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ABSTRACT

Alumina-forming commercial Ti₂AlC (MAXthal 211)TM phase samples were exposed in a jet-fueled, high pressure burner rig (HPBR) at 1100°, 1200°, and 1300 °C, operating at 6 atm (bar) and 25 m/s, in ~10% water vapor. Weight change exhibited a rapid initial uptake associated with a TiO₂ transient phase followed by cubic kinetics of a slow-growing α-Al₂O₃ underlayer. The cubic rate constants, *k_c*, were approximately 20% of those measured in static thermo-balance furnace tests. A small recession rate of −0.012 mg/cm²/h was measured at 1300 °C for a pre-oxidized sample. The loss rate was ~15% that observed for SiO₂ scales subject to volatile Si(OH)₄ formation for SiC tested under similar conditions. These kinetic features were fitted in a modified cubic-linear law. From thermodynamic, XRD, and SEM analyses, it is proposed that volatile TiO(OH)₂ was formed by the reaction of water vapor with TiO₂ and TiAl₂O₅ outer layers.

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1. Introduction

The evaluation of ceramics for turbine applications has often addressed the issue of oxide or scale volatility in flowing high pressure water vapor due to the formation of volatile metal hydroxides. For the case of SiC and SiC composites, this entails the formation of the volatile Si(OH)₄ species [1,2]. A number of test techniques have evolved to study the phenomenon, including standard furnace thermogravimetric (TGA) and steam-jet [3,4]. Early demonstrations also used high pressure burner rigs where jet fuel was combusted and projected at high velocity over SiC and Si₃N₄ based samples [5–8], as well as a turbine combustor demonstration test [9]. SiO₂ scale volatility issues have since achieved a level of prominence. The recession rate under turbine conditions (high temperature, pressure, and velocity) is sufficient to remove typical SiC seal coats on CMC composites, exposing fibers and fiber coatings susceptible to oxidative degradation. Ultimately major emphasis has been placed on the development of various moisture-resistant environmental barrier coatings (EBC) [10–14]. Since these materials were designated for temperatures greater than 1200 °C, new high temperature regimes of burner rig testing have been employed. However, conventional metallic components rarely exceed 1150 °C, resulting in much less opportunity to observe these scale volatility effects. With less water vapor attack of the Al₂O₃ scales associated with metal-

lic coatings and superalloys used at lower temperatures, similar volatility phenomena are not expected and have not been reported for conventional turbine materials.

In another field, much attention has been directed toward the novel class of ceramic carbide and nitride materials known as MAX phases because of their unique structure and properties [15,16]. They are characterized by their damage tolerance, machinability, high temperature stability (1400 °C), thermal shock resistance, and thermal conductivity. Additionally, some MAX phases possess excellent oxidation resistance because of their Al₂O₃-forming ability. These would include Ti₃AlC₂, Ti₂AlC, and Cr₂AlC [17]. As candidates for various high temperature applications, it is reasonable to envision MAX phases in turbine environments for some novel uses, including bond coats for TBCs [18,19]. Recently, extended oxidative durability has been demonstrated for YSZ-TBC coatings on Ti₂AlC MAX phase substrates [20]. Here, up to 2500 h coating life was observed in intermittent, stepped furnace tests from 1100°–1300 °C, tolerating much greater exposures (1300 °C) and Al₂O₃ scale thickness (40 μm) than on superalloy substrates (1200 °C, 150 h, 7 μm) [21].

Finally, the volatility of Al₂O₃ scales above 1200 °C in turbine environments has not been explicitly demonstrated or excluded. Therefore, the purpose of the present study was to examine the durability of a commercial Ti₂AlC material (MAXthal 211 from Kanthal/Sandvik) under high temperature, high pressure, burner rig conditions. Special attention is given to both TiO₂ and Al₂O₃ scale growth and volatility.

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2. Experimental

Basic operation of the HPBR entails pressurized fuel and air injection in a commercial turbine air blast nozzle and swirl plate dome section. Ignition is accomplished by hydrogen gas at a spark plug. Combustion occurs in an air-cooled, thermal barrier-coated superalloy combustor can. The gaseous combustion products proceed through a water-cooled, pressurized stainless steel transition section, losing heat in the process. The gas temperature is measured by a Pt–Pt 13Rh thermocouple at a position just behind the samples. Sample temperature is measured by two-color optical and laser pyrometry. Temperature is controlled by fuel-to-air ratio, nominally in the range of 0.04–0.06 by mass. High pressure is achieved by the input compressed air mass flow, combustion expansion, and exhaust pressure. The exhaust is choked by a pneumatic Annin valve downstream of the sample section. Velocity is somewhat of a dependent variable, but can be adjusted through the various rig pressure, temperature, and mass flow operational parameters. Nominal fuel-lean combustion, at the molar equivalence ratio of $\phi = 0.8$ to 0.9, can produce sample temperatures from 1200 to 1450 °C. More details of the rig construction and operation have been provided previously [22,6].

Sintered 'MAXthal 211'™ Ti_2AlC was obtained (Kanthal/Sandvik) and sliced by a band saw. $\sim 3 \times 11 \times 35$ mm HPBR specimens were sectioned from the slices and polished to a 600 grit finish, with rounded corners to prevent chipping. Both ends of the samples were inserted into loosely fitting slots machined into cylindrical Rene'N5 superalloy end blocks, resulting in ~ 3.0 cm long Ti_2AlC exposed hot section and 9.2 cm^2 hot area. The blocks were held in two opposing water cooled stainless steel rods. These extended to opposite sides of a removable specimen chamber ring

Table 1

Average run conditions for HPBR testing. Mass air flow = 0.57 kg/s; pressure = 0.61 MPa (6 atm).

