

## Durability of YSZ Coated Ti<sub>2</sub>AlC in 1300°C High Velocity Burner Rig Tests

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### Abstract

A thermal barrier coating system survived 500 h in cyclic burner rig tests at 1300°C, exceeding the life of all previous systems. An yttria stabilized zirconia (7YSZ) thermal barrier coating (TBC) was plasma sprayed on the oxidation resistant Ti<sub>2</sub>AlC MAX phase and tested in a jet fuel burner. No coating spallation or recession was observed, only a 2.4 mg/cm<sup>2</sup> mass gain due to typical cubic Al<sub>2</sub>O<sub>3</sub> oxidation kinetics. The modest weight gain contrasted with large TBC spallation or oxide volatility losses that might occur under cyclic, high velocity (~100 m/s) burner conditions. The coating surface exhibited colonies of [111]<sub>fluorite</sub> fiber-textured columns separated by craze crack patterns, but with no visible moisture attack. The thickness of the alumina scale under the YSZ face was >20 μm, more than twice that formed on TBC/superalloy systems at failure. TiO<sub>2</sub> nodules, initially formed on the uncoated backside, were then removed as volatile hydroxides formed in high temperature, high velocity water vapor (~10%). Overall, the test indicated the exceptional stability of the YSZ/Ti<sub>2</sub>AlC system under turbine conditions, due in large part to good thermal expansion matching.

## 1.0 Introduction

MAX phases have been keenly studied because of their unique layered hexagonal crystal structure (space group  $P63/mmc$ ) and intriguing properties.[1][2] Having the  $M_{n+1}(Al,Si)(C,N)_n$  general composition, they are defined as ceramics, but possess unusual desirable attributes such as high conductivity, thermal shock resistance, easy machinability, and deformation tolerance. The mechanical properties derive from weak M-(Al,Si) bonding in the basal plane that leads to sliding and kinking in preference to catastrophic crack growth. But, like most ceramics, they are phase stable at high temperatures, generally up to 1500°C. High temperature oxidation resistance is excellent for alumina-forming  $Ti_3AlC_2$ ,  $Ti_2AlC$ , and  $Cr_2AlC$ , as reviewed by Tallman, et al.[3] Compatibility with  $\alpha-Al_2O_3$  scales is further enhanced in cyclic exposures by a close matching of thermal expansion coefficients,[4] i.e., ( $\sim 9.3, 10.2, 11.3 \times 10^{-6}/K$  for  $Al_2O_3$ ,  $Ti_2AlC$ , and YSZ, respectively, to be discussed).

Gas turbine environments generally contain 10% water vapor in the hot combustion gases, therefore moisture effects can be a concern for some materials at high material temperatures.[5] Furnace tests of MAX phases in high temperature steam generally showed little effect on  $Al_2O_3$  scale growth.[6] However, high velocity and high pressure gas can influence scale losses by the formation of volatile reaction products, such as  $Si(OH)_4$ ,  $TiO(OH)_2$  and  $Al(OH)_3$ . [7][8][9][10] This phenomenon had been discussed for 1100°C-1300°C high pressure (6 atm) burner rig tests (HP-BRT) of  $Ti_2AlC$ [11]. The cubic growth rate parameter here ( $k_{cubic}$ ) was measurably lower than that measured in comparable furnace TGA tests. The discrepancy could be resolved by incorporating a slight linear loss (i.e., volatility) term, that decreased with time. In general, a two-parameter, cubic-linear, (growth-volatility) law was believed to apply. Corresponding HP-

BRT scale volatility loss rates, directly measured at 1300° on a furnace pre-oxidized sample, were moderate (0.012 mg/cm<sup>2</sup>/h) and largely attributed to removal of the initial TiO<sub>2</sub> transient scale.

