen pressure environments. At a test pressure of 17.2 MPa, porous SiC/SiC (Dupont/Lanxide) composite with carbon-rich layers was ample fuel for combustion (30% consumed). Eighty-six percent and 100% of the composites were consumed at 20.7 and 41.4 MPa, respectively. Silicon nitride (AS800-Allied Signal), in contrast to SiC, showed excellent resistance to ignition. At 41.4 MPa, sustained combustion did not occur. Both SiC based materials and Si_3N_4 display distinct heterogeneous burning characteristics. The amount of oxygen solubility and the nature of oxygen–silicon bonding in the structure are both critical factors for the accurate prediction of combustion resistance. It is recommended that future users of ceramic materials at very high oxygen pressures focus utilize on materials containing a high degree of ionic characteristics, such as oxides, Si_3N_4, Si-O-N systems, and potentially silicon oxycarbide (Si-O-C).

Extremely elegant and sophisticated continuum models have been developed, and respectable progress has been achieved, to describe heat, mass, and momentum transfer conditions for ignition and combustion of materials [1, 7 and 11]. The skills that the continuum mechanics investigators have exhibited contrast with the relative meagerness of our experimental data and the crudeness of our experimental methods. Promoted combustion test results, including those results reported in present investigation, merely serve to rank different materials for use in high-pressure oxygen systems with respect to each other. The promoted combustion test is a severe damage tolerance evaluation, and as such, provides limited information to assess the mechanisms responsible for the ignition and combustion resistance of the materials tested. Until experimental methods, and therefore the resulting data, have been distinctly improved, there is little that can be done with the best of theories. Experimental measurements of heat of formation, activities and phase diagrams of metal and oxygen systems under practical conditions (especially for the systems with non-equilibrium phases) are required. The advancement of the fundamental understanding of the combustion of materials requires a fusion of sciences to understand the formation of non-equilibrium phases, as well as physical modeling that incorporates computational tools from *ab-initio* principles.

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