	T (°C)	v_{gas} (m/s)	fuel-to-air (mass)
pre-ox A	1100	20.5	0.038
	1203	25.5	0.048
	1300	24.5	0.053
	1303	25.1	0.059

fitting between segments of the pressurized housing, as a modification of the original specimen holder. The high-pressure burner rig was operated under lean-burn conditions, appropriate to most current aircraft turbines, using Jet A fuel ($\sim$ kerosene). Standard operating pressure and velocity were ~ 6 atm and ~ 25 m/s, respectively, and the specific (average) run conditions for the present study are summarized in Table 1. Oxidation was monitored by weight change and appearance after the first 2 h followed by repeated 6 h run durations for a total of 50 h. Weights were obtained on an analytical balance sensitive to 0.01 mg. The same 5 g standard was also weighed for each measurement. Since this was a constant, it allowed for correction of any balance drift errors, commonly on the order of ± 0.05 mg, yielding a more accurate final weight.

Post-test analyses of the samples included standard optical and scanning electron microscopy and x-ray diffraction. Since scale volatility effects can be more easily observed for slow growing scales, one sample was furnace pre-oxidized at 1300 °C for 300 h. It was weighed at numerous intervals intermittently, then subjected to the HPBR environment for 80 h. Weights were obtained throughout the HPBR test as before, with XRD analyses after 62 h of HPBR exposure during the same run. Many of the results were compared

Fig. 1. Intact Ti_2AlC MAX phase coupons for 50 h HPBR testing at 1100°–1300 °C. (6 atm, 25 m/s).

Fig. 2. Well-behaved weight gain behavior for Ti_2AlC in HPBR test (solid: HPBR; dashed: TGA).

to findings from isothermal TGA furnace tests in air of the same material, as described in detail previously [23].

In summary, a total of 4 HPBR samples were run: one each at 1100°, 1200°, and 1300 °C, each for 50 h. The fourth was furnace pre-oxidized for 300 h, then HPBR tested for an additional 80 h, all at 1300 °C. Also, comparisons are made to 4 TGA samples from a previous publication: again, one each at 1100°, 1200°, and 1300 °C, but for 100 h. The fourth was only heated for about 5 min until 1300 °C was achieved, then heating was terminated with no forced cooling.

3. Results

The nominal appearance of the samples and weight change results after 50 h exposures at 1100°, 1200°, and 1300 °C are presented in Figs. 1 and 2. No indication of non-uniform breakaway oxidation or spallation was apparent. A rapid uptake occurred over the first exposure or during heatup, followed by a much more modest rate of oxidation at all three temperatures. This behavior is similar to that often reported for furnace tests of Ti_2AlC , wherein the initial uptake was often attributed to an initial, ~ 0.1 h rapid transient of TiO_2 followed by a healing underlayer of protective Al_2O_3 [23–26]. This initial rise was similar to the 0.4, 0.6, and 0.9 mg/cm^2 observed in the first hour of oxidation at 1100°, 1200°, and 1300 °C in the TGA (dashed lines). Whereas, at 50 h, the approximate HPBR instantaneous weight gain rates were all less than 0.01 $\text{mg}/\text{cm}^2/\text{h}$. Note also that the steady state gains in TGA were higher than those recorded for the HPBR test (at equivalent times). This will become an important point in discussing scale volatility later.

In order to accurately define the Al_2O_3 growth kinetics, graphical techniques were devised to correct for weight contributions that occurred at an initial distinctive ‘knee’ (at t_k), or change in slope, that occurs for $t < 1$ h in a log–log representation of the weight change vs time behavior [23]. Accordingly, the same approach was attempted for the HPBR data, correcting for the time, t_k , and weight change per unit area, $(\Delta W/A)_k$ by:

$$\left(\frac{\Delta W}{A}\right) - \left(\frac{\Delta W}{A}\right)_k = k_c(t - t_k)^{1/3} \quad (1)$$

The corrections (Eq. (1)) resulted in relatively well-behaved cubic kinetics for the entire test, as presented in the $t^{1/3}$ ‘cubic’ plot of corrected weight, Fig. 3. Similarly, a log–log plot in Fig. 4 shows time exponents, $1/n$, on the order of 0.30–0.33, as expected.

Fig. 3. Cubic oxidation behavior of Ti_2AlC in HPBR tests at 1100°–1300 °C. (corrected weight and time; regression fitted dashed lines).

Fig. 4. Log-log plots of corrected weight and times for oxidation behavior of Ti_2AlC in HPBR exhibiting exponents consistent with cubic rates.

However it was unexpected to see systematically lower values compared to similar TGA data, i.e., only about 20% TGA k_c , as plotted in the Arrhenius diagram of Fig. 5. (The weights produced by HPBR tests are ~ 50 –60% those from TGA, since these scale only as $k_c^{1/3}$). An activation energy of 284 kJ/mol was measured for the present data, which is somewhat below that determined more precisely at 338 kJ/mol for the TGA testing of the same material [23,20]. The value of 279 kJ/mol was measured for another Ti_2AlC material in air (and 261 kJ/mol in 100% H_2O) by intermittent oxidation testing [27]. By comparison, the value estimated for grain boundary diffusion of oxygen in alumina scales was ~ 375 kJ/mol [28]. An example of Zr-doped FeCrAl oxidation data used for grain boundary diffusivity is also shown in Fig. 5 (right axis) [23,28,29], where it was suggested that Al_2O_3 scale growth was controlled by similar oxygen grain boundary diffusivity for Ti_3AlC_2 , Ti_2AlC , Cr_2AlC , and FeCrAl. These activation energies are offered for completeness and some noted similarities. A more critical comparison is not possible without factoring in the rate-controlling scale grain size of each material, which is not currently available. However the difference between the burner rig and furnace TGA values, on the same material, may be significant due to moisture-induced volatility issues (i.e., losses in 1300 °C HPBR testing) discussed at length later.

Fig. 5. Arrhenius diagram of cubic oxidation rates of Ti_2AlC measured for HPBR testing (horizontal half diamonds) compared to TGA values (vertical half diamond). Estimate of grain boundary diffusivity of oxygen from FeCrAl(Zr) oxidation (circles and dashed regression line) [23] is also shown, right axis, with similar activation energy to Ti_2AlC oxidation.