A related CH<sub>4</sub> burner study of high purity Cr<sub>2</sub>AlC MAX phase demonstrated 1200°C durability after 500 rapid (5 min. heat and 2 min. cool) thermal shock cycles (29 h hot time).[12] Heating and cooling rates were ~ 1000°C and 500°C per minute, with a gas velocity of ~10 m/s, that produced a 75°C/mm gradient through the thickness. A 7 μm Al<sub>2</sub>O<sub>3</sub> surface scale and a 13 μm Cr<sub>7</sub>C<sub>3</sub> depletion zone formed with no signs of failure. No evidence of scale volatility was evident. However, the velocity was moderate, and the total hot time was not extensive (weight change not provided). The same high gradient BRT was used to produce 1400°C surface temperatures for a YSZ/Cr<sub>2</sub>AlC/IN738 system in the first study of MAX phases used as bond coats for thermal barrier coatings (TBC).[12] Here TBC failure was reported after 745 cycles (62 h), with only 1.5 μm Al<sub>2</sub>O<sub>3</sub> scales entrained within Cr<sub>7</sub>C<sub>3</sub> depletion zone porosity.

YSZ (yttria-stabilized zirconia) thermal barrier coatings have been considered as a compatible complement to Al-MAX phases because of thermal expansion matching and *extremely* low YSZ volatility in water vapor. Initial studies showed superior oxidative stability up to 1300°C for long times, (at least 500 h) for Ti<sub>2</sub>AlC substrates and less (268 h) for Cr<sub>2</sub>AlC, while withstanding large alumina scale thickness (~35-40 μm).[13][14] By comparison, typical superalloy systems could only survive 1150°C maximum interface temperatures for extended periods, with failure generally occurring below a maximum sustained thermally grown oxide (TGO) of 10 μm.[15]

SiC ceramic matrix composites are very attractive substitutes for Ni-base superalloy turbine components. SiC based systems are known to form slow-growing SiO<sub>2</sub> scales at very high

temperatures. But these materials are subject to rate enhancement and volatile  $\text{Si(OH)}_4$  products in the presence of water vapor, as described comprehensively by Opila, et al.

[16][17][18][5][19]. Net weight losses are generally observed in high velocity, high pressure burner rig studies (e.g., 0.084 mg/cm<sup>2</sup>/h at 1300°C).[20] Furthermore, the loss rates have been shown from chemical physics to scale with  $v^{1/2}$  and  $p_{\text{H}_2\text{O}^2}$ . [16] Low activity, moisture-resistant environmental barrier coatings (EBC), such as rare earth silicates, are needed to prevent substrate recession under turbine conditions.[21][22][23]

YSZ is eminently qualified as a non-reactive, moisture-resistant material.[24], but with a coefficient of thermal expansion (CTE) too large to be compatible with SiC as an environmental barrier coating (EBC). However, YSZ is seen as a natural complement to MAX phases. Indeed, recent burner tests of YSZ TBC-coated  $\text{Cr}_2\text{AlC}$  bond coats have shown potential above 1200°C. [25] TBC/EBC protection of MAX phases in high velocity water vapor environments is therefore intriguing. The purpose of the present study was to demonstrate the durability of a 7YSZ TBC/ $\text{Ti}_2\text{AlC}$  system under aggressive 1300°C Mach 0.3 (~100 m/s) burner conditions for 500 h. A secondary objective was to examine the oxidation/volatility behavior of uncoated  $\text{Ti}_2\text{AlC}$  regions exposed to the same environment. While this 1 atm burner exposure did not produce high water vapor pressure, its simplicity allowed for long term, cyclic endurance testing.

## **2.0 Materials and Experimental Methods**

**2.1 Sample preparation.** The material tested in this study was Sandvik Kanthal  $\text{Ti}_2\text{AlC}$  MAX phase (MAXthal® 211) obtained in the form of large sintered ingots. Two slabs 6.4 x 38 x 82 mm (1/8 x 1½ x 3¼ ") were EDM machined from the ingot and hand polished thru coarse (60, 30, 15 μm) diamond wheels and finished with finer SiC carborundum grits to a 2400 grit finish. One slab, prepared to this finish, had one side lightly grit blasted for coating adhesion.