Table 2

Relative XRD peak intensities from Ti_2AlC scale phases after various furnace and burner rig exposures. $d_{(110)} \text{TiO}_2 = 3.25(\text{\AA})$; $d_{(104)} \text{TiAl}_2\text{O}_5 = 3.36(\text{\AA})$; $d_{(113)} \text{Al}_2\text{O}_3 = 2.08(\text{\AA})$.

sample	$T, ^\circ\text{C}$	t, h	$d (\text{\AA})$ 3.25 TiO_2	$d (\text{\AA})$ 3.36 TiAl_2O_5	$d (\text{\AA})$ 2.08 Al_2O_3
TGA	as-recd	0	0	0	1.7
	1100	100	24.9	0	47.9
	1200	100	44.4	0	100
	1300	100	10.6	28.2	100
	1300	10 min	20.7	10.2	20.8
HPBR	1100	50	2.9	0	20.4
	1200	50	1.6	0	50.7
	1300	50	4.8	3.8	96.1
	1300	300	1.1	23.9	100
Furnace pre-ox +HPBR	1300	62	<0.1	1.4	100

Fig. 7. Optical micrographs showing dispersed bright TiO_2 colonies (arrows) produced by a) 1200°C TGA exposure of Ti_2AlC (100 h), but absent in b) 1200°C HPBR exposure (50 h).

Fig. 6. XRD peak intensities for $3.25 \text{\AA}$ (110) TiO_2 , $3.36 \text{\AA}$ (104) TiAl_2O_5 , and $2.08 \text{\AA}$ (113) Al_2O_3 peaks for 50 h HPBR tested Ti_2AlC samples (filled symbols) compared to 100 h TGA tested samples (open symbols). Ti-oxides are reduced in HPBR tests.

X-ray diffraction was used to characterize the scales formed in both TGA (100 h) and the HPBR (50 h). The intensity (relative to the strongest observed peak) of characteristic (110), (104), and (113) peaks for TiO_2 , TiAl_2O_5 , and Al_2O_3 scale phases, respectively, (Table 2) are shown in Fig. 6, analogous to the approach followed

by Li et al. [30]. TiAl_2O_5 is seen to form at or above 1300°C from reaction of the TiO_2 and Al_2O_3 scales [31,23]. The Al_2O_3 peaks were always much higher, eventually reaching 100% with temperature, depending on the exposure times. The results for the HPBR samples show significant reductions in Ti-rich phases at all three temperatures, consistent with removal of the fast initial transient scale. (In general, increased test time also reduces the relative amount of Ti-oxides, so the same conclusions are obtained even though the HPBR data was obtained at half the duration of the TGA exposures).

The surface appearance of the scale formed at 1200°C is shown in Figs. 7 and 8. Here island colonies of a bright (nodular) phase can be seen on the Ti_2AlC sample oxidized in the TGA furnace for 100 h (Figs. 7a, 8a, b). These correlate with the TiO_2 phase identified by XRD with a relative intensity of 44%. The islands can be seen to be composed of large, faceted $5\text{--}10 \mu\text{m}$ TiO_2 grains, typical of outward growing TiO_2 scales. EDS spectra reveal only Ti and O for these bright grains and Al and O for the underlying darker fine grains. Accordingly, it is assumed that the underlying scale is Al_2O_3 .

In contrast, the scale formed after 50 h at 1200°C in the burner rig (Fig. 8c) does not show these bright colonies, but rather a more uniform surface. At higher magnification (Fig. 8d), it can be seen that the surface is composed of $\sim 0.5 \times 5 \mu\text{m}$ platelets decorated with a dispersion of fine $1 \mu\text{m}$ light, nodular crystallites. EDS of the underlying platelets again reveals primarily Al and O, indicating Al_2O_3 . However the fine nodules contain high amounts of Ca and Ti, in addition to Al, with lower, sometimes trace levels of Si

Fig. 8. SEM/BSE micrographs showing dispersed bright TiO_2 colonies produced by a,b) 1200°C TGA exposure of Ti_2AlC (100 h), changed to a fine dispersion in c,d) 1200°C HPBR exposure (50 h).

and Mg, depending on the particle. Since these features are on the order of the electron beam spot analysis size ($1\ \mu\text{m}$), contributions from the underlying Al_2O_3 scale are expected. The reduced feature amounts are consistent with the low 1.6% relative TiO_2 peak intensity observed in XRD scans of this sample, as compared to 44% for TGA (Fig. 6, Table 2). Impurity elements suggest possible minor upstream contaminants from dust or cooling water that may unintentionally enter the gas stream from various facility supply systems.

One mechanism for removal of TiO_2 is by reaction with water vapor in the combustion atmosphere to form volatile $\text{TiO}(\text{OH})_2$ species. [32]. Yet no clear weight loss trends were observed Figs. 2–4. Very small loss rates may be obscured by Al_2O_3 growth. Part of this condition is related to the short times preordained by expensive rig testing. This does not allow the growth rates to moderate or for losses to accumulate as they might for much longer times. To resolve this difficulty, an extensive 300 h pre-oxidation was performed at 1300°C in a box furnace, then exposed to water vapor in the 1300°C HPBR test. The pre-oxidation results are presented in Fig. 9 and do show $\sim 2.5\times$ lower instantaneous growth rate at 300 h for this sample compared to that at 50 h. The subsequent burner rig results now show a consistent weight loss rate of $\sim 0.012\ \text{mg}/\text{cm}^2/\text{h}$ for the first 38 h, Fig. 10. This is compared to the steady growth exhibited without pre-oxidation (upper curve). (At 44 h, an operational anomaly occurred in the combustor section causing some steel melting and spot deposits giving a weight gain. Subsequent exposure to 80 h total HPBR time resumed a similar weight loss behavior, at a slightly lower rate.)