Thermal Barrier coating was accomplished in a Sulzer-Oerlikon-Metco plasma spray physical vapor deposition (PS-PVD) facility at the NASA Glenn Research Center [26]. Samples were coated normal to the torch with a standoff distance of 1.68 m. The torch power was 94 kW, plasma gases were 40/80 Ar/He, and the feedstock powder was Metco 6700 7YSZ. Coatings were deposited in 1.51 mbar (1.13 torr) partial vacuum, mostly via the vapor phase, achieving approximately 160  $\mu\text{m}$  of YSZ in a segmented, columnar ‘cauliflower’ microstructure, typical of EB-PVD morphologies. Both samples were given a mild preconditioning furnace oxidation exposure at 1000°C for 10 h. This completed the primary transient  $\text{TiO}_2$  stage and set up stable  $\text{Al}_2\text{O}_3$  growth. [kinetics]. It also helped insure against any unexpected, premature ‘infant mortality’ TBC failure and transformed the ‘black’ oxygen-deficient PS-PVD as-deposited structure to ‘white’  $\text{ZrO}_2$ .

**2.2 Burner test protocol.** The bare slab sample was tested first as a preliminary shake out run and baseline comparison for the coated sample. In addition to overall oxidative durability, some moisture induced scale volatility was indicated, given that the combustion gas contained about 10% water vapor and was flowing at about 100 m/s (vs 25 m/s in previous high pressure burner rig (HP-BRT) tests). Automatic cycling to ambient temperature was accomplished every 5 h, with weighing and inspection over graduated time intervals.

A description of the atmospheric Mach 0.3 burner can be found in Fox et al. [27]. The rig utilized 800 kPa (120 psig) filtered shop air measured with turbine flow meters (data logged) and rotometers (visual). At Mach 0.3, approximately 1.1 kg (2.5 lb)/min airflow was used (with up to 3.2 kg (7.0 lb)/min possible for higher Mach numbers). Preheated 288° C (550° F) compressed lab air was mixed with atomized Jet-A fuel in a swirl plate nozzle and delivered to the combustion chamber. Pressure within the combustor was 6.9 kPa (1 psi) above ambient to

produce a Mach 0.3 flame velocity. An aircraft-type igniter-initiated combustion. The inner liner was made of Inconel 601 with a 5.1 cm (2 inch) inner diameter and a 2.5 cm (1 inch) exit nozzle. Flame temperature was monitored by thermocouple. Sample temperature was measured by optical pyrometers (8  $\mu\text{m}$  wavelength for YSZ, emissivity set at 0.92, and 2-color pyrometer for bare  $\text{Ti}_2\text{AlC}$  MAX phase). Temperature was controlled  $\pm 5\text{ C}^\circ$  by a feedback loop between the optical pyrometer (sample temperature) and the fuel flow control valve that adjusted the fuel-to-air ratio. Heating typically took place in 1 min. Cycling was produced by pneumatically pivoting the burner apparatus away from (10 min cool) and back onto direct sample impingement (5 h heat). No backside cooling was used. Sample weights were measured on an analytical balance sensitive to 0.01 mg.

**2.3 Preliminary trials.** Initially, the uncoated slab, clamped with a vise, was exposed for 50 h,  $100^\circ\text{C}$  increments from  $1000^\circ\text{C}$ - $1300^\circ\text{C}$  to demonstrate test feasibility. Face-on heating resulted a uniform hot section, with the backside temperature only  $10^\circ\text{C}$  lower. This configuration suffered from temperature limitations due to flame deflection and inefficient heating above  $1100^\circ\text{C}$ . Edge-on heating was more efficient, enabling  $1200^\circ\text{C}$ , then  $1300^\circ\text{C}$ , to be achieved, but resulted in a sample-wide crack and runaway oxidation after 38 h at  $1300^\circ\text{C}$ .