In order to connect this behavior of the pre-oxidized sample to scale phases, the surface was analyzed by XRD before and after HPBR exposure, Fig. 11 and Table 2. Results are also shown for 0.1 and 100 h TGA furnace exposures from [23]. It is seen that the relative intensity of the TiAl_2O_5 peak is high for the 300 h box furnace pre-oxidation, but drops off dramatically (from 24% to 1.4%) with subsequent HPBR exposure for 62 h. This confirms that the weight loss for the pre-oxidized sample in Fig. 10 was due in part to volatile Ti-oxides. In contrast, predictably, the peak for Al_2O_3

Fig. 9. Weight change response for 1300°C furnace pre-oxidation of Ti_2AlC showing lower instantaneous rates at 300 h compared to those at 50 h.

was maintained at a 100% level. It is not clear whether some Al_2O_3 was also being lost due to volatilization or whether some degree of continuing Ti-rich scale growth occurred after the large initial transient. Prior to the HPBR exposure, both Ti-rich scale intensities drop somewhat with respect to Al_2O_3 because the former is nearly fixed from the initial transient, while the latter keeps thickening from steady-state, cubic growth.

As with the TGA sample, the scale formed by extensive 300 h pre-oxidation at 1300°C in a box furnace shows large expanses of light granular islands, Figs. 12 and 13a, but has higher Al and lower Ti contents in EDS spectra. These presumably correspond to the appreciable amounts of TiAl_2O_5 found in xrd, Fig. 11. A few brighter particles remained, Fig. 13b, probably as original TiO_2 particles that

Fig. 10. Weight loss of 1300 °C pre-oxidized sample from Fig. 9 in subsequent 1300 °C HPBR test. Linear loss rate $\sim 1.2 \text{ mg/cm}^2$ per 100 h (lower curve) compared to cubic gain for no pre-oxidation (upper curve).

Fig. 11. XRD peak intensities for 3.25 Å (110) TiO_2 , 3.36 Å (104) TiAl_2O_5 , and 2.08 Å (113) Al_2O_3 peaks for Ti_2AlC samples after 1300 °C furnace pre-oxidation compared to subsequent HPBR testing. Ti-oxides reduced in HPBR tests.

have not yet reacted to form TiAl_2O_5 . The underlying scale was again very Al-rich (Al_2O_3).

However, after testing in the HPBR at the same temperature for an additional 80 h, the surface appeared much more uniform and with less indication of the bright islands Figs. 12b, 13c, d. This corresponds to the order of magnitude reduction in characteristic peak intensity for TiAl_2O_5 after burner rig testing (reduced from 24% to 1.4% relative intensity obtained at 62 h), while maintaining a 100% relative peak intensity for Al_2O_3 (Fig. 11). The irregular porous surface colonies of the slightly lighter phases were primarily Al_2O_3 , but contained some Ca. These colonies are believed to be residue scale from decomposition and volatilization of the large expanses of TiAl_2O_5 initially formed by the pre-oxidation treatment and shown in Fig. 13a, b. A few dispersed small bright particles were present, high in Al, but also containing Ti and Zr with lower levels of Ca. These particles are believed to correspond to the small amount of residual TiAl_2O_5 , along with impurities deposited from the rig. The underlying 10 μm granular structure was relatively pure Al_2O_3 . These originally developed as the heavily pre-oxidized scale (300 h

Fig. 12. Optical micrographs showing dispersed light TiAl_2O_5 colonies (arrows) remaining after 1300 °C pre-oxidation exposures of Ti_2AlC (300 h), then, b) reduced in subsequent 1300 °C HPBR exposure (80 h).

at 1300 °C) and are now more clearly revealed after the Ti-rich surface oxides were removed.

4. Discussion

4.1. Weight change behaviors

It is shown that Ti_2AlC -based Maxthal 211TM can survive aggressive exposures in a high pressure burner rig. The oxidation rates follow cubic kinetics controlled by Al_2O_3 growth. This behavior has been widely studied in the literature and related to grain growth in the scale, with rate control by oxygen grain boundary diffusion. [24,25,17,23,27,28] Little differences are noted between Ti_2AlC or Ti_3AlC_2 substrates [17]. Static furnace oxidation in water vapor has not been shown to produce significant changes in the kinetic law or rate constants. At 1000 °C, even an increase in weight gain was observed due to 10% water vapor [33]. Another study showed very little difference in weight change or scale thickness due to oxidation in 100% water vapor. [27] However it was shown there that the TiO_2 present on top of the Al_2O_3 layer was absent at 1300 °C in water vapor. This was attributed to the formation of a volatile $\text{TiO}(\text{OH})_2$ reaction species and will be discussed later.

The steady state growth behavior in the burner rig gave no direct indication of Al_2O_3 scale volatility, except that the absolute value of the rates was about 20% of those in comparable static furnace TGA tests. This would be unexpected for a volatility mechanism, which should lead to a 'parabolic-type' weight gain curve, not cubic [3].

Fig. 13. SEM/BSE micrographs showing dispersed light TiAl_2O_5 colonies (arrows) a,b) remaining after 1300°C pre-oxidation exposures of Ti_2AlC (300 h), then c,d) largely removed by subsequent 1300°C HPBR exposure (80 h).

That is to say, no apparent decrease was noted with time as would be expected for a large superimposed linear loss rate. Nevertheless, an extensive pre-oxidation experiment, where the initial transient growth had already occurred, allowed a small linear weight loss to be measured in the burner rig. This appears to correlate with the elimination of surface Ti-rich scale features, as documented by optical microscopy, SEM/EDS and XRD. In general, the HPBR tested samples exhibited less of these Ti-oxides than comparable furnace tests.