To avoid both these complications, narrow  $\sim 15$  mm wide strips were sectioned lengthwise from the coated slab and subjected to face-on exposure. These were mounted via set screw in a slotted superalloy mounting pedestal. A shake out run, performed at  $1200^\circ\text{C}$  for 500 h, revealed less flame deflection and no edge cracking. Rather, TBC abrasion in the grip area compromised oxidative weight change measurements. Once that portion was ground off, the sample produced well-behaved weight gains amounting to only  $\sim 1\text{ mg/cm}^2$  at the end of the test. These details can be found in a preliminary report. [28]

**2.4 1300°C durability test.** This test protocol was used for the second YSZ-coated strip.

Sample dimensions were 3.6 x 15.2 x 62.3 mm. Initially, the coating was ground off in the grip end region as before, leaving a 50 mm coated length exposed to the 25 mm dia. combustion flame. Fuel-air ratio was used to set the front surface coating temperature at  $1300 \pm 5^\circ\text{C}$ , controlled by the 8  $\mu\text{m}$  pyrometer ( $e = 0.92$ ). Further measurements were obtained by 2-color optical pyrometer for the bare backside and by thermocouple in the combustion gas. Sample deflection was also monitored by caliper measurements of the bending gap.

**2.5 Analyses.** Microstructures were characterized by optical microscopy and field emission gun scanning electron microscopy (FEG-SEM) of exposed surfaces and polished Ni-plated cross sections (15 kV, Hitachi S-4700 FESEM, Tokyo). X-ray diffraction analyses (XRD) were used to identify coating and oxide phases, (Malvern Panalytical Empyrean diffractometer (Westborough, MA) using  $\text{Co K}\alpha$  radiation and Bruker, D8 Advance diffractometer with  $\text{Cu K}\alpha$  radiation (Madison, WI) from both sides of the sample. The instrument was configured to limit the x-ray beam width to 5 mm and prevent spillage off the face of the sample at all diffraction angles. A 5-axis cradle was used to achieve desired sample orientations. Phases were identified using the ICDD 2018 PDF4+ Inorganic database and Jade 2010 software. Raman spectra were obtained on select YSZ coatings as a more sensitive technique for identifying YSZ phases (Thermo Scientific, Nicolet DXR microscope, Waltham, MA). Operating conditions were 1sec, 633 nm laser at 5 mW, 600 lines/mm, 25  $\mu\text{m}$  pinhole.

## 3.0 Results

### 3.1 1300° C Mach 0.3 Burner

**Figure 1** shows the coated strip sample in the burner rig test (BRT). Photo (a) indicates the hot gas flow from the burner nozzle across the sample from a top right view angle. The mounting base, with FeCrAl and CMC shims, are visible below the hot zone of the sample. The sample hot zone corresponds to the 2.5 cm (1”) inner diameter of the exhaust nozzle, as observed in the low light exposure photograph, (b).

The weight change behavior of this YSZ-coated Ti<sub>2</sub>AlC MAX phase sample is shown in **Figure 2a**. The furnace preconditioning treatment at 1000°C is presented as time before zero and reflects the rapid growth of TiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> scales to ~0.8 mg/cm<sup>2</sup>. The remainder of the curve displays the subsequent response to the BRT (burner rig test). It shows well-behaved, continuous behavior with decreasing oxidation rate, as occurs for common parabolic or cubic growth laws. It is not suggestive of any spallation events. The final weight gain is a modest 2.40 mg/cm<sup>2</sup>.

This is less than the 4.55 mg/cm<sup>2</sup> calculated from the steady-state, cubic growth rate constant ( $5.229 \times 10^{-11}$  kg<sup>3</sup>/m<sup>6</sup>s, i.e., 0.200 mg<sup>3</sup>/cm<sup>6</sup>h) measured for the same material by isothermal furnace TGA kinetics. Furthermore, the isothermal test produced an initial TiO<sub>2</sub> transient scale of 0.4 mg/cm<sup>2</sup>. In total, the final predicted weight is ~5 mg/cm<sup>2</sup>, i.e., substantially higher than the 2.4 mg/cm<sup>2</sup> produced in the burner rig here. Nevertheless, a very good fit to cubic  $t^{1/3}$  kinetics could be still produced by correcting the burner rig data for the initial TiO<sub>2</sub> transient (0.5 mg/cm<sup>2</sup>), **Figure 2b**. Here  $k_c = 0.012$  mg<sup>3</sup>/cm<sup>6</sup>h ( $r^2 = 0.998$ , intercept = -0.008 mg/cm<sup>2</sup>) or about 1/8 that measured in static dry air furnace tests (TGA). More detailed comparisons will be presented and discussed later.

A comparison of the YSZ-Ti<sub>2</sub>AlC results with uncoated SiC Mach 0.3 and HP-BRT tests is presented in **Figure 3**. Overall, weight gains exhibited for Ti<sub>2</sub>AlC in the present Mach 0.3 BRT

are in contrast to weight losses due to SiO<sub>2</sub> scale volatility and recession. [20] [Opila, Smialek, Cuy, unpublished research]. Similar high pressure burner rig results are also presented with similar conclusions. The specifics and implications will be discussed in detail later.

**Figure 4** presents visual appearances of the burner sample: YSZ coated front face before and after the test and the uncoated backside after test. (The coating was ground off at the grip end (dashed line) to avoid fretting in the clamp and anomalous weight losses). Brown discoloration above the grip resulted from Fe-oxide staining from the FeCrAl gripping shims. The backside was relatively uniform, slightly lightened due to oxidation. No spallation or deterioration of the coating was apparent.

**Figure 5** shows the total bending by hot flame impingement after 500 h of testing, as monitored by the chord width ( $\Delta$ ) of the curved sample. The continuous development of that curvature was presented in **Figure 2**. (Note: measurements were only made after 100 h when they were first noticed). The deflection rate was somewhat less than linear because sample bending shortens the moment arm of maximum force. Work hardening may also decrease the rate of bending/deflection.

### **3.2 Microstructures.**

#### **3.2.1. Coated face**

The overall plan view of the coating surface after testing was first examined by optical microscopy. The maximum temperature hot zone (a) showed nodular colonies of columns, separated by wide-gapped, cellular mudflat craze-crack boundaries. In contrast, the ‘warm’ zone surface, corresponding to the top of the bar, appeared much more uniform.[28] It may be that the hottest region fostered sintering and shrinkage, whereas the warm regions allowed TBC

expansion and compaction with respect to the underlying cooler substrate. Sintering is a known phenomenon for YSZ thermal barrier coatings, especially above temperatures in the vicinity of 1250°C.

SEM images of the craze cracking and colonies of TBC growth columns in the hot section are presented in **Figures 6a, b, and c**. At higher magnifications (**6d**), the granular surface structure of an individual column can be discerned, with ~1-3  $\mu\text{m}$  YSZ grain diameters ( $2.6\pm 0.6 \mu\text{m}$ , on average). No surface attack features nor grain boundary etching due to water vapor was apparent. No elemental peaks were observed by electron dispersive spectroscopy (EDS) for the hot zone coating other than Zr, Y, and O.

Polished cross sections of the tested coating at the center of the hot zone and at the cooler grip end (about 1 mm above the clamping) were also examined by optical microscopy [28] and SEM, **Figure 7a,b**. They show an uneven YSZ surface encapsulated by Ni plating. The bulk of the ~160  $\mu\text{m}$  thick coating exhibited a bimodal porosity – both finely dispersed and coarse columnar. Broad vertical separations, extending part way to the substrate, were frequently observed, corresponding to the craze patterns observed in plan views, with an average spacing of ~80  $\mu\text{m}$ . However, no lateral interface or fine vertical through-cracks were observed in these or any other regions examined. By comparison, the YSZ structure near the cooler grip end (**7b**) showed that most porosity was highly aligned along the initial column boundaries. In general, these morphologies mirror those described in a recent study of PS-PVD YSZ coatings.[29]

SEM imaging also revealed details of the microporosity within the YSZ. Coarsening to > 1  $\mu\text{m}$  and uniform dispersal in the hot zone (**7a,c**) is compared to the regular arrays of fine as-coated porosity (~100 nm) remaining at the grip end (**7b, d**). Microporosity had been seen to coarsen in the recent PS-PVD study as well.[29]