A preliminary examination of polished cross sections of the initial 1300°C HPBR sample (50 h) revealed a scale thickness of $\sim 15.0\ \mu\text{m}$. Part of the outer scale was missing or lost, presumably during polishing (metallographic pullout). It will require SEM/EDS to determine if this was associated with the outer TiO_2 layer and/or volatility reactions at the surface. The measured weight change should correlate with the thickness according to the density of the major phase (Al_2O_3 , $3.99\ \text{g/cm}^3$) and the stoichiometric ratio of oxygen gain to oxide present ($48/102\ \text{g atom oxygen/g mol Al}_2\text{O}_3$). Using a simple mass/volume equivalency, this scale thickness predicts a $2.83\ \text{mg/cm}^2$ oxygen gain. This substantially exceeds the $1.64\ \text{mg/cm}^2$ measured from that test (Fig. 2). The difference ($1.2\ \text{mg/cm}^2$) could be made up from a loss of rate of $0.024\ \text{mg/cm}^2/\text{h}$ over the 50 h test for that sample. This rate, however, exceeds the $0.017\ \text{mg/cm}^2/\text{h}$ estimated from the pre-oxidized sample in Fig. 10 (measured loss of 0.0122 plus Al_2O_3 growth of $0.0045\ \text{mg/cm}^2/\text{h}$ projected from Fig. 9). It is not possible to unequivocally explain the discrepancy (0.024 vs $0.017\ \text{mg/cm}^2/\text{h}$). However it may be related to higher initial surface area coverages of Ti-oxides for a freshly exposed sample ($\sim 50\%$ relative intensity) vs the pre-oxidized sample ($\sim 25\%$).

Finally, it should be pointed out that oxidation of Ti_2AlC could potentially release $0.50\ \text{g-atom of C}$ for every g-atom of O gained to form Al_2O_3 . If this were released as gas preferentially for the burner rig case, it would result in weight gains only 50% that of TGA tests, as compared to the actual $48\text{--}63\%$ levels observed, and could be another source of weight loss. While not specifically addressed experimentally in the literature, this free carbon

Fig. 14. Arrhenius diagram of linear mass loss rates for SiC (Robinson, 1999) and Ti_2AlC (this study) showing about $7\times$ lower value for the MAX phase at 1300°C .

is generally implied to back diffuse into the greater mass of the carbide substrate with slight effects on stoichiometry rather than loss through the scale, for example [27,30].

The linear weight loss rate can be compared to those obtained from similar tests performed on SiC samples, using nominally the same fuel, 10% moisture content, $6\ \text{atm}$ pressure and $20\text{--}25\ \text{m/s}$ gas velocity [6]. These rates are presented as a function of sample temperature in Fig. 14. Also shown is the proposed TiO_2 loss rate determined from Fig. 10, assuming Al_2O_3 is simply left behind from TiAl_2O_5 decomposition. It is seen to be approximately $7\times$ lower than that corresponding to SiC loss rates from steady state SiO_2 scale growth and volatility. Using stoichiometry and atomic weights (SiC – 42 vs TiO_2 – $80\ \text{gm-mol}$) to suitably compare molar loss rates, the Ti molar loss rate was reduced by a factor of $\sim 13\times$ as compared to Si (i.e., TiO_2 compared to SiO_2). It is not clear whether this

rate would moderate at longer times as the partial surface coverage of Ti-oxide is depleted or whether it reflects more constant losses from continuous Ti-oxide scale growth.

4.2. Volatility rates and cubic-linear behavior

In order to gain more insight regarding the loss rates and pertinent species, an attempt was made to predict volatility rates according to mass transport models used previously [1,4,34]. This exercise is meant to give a general perspective rather than precise modeling since uncertainties will always remain regarding the appropriate species. Furthermore, only one experiment (pre-oxidized sample) directly lends itself to this discussion since the other tests exhibit only weight gains. Volatility rates of oxides can be calculated from the equilibrium vapor pressure of the hydroxide species and the gas conditions in the burner using the mass transport equation for laminar (or turbulent) flow in a moving boundary layer [32–34,1,4]. Using published values for the thermodynamic energy of compound formation, these pressures and fluxes were calculated (i.e., Jacobson) and listed in Table 3 [32,37,38]. More details related to the calculation are presented in Appendix A. It is seen that the volatile species fluxes for laminar flow conditions translate into scale loss rates, r , of approximately 7.1×10^{-3} , 3.4×10^{-3} , and 1.1×10^{-1} mg/cm² h for Al₂O₃, TiO₂, and SiO₂, respectively. (Using the turbulent flow model, the predicted rates are only 17.4% higher for all three oxides than these predicted for laminar flow).

Both Al(OH)₃ and Ti(OH)₂ pressures and calculated loss rates are low compared to Si(OH)₄. Furthermore, these estimated loss rates appear somewhat less than the linear fit measured at ~ 0.012 mg/cm². (This value increases to 0.017 mg/cm² if the gain projected from further Al₂O₃ growth over that time interval, from Fig. 9, is included with the measured loss rate). Thus the measured rate of weight loss is on the order of $2.3 \times$ that predicted above for $r_{\text{Al}_2\text{O}_3}$ and $5.0 \times$ that for r_{TiO_2} . It is expected that the loss rate would increase with higher surface coverage by Ti-oxides, here seen to cover just a fraction of the surface and be measurably reduced by HPBR exposures. Furthermore, from surface microstructures, it was seen that the Ti-oxide surface coverage after pre-oxidation was measurably less than that initially produced, e.g., at ~ 10 min of the TGA exposure.

Other studies also indicate high rates for Ti(OH)₂ volatility [39,4]. Some uncertainty has been raised regarding the thermodynamic data used for Ti(OH)₂ due in part to analysis difficulties for the low yields of condensed species in the transpiration experiment [4,32]. Thus it appears that experimental rates are higher than those predicted for Ti-oxide losses in water vapor. In contrast, most measurements for Al₂O₃ volatility in water vapor are in good agreement with thermodynamic/fluid transport projections, which also predict a low rate under these conditions. [37] It is therefore doubtful the loss exhibited in the burner rig here would be entirely by Al₂O₃ volatility, if at all.

Finally, the classic ‘paralinear’ model of scale growth attributed to volatile oxides, e.g., SiO₂, Cr₂O₃, [3,40] is not readily exhibited by the burner rig data. Ideally, this should show a parabolic (or cubic for the case of Ti₂AlC) initial growth behavior, pass through a maximum, then approach a constant linear rate of weight decrease. This behavior has been demonstrated for SiC and Si₃N₄ [5,6,34]. However, the burner rig data in the present study does not show a maximum and appears to follow cubic kinetics for the full 50 h, albeit at a rate less than that provided by static dry TGA tests. It will be argued later that the loss rate is too low to produce a maximum in the 50 h of testing. The uncertainty surrounding any continued Ti-oxide growth or Al₂O₃ volatility prevents a more precise analysis.

Some elaboration can be provided concerning the effects of a slight amount of volatility on the apparent cubic growth kinetics.

Fig. B1. Transient-corrected 1300°C HPBR weight change data (triangles) and superimposed cubic-linear fit (dot-dot-dash). Corresponding cubic growth, with no volatility, (solid) and scale loss curve (dashed) also presented.

To that end, a cubic analogy to the classic paralinear formalism may be envisioned:

$$x^3 = k_c t(\text{cubic}) \quad (2)$$

$$\frac{3x^2 dx}{2dt} = k_c(\text{differential}) \quad (3)$$

$$\frac{dx}{dt} = \frac{2k_c}{3x^2} - k_l(\text{cubic} - \text{linear}) \quad (4)$$

A numerical approach was useful and convenient to approximate this type of behavior using the cyclic oxidation spalling program, COSP [41]. Instead of usually describing an iterative spalling event ($\Delta W/\Delta t$) of a uniform outer layer of the scale, it can also approximate a continuous process (dW/dt) by using progressively shorter cycle durations. For a sample case, the oxide stoichiometry (Al₂O₃), cubic rate constant ($0.2116 \text{ mg}^3/\text{cm}^6/\text{h}$ measured in 1300 °C TGA), and cubic time exponent (3.0) are specified. The spall constant (Q_0), and spalling time-exponent (α) were then adjusted to reproduce the experimental data, corrected for the rapid initial transient discussed previously. The resulting fit to the weight change curve is described and justified in Appendix B, and shown as Fig. B1. The corresponding scale loss produced by the same model parameters is seen to correspond remarkably well to the loss (as cation weight) presented in Fig. 10, namely $-0.012 \text{ mg/cm}^2/\text{h}$.

Given the liberties taken in producing this approximation, this general agreement is taken to suggest that some form of cubic-linear kinetic behavior can apply for the weight change curves observed. It also accounts for the reduced apparent k_c produced in the HPBR tests as compared to TGA. That is, some scale volatility in high pressure, high velocity water vapor may also be the reason for the apparently lower, but still effectively cubic, oxidation rates. A low rate of volatility can thus result in an apparent cubic kinetic law without the signature maximum followed by negative weight change classically associated with para-linear behavior.

Table 3

Estimated vapor pressures, volatile species flux, and scale phase rates of loss for Ti₂AlC and SiC substrates under 1300 °C, 6 atm, 25 m/s, ~10% H₂O burner rig conditions. (Chapman-Enskog corrections applied for gas diffusivity).

vapor species, s	oxide	vapor pressure P _s (bar)	laminar flow			turbulent flow		
			hydroxide flux J _s (mol/cm ² -s)	hydroxide flux J _s (mg/cm ² -h)	oxide recession r _{ox} (mg/cm ² -h)	hydroxide flux J _s (mol/cm ² -s)	hydroxide flux J _s (mg/cm ² -h)	oxide recession r _{ox} (mg/cm ² -h)
Al(OH) ₃	Al ₂ O ₃	1.38E-07	3.89E-11	1.09E-02	7.13E-03	4.56E-11	1.28E-02	8.38E-03
TiO(OH) ₂	TiO ₂	3.54E-08	1.19E-11	4.19E-03	3.42E-03	1.39E-11	4.92E-03	4.01E-03
SiO(OH) ₄	SiO ₂	1.66E-06	5.05E-10	1.75E-01	1.09E-01	5.93E-10	2.05E-01	1.28E-01

Fig. B2. Cubic-linear Chen-Tedmon scale growth curves; (a) Dimensionless thickness-time plot of Eq. (B3). (b) similar form using specific cubic-linear curves for Chen-Tedmon solution (circles) and COSP fit (dashed line); HPBR parameters with linear (constant) mass removal rate, $k_1 = Q_0$.

As a note added in proof, an analytical solution to the cubic-linear behavior was cited [42], with the general form presented in Fig. B2a. It is also shown that the COSP model can reproduce the analytic expression, with an example produced from parameters taken from the TGA value for k_c and the COSP fitted value for $Q_0 = k_l$, Fig. B2b. However it should be noted that the analytic expression is for constant k_l , (COSP $\alpha = -1$), whereas the fit of the experimental data required $\alpha = -3$ to account for the decreasing amount of volatile TiAl₂O₅ on the surface.

The model fit (Fig. B1) thus indicates weight loss as Ti-scales were continually removed by water vapor. That is, the clusters of large Ti-oxide grains have largely been removed, leaving only a fine

dispersion of small crystallites at less surface coverage. Also, the Al₂O₃ tabular grains appear to be hydro-thermally etched (Fig. 8d) revealing a platelet morphology with selectively attacked surfaces, presumably crystallographic facets.

5. Summary and conclusions

The durability of a commercial Ti₂AlC-based MAX phase has been demonstrated in a high pressure burner rig for temperatures up to 1300 °C. The oxidation kinetics demonstrated rapid initial weight gains due to patches of initial transient TiO₂ formation residing on the outer surface of the protective healing underscale of Al₂O₃. The subsequent kinetics were successfully fitted to a cubic rate law corresponding to slower Al₂O₃ scale growth. The cubic rate constant, k_c , exhibited a strong temperature effect with an activation energy of ~280 kJ/mol. These behaviors were similar to those observed in static furnace oxidation (TGA), which had an activation energy of ~340 kJ/mol. However, the values of k_c determined in the HPBR tests were only ~20% those found for TGA tests, implying weight gains of only about 50–60% of the TGA results.