Some fine porosity is observed in the  $\text{Al}_2\text{O}_3$  scale, **Figures 7c, d**, but undoubtedly includes metallographic pullout as well. The dark grey features in the  $\text{Ti}_2\text{AlC}$  MAX phase substrate were again identified as  $\text{Al}_2\text{O}_3$  particles by EDS. No other first-order chemical inhomogeneity within the substrate, the  $\text{Al}_2\text{O}_3$  TGO, or YSZ TBC was identified by EDS, although contrast variations can be seen at the YSZ/TGO interface, **Figure 7c**. These may correspond to the  $\text{TiAl}_2\text{O}_5$  remnants of  $\text{TiO}_2$  transient oxidation observed previously. The alumina scale thickness was measured by SEM as 20.7 and 22.2  $\mu\text{m}$  for two regions in the hot zone and as 12.4  $\mu\text{m}$  in the grip end. These values are within experimental variations of those measured by optical microscopy (22.8 and 11.4  $\mu\text{m}$ , respectively). The inner growth interface was seen to follow a faceted morphology, intimately following lenticular  $\text{Ti}_2\text{AlC}$  granular features.

### 3.2.2 Uncoated backside.

Cross section SEM/BSE micrographs of the uncoated backside in **Figure 8** revealed an irregular scale/gas surface, possibly a vestige of moisture attack by  $\text{TiO}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  volatile oxide formation. Here the backside scale thicknesses were approximately 12.4/13.8  $\mu\text{m}$  (hot) and 9.0  $\mu\text{m}$  (grip end), respectively (compared to 14.7 and 8.2  $\mu\text{m}$  thick from optical microscopy[28]). The reduced scale thickness, compared to 22  $\mu\text{m}$  at the coated front side having direct flame impingement, can therefore be attributed to both reduced backside temperature combined with volatility losses from the bare scale. At higher magnification (**8c, d**) the SEM images reveal detail regarding the faceted, convoluted, open  $\text{Al}_2\text{O}_3$  structures formed by hydroxide volatility etching effects. The relative thickness of this filamentary surface  $\text{Al}_2\text{O}_3$  is greater (and more dense) for the cool grip end (~68%, at 6.2  $\mu\text{m}$ ) vs the hot zone (~35%, at 4.8  $\mu\text{m}$ ). That is, the volatility effects (surface removal) and oxidation (inward layer growth) are expected to be greater for the hot zone compared to the grip end.

The weight change for various scale thicknesses can be projected by the  $3.99 \text{ g/cm}^3$  density of  $\text{Al}_2\text{O}_3$ , i.e., by dividing the thickness by  $5.339 \text{ } \mu\text{m} / (\text{mg/cm}^2)$ . Weight changes of  $\sim 4.1$  and  $2.6 \text{ mg/cm}^2$  are thus projected for scales corresponding to the hot zone face and backside (at  $\sim 22$  and  $14 \text{ } \mu\text{m}$ , respectively). Similarly  $2.2$  and  $1.7 \text{ mg/cm}^2$  correspond to the grip end (face, backside at  $12$  and  $9 \text{ } \mu\text{m}$ , respectively). These reductions in specific weight gain are expected for cooler portions of the strip sample where the exposed length ( $50 \text{ mm}$ ) was about twice the diameter of the exit nozzle ( $25 \text{ mm}$ ) and impinging hot gas stream. Allowing for typical vertical temperature gradients from the hot zone (front and backside  $\text{Ti}_2\text{AlC}$  at  $\sim 1244^\circ\text{C}$  and  $1216^\circ\text{C}$ ), the specific weight gain could be estimated from established alumina kinetics as  $\sim 2.7 \text{ mg/cm}^2$ . The net measured weight gain was  $2.4 \text{ mg/cm}^2$ . The differential is consistent with a slight volatility loss of  $\text{Al}_2\text{O}_3$  from the backside.