The 50 h HPBR weight change curves displayed monotonic growth with no obvious or direct indication of scale volatility. This is in contrast to SiO₂ scales formed on SiC and Si₃N₄ materials, which clearly exhibit a linear rate of weight loss due to the volatile Si(OH)₄ reaction product. An extensive pre-oxidation treatment of the Ti₂AlC did allow a linear loss rate to be revealed, amounting to 0.012 mg/cm²/h or about 15% that measured for SiC. This level was higher than those predicted from thermodynamic data and fluid dynamics models for either TiO(OH)₂ or Al(OH)₃ volatility rates. A model weight change curve fit showed that a small negative loss factor could be superimposed on cubic growth and still result in apparent cubic growth, but of a lower magnitude, and with volatility loss rates consistent with the HPBR result. The distinct changes in surface morphology and relative amounts of phase constituents confirmed that loss of Ti-oxides did occur in high temperature, high pressure, high velocity combustion products (water vapor).

The primary conclusions are therefore summarized as:

- Ti₂AlC MAX phase has survived 1100°–1300 °C exposures in a high pressure burner rig.
- Steady state cubic oxidation kinetics were produced by a healing Al₂O₃ scale underlayer.
- The oxidation rates were measurably lower than those produced in laboratory furnaces.
- Transient surface Ti-oxides were removed by reactions with water vapor.

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Table A1

Parameters used in Chapman–Enskog estimates of gas species diffusivity. (Ti, Al, and Si species from Ti₂AlC and SiC substrates, 1300 °C, 6 atm burner rig conditions).

	Al(OH) ₃	TiO(OH) ₂	Si(OH) ₄	units
M_A (Air)	28	28	28	g/mol
M_B (M(OH) _x)*	78	98	96	g/mol
σ_A (Air)	3.8	3.8	3.8	Å
σ_A (M(OH) _x)*	5.13	4.08	4.88	Å
$\sigma_{A,B}$	4.46	3.94	4.34	Å
ε_A/k_B (N ₂)	71.4	71.4	71.4	K
ε_B/k_B (M(OH) _x)*	472	318	172	K
$\varepsilon_{A,B}/k_B$ rms force constant	183.6	150.7	110.8	K
Reduced T	8.57	10.44	14.2	
Collision Integral, Ω	0.76	0.74	0.7	
D_{AB} (1 atm)	1.68	2.17	1.89	cm ² /s
D_{AB} (6 atm)	0.28	0.36	0.32	cm ² /s
* model species:	AlCl ₃	CH ₂ F ₂	SiF ₄	
($k_B = 1.381 \times 10^{-23}$ J/K)				
Boltzman constant				

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Appendix A. : Estimates of scale volatility and recession rates

The method for estimating the volatility rate follows that presented by Opila, et al. [5,4,34] based on transport phenomena [35,36]. Fluid flow transport equations describe the diffusive flux (of the volatile species) from a flat plate into a moving boundary layer. The following two equations apply for laminar (L) or turbulent (T) flow, respectively [35,36]:

$$J_L = 0.664 \left(\frac{v_\infty \rho_\infty L}{\eta} \right)^{0.5} \left(\frac{\eta}{D_i \rho_\infty} \right)^{0.33} \frac{D_i P_i}{RT L} \quad (A1)$$

$$J_T = 0.0365 \left(\frac{v_\infty \rho_\infty L}{\eta} \right)^{0.8} \left(\frac{\eta}{D_i \rho_\infty} \right)^{0.33} \frac{D_i P_i}{RT L} \quad (A2)$$

Here J is the outward flux in moles/cm² s and L and T subscripts correspond to laminar and turbulent gaseous flow, respectively. The first term in parentheses is the non-dimensional Reynold's number, Re , and the second is the Schmidt number, Sc . v is the free-stream velocity (~ 25 m/s), $\rho(T, P_T)$ the density, and $\eta(T)$ the viscosity of the gas. L is a characteristic sample dimension generally referring to the gas transit distance from the start to the end of the flow direction across the material. $D(T, P_T)$ is the diffusivity and P the partial pressure of the volatile species. R and T again are 82.06 cm³/mol K and 1573 K.

The pertinent chemical reactions under discussion, leading to the calculations of the vapor pressures, are given below:

The thermodynamic data giving the free energy of the reaction and corresponding equilibrium constant are listed in Table A1. The equilibrium constant and vapor pressure are given by the law of mass action and reaction energy, for example for reaction (A3):

$$\Delta G_{\text{rxn}} = -RT \ln K; \text{ where } K = P_{\text{Al(OH)}_3} / 1 \times P^{3/2}_{\text{H}_2\text{O}} \quad (A6)$$

In the present experiment, v was approximately 2500 cm/s and $L \approx 1$ cm. $\rho(1300^\circ\text{C}, 6 \text{ atm})$ is determined from an average molecular weight of air ($\sim 79\% \text{ N}_2$, $21\% \text{ O}_2$) of 28.97 g/mol and the ideal

Table A2

Thermodynamic data and equilibrium vapor pressure estimates for volatile. Ti, Al, and Si species from Ti₂AlC and SiC substrates. (1300 °C, 6 atm, 10% H₂O burner rig conditions).

	Al(OH) ₃	TiO(OH) ₂	Si(OH) ₄	units
n_{rxn} , in $P_{\text{H}_2\text{O}}^n$	1.5	1	2	
ΔG_{rxn}	196	218	161	kJ
$K_{\text{rxn}} \cdot P_{\text{M(OH)}_x}$ at $P_{\text{H}_2\text{O}} = 1 \text{ atm}$	2.96E-07	5.91E-08	4.60E-06	atm
$K_{\text{rxn}} \cdot P_{\text{M(OH)}_x}$ at $P_{\text{H}_2\text{O}} = 0.6 \text{ atm}$	1.38E-07	3.54E-08	1.66E-06	atm

gas equation applied to the high temperature, high total pressure gas, giving $\rho = 1.347\text{E}-03 \text{ g/cm}^3$. The viscosity term can be obtained from Svehla (R-132) as $6.40\text{E}-4 \text{ g/cm s}$ [43]

The diffusion coefficient of the volatile species would be similar to the nominal diffusivity of any gaseous species in a gas at $\sim 2 \text{ cm}^2/\text{s}$. More precise approximation can be given by the Chapman–Enskog treatment of gas diffusivities [35]:

$$D_{AB} = 0.001853 \sqrt{1/M_A + 1/M_B} T^{3/2} \left\{ \frac{1}{P_T \times \sigma_{AB}^2 \times \Omega} \right\} \quad (A7)$$

Here the molecular weights of the solvent carrier gas (A), at 28, and volatile species (B) and are needed along with an average collision diameter σ_{AB} and effective collision integral $\Omega(T)$. The latter two parameters are approximated here from similar molecules for Al(OH)₃, (i.e., AlCl₃), TiO(OH)₂, (i.e., CH₂F₂), and Si(OH)₄, (i.e., SiF₄). Ω is obtained from a calibration table (or cubic fit to the data) and input values for reduced temperature, as defined by ε_{AB} , the root mean square of the molecular force constant parameters, normalized by the Boltzman constant, k_B , and available from the Svehla compilation [43]. These parameters and values are all summarized in Table A2. These values are used to calculate the flux J_L , J_T from Eqs. (A1), (A2) and are listed in Table 3. The results are compared to the experimental loss value ($-0.012 \text{ mg/cm}^2/\text{h}$) in the Discussion.

Appendix B. : Cubic-linear fit using COSP program

A cubic growth –linear spallation COSP model was employed to fit the 1300 °C experimental HPBR data [41]. Here the weight gain (W) and the ‘spalled’ (removed or volatilized) weight (W_s) are given by:

$$W^3 = k_c t (\text{cubic}) \quad (B1)$$

$$W_s = Q_0 W_r^{(\alpha+1)} \quad (B2)$$

where W_s is the weight of scale removed each cycle, Q_0 is a ‘spall’ (i.e., loss) constant, W_r is the weight of retained scale prior to the loss, and α is a spall constant. For cyclic oxidation, the degree of loss increases with W_r and α is often 1. However for the volatile TiO₂ loss analogy, the loss rate is constant or decreases as the surface coverage decreases with time and can be specified by $\alpha \leq -1$. The 1300 °C baseline (non-volatile) isothermal curve was provided by the isothermal growth constant, k_c , ($0.2116 \text{ mg}^3/\text{cm}^6/\text{h}$) and the cubic time exponent (3.0). The volatilization model employed shortened cycle durations (0.1 h), allowing the cyclic curves to converge to a ‘continuous’ cubic-linear behavior. The values of Q_0 and α corresponding to a good fit were found to be 0.02204 and -3.023 , respectively. This value of Q_0 corresponds to a time cycle of 0.1 h for smoothness, where an equivalent but more discontinuous fit could be constructed for 1 h cycles at $Q_0 = 0.2204$. The model curve and experimental data (dot-dot-dash vs triangles) are shown to essentially overlap, Fig. B1, and both are much reduced from the simple cubic TGA (solid, smooth) curve.

In further agreement, the oxide (volatility) loss is indicated by the negative dashed line, reflecting cation mass in the Al_2O_3 scale removed. (In the actual exposure, oxygen is gained and lost each cycle and not reflected in the linear net sample weight loss). It is seen that the loss rate equals the measured values of $-0.012 \text{ mg/cm}^2/\text{h}$ at about 21 h into the run. It fits the average from 6 to 38 h and corresponds to the average linear rate measured experimentally from 2 to 38 h. (COSP only models one scale chemistry at a time for both growth and removal. When the case of TiO_2 scales is modeled, a similar good fit can be obtained with different ‘spalling’ parameters, but still achieves the loss rate of $0.012 \text{ mg/cm}^2/\text{h}$, similarly at about 22.5 h.)

An analytic form of the cubic-linear behavior derived from the differential equation has been provided by Chen et al. [42]. The Tedmon-like result is given as Eq. (B3):

$$\tau = -X - \frac{1}{2} \ln \left(\frac{1-X}{1+X} \right) \quad (\text{B3})$$

where:

$$\tau = \frac{t \times k_l}{x_L}; X = \frac{x}{x_L}; x_L = \left(\frac{k_c}{3k_l} \right)^{1/2} \quad (\text{B4})$$

and x refers to the scale thickness, x_L to the limiting scale thickness (where growth rate = removal rate), and k_c , k_l refer to the cubic growth and linear loss rates of scale thickness. The overall form of retained scale thickness in dimensionless form as Eq. (B3) can be viewed in Fig. B2a, blue circles. For the specific case under discussion, the values for the parameters in Eqs. (B4)–(B6) can be substituted to yield Fig. B2b, again as blue circles. Here k_l was taken as Q_0 from the prior COSP fit as $0.22043 \text{ mg/cm}^2/\text{h}$ and k_c as $0.2116 \text{ mg}^3/\text{cm}^6/\text{h}$ of oxygen gain. The latter was converted to k_c for retained oxide, x , by multiplying by the stoichiometric constant cubed, given by $(102/48)^3$ for Al_2O_3 . Then, the same parameters are used in the COSP program to generate an oxidation curve, capturing the prediction for retained oxide as the red dot-dashed curve in Fig. B2b. This shows near perfect correspondence to the derived analytical expression of Chen et al., Eq. (B3). Therefore the appropriate use of the COSP program is considered to provide an acceptable approximation of strict cubic-linear behavior ($\alpha = -1$). Furthermore, the well-fitted curve in Fig. B1 and conclusions regarding the magnitude and diminishment of loss rates and other kinetic issues are thus deemed to be meaningful.

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