In plan, optical micrographs revealed zonal differences on the uncoated backside of the sample.[28] The hot zone appeared rather fibrous and filamentary at low magnification and a more uniform granular structure at the top (warm zone) of the bar. Similarly, SEM images of the hot zone backside **Figure 9**, reveal an ‘open’ structure at low magnification (a) and unsupported protruding etched platelets (P) at high magnification (**9b**). The EDS spectra show the granular regions (G) to be  $\text{Al}_2\text{O}_3$ , while the platelets (P) exhibit Ca, Ti, Mg contributions. Ti contamination is probably a remnant of  $\text{TiO}_2$  transient oxide features.  $\text{TiAl}_2\text{O}_5$  and  $(\text{Ca,Mg})\text{TiO}_3$  are possible as stable reaction phases, though the  $1 \text{ } \mu\text{m}$  nodules are small to isolate their EDS response that of the from the underlying alumina. No Ca, Mg, Al, or Si EDS peaks were observed on the YSZ TBC face, only Y, Zr, and O.

By contrast, the plan view of the backside cooler grip end (**Figure 10**) exhibits a relatively uniform granular structure, dispersed with bright nodules. Again, the granular regions (G) are

relatively pure  $\text{Al}_2\text{O}_3$ , while nodules (N) contain more appreciable levels of Ti and Ca. The higher levels of Ti are vestiges of previous transient  $\text{TiO}_2$  particles, while, again, Ca was likely an air supply contaminant. The granular regions exhibit grain boundary porosity and open spaces that may indicate some level of etching by volatile  $\text{Al}(\text{OH})_3$  formation. Finally, the ‘warm’ top end represented an intermediate temperature and showed less Ti, Ca-rich nodules remaining atop the pure  $\text{Al}_2\text{O}_3$  grains, with similar intergranular porosity.

### 3.3 X-ray Diffraction and Raman.

Xrd diffractometer scans of the back (bare) and front (coated) phases are shown in **Figure 11**. They correspond to positions along the length for samples exposed briefly at  $926^\circ\text{C}$  (S1) and long term at  $1300^\circ\text{C}$  (S2). (The burner was immediately shut down for sample S1 because a leading-edge crack was observed on heat up). It is first noted that the uncoated backside phases corresponding to the previous microstructures have identified  $\alpha\text{-Al}_2\text{O}_3$  as the principal scale phase along with the hexagonal 211 MAX phase (M) substrate.  $\text{TiO}_2$  rutile (R) was more prominent for the short initial exposure (10 min.). Secondly, the YSZ phases on the front coated surface indicate primarily overlapping tetragonal and cubic peaks (Y), with a minor level of Fe-oxide (F) from grip end contamination.

**Table 1** lists the estimated wt.% of phases identified in **Figure 11** calculated by Rietveld whole pattern fitting for these BRT and previous furnace tests (not shown in **Figure 11**). It is acknowledged that these values can only indicate relative major trends and are not fully accurate because of layered structure absorption. The top section of the table corresponds to the scale phases formed on the uncoated backside, showing results for short  $926^\circ\text{C}$  exposure and for various positions after  $1300^\circ\text{C}$  testing. The hot zone became dominated by  $\alpha\text{-Al}_2\text{O}_3$  (97%), the MAX phase was still evident (3%), and  $\text{TiO}_2$  was reduced from 10% to just a very weak trace

(0.1%). This was indicative of a strong tendency for initial  $\text{TiO}_2$  transients to become greatly diminished with respect to the steady state  $\alpha\text{-Al}_2\text{O}_3$  growth. It is also consistent with preferential volatility of  $\text{TiO}(\text{OH})_2$  compared to  $\text{Al}(\text{OH})_3$  (as suggested by **Figures 9 and 10**).

The second section of **Table 1** summarizes phases observed on the YSZ coating (front side).

The first entry corresponds to previous long term, consecutive furnace exposures, lasting 500 h each at 1100-1300°C, in 50°C increments (2500 h total).[30]. This produced a large amount of monoclinic, with no residual  $t'$ . The low temperature and short time BRT exposure produced nearly an as-coated value, i.e., a high level of metastable  $t'$  tetragonal phase, balance cubic, with a trace of monoclinic. The third grouping was for the 1200°C Mach 0.3, 500 h pre-test.[28] A high cubic level again resulted, but a 'transformable' tetragonal made up the residual. It is not clear why this low-Y tetragonal (3-5 wt.%) did not transform to monoclinic upon cooldown. (The %  $\text{YO}_{1.5}$  mole % was estimated for the YSZ phases by the established lattice parameter or c/a ratio empirical correlations, **Table 2**).[31][32]–[34]

The highest material temperature corresponds to the middle hot zone, with a 'warm' top of the bar and 'cool' grip end bottom. For the 1300°C test here, a very high level of cubic resulted. The cool grip end still showed a large amount of high Y (7 wt.%) tetragonal. Surprisingly, none of the burner rig samples exhibited high levels of monoclinic. Typically, aged YSZ will phase separate into low Y tetragonal (transforming to monoclinic on cooling) and high Y cubic phases at their respective ends of the tie line, e.g., as did the 2500 h furnace sample. The high cubic contents for the 1200°C, 500 h burner sample is consistent with this projection. However, the low Y tetragonal unexpectedly did not transform to monoclinic. Furthermore the 1300°C/500 h burner sample became primarily cubic with neither tetragonal phase and little monoclinic.

Further comparisons are available in the recent PS-PVD phase stability study that did show transformation to monoclinic.[29]

Some preferred deposition growth orientation (fiber texture) of the YSZ columns was observed, as indicated by the inverse pole figure of **Figure 12**. The strongest orientation (max relative intensity of 450) was for  $(111)_{\text{fluorite}}$ , with secondary weak orientations (1.5 max intensity) of  $(200)_{\text{fluorite}}$  and  $(220)_{\text{fluorite}}$

While monoclinic appears to be missing in many cases from the XRD results, Raman analyses were able to discern small peaks for monoclinic in related, furnace tested, PS-PVD samples[28] with typical wavenumbers indicating 178, 190, 381  $\text{cm}^{-1}$  peaks typically associated with monoclinic (M) YSZ and 142, 258, 322, 467, and 637  $\text{cm}^{-1}$  associated with tetragonal (Ramos, 2015) [35]. It is also noted that monoclinic may not appear instantaneously upon cooling, but require additional stress (grinding APS YSZ)[36] or some time interval of nucleation for ‘isothermal’ martensite to appear at room temperature (in EB-PVD YSZ after aging at 1425°C)[37]. The PS-PVD YSZ – TGO –  $\text{Ti}_2\text{AlC}$  interfaces in this study are being studied in a subsequent FIB-STEM investigation.

#### **4.0 Discussion of TBC Durability and Volatility**

The exceptional durability of this YSZ- $\text{Ti}_2\text{AlC}$  system has again been demonstrated, but now under more extreme environmental conditions. Its success was due to beneficial matching of thermal expansion coefficients between the YSZ top coat,  $\text{Al}_2\text{O}_3$  scale, and  $\text{Ti}_2\text{AlC}$  substrate ( $\sim 11.7, 9.3, \text{ and } 10.2 \times 10^{-6}/\text{K}$ ) combined with the excellent oxidation resistance of Al-MAX phases. Compared to the previous furnace tests, the present test provided the added factors of long-term testing, high velocity (100 m/s) gas, water vapor (10%), and cyclic thermal shock.

In our related burner studies, uncoated  $Ti_2AlC$  had also been shown to survive oxidation, moisture-induced recession (scale volatility), and thermal shock in 50 h high pressure burner rig (HP-BRT) exposures up to  $1300^{\circ}C$ [11]. That data, shown in **Figure 3**, is similar to the present data, but necessarily of much shorter duration and fewer cycles because of rig complexity. The HP-BRT (6 atm., 25 m/s) also produced moderate weight gains. A pre-oxidized sample revealed slight net weight losses ( $\sim 0.01 \text{ mg/cm}^2\text{h}$ ), proving some scale volatility in water vapor.

It is generally agreed that  $Al_2O_3$  growth on  $Ti_2AlC$  occurs by grain boundary diffusion of oxygen through the scale[3][38]. Coupled with nearly cubic grain growth, this results in sub-parabolic, cubic scale growth. The weight gain kinetics of the Mach 0.3 test were therefore analyzed in a manner similar to the TGA and HPBR studies.[11],[39] The good fit to  $t^{1/3}$  cubic kinetics (**Figure 2**) produced  $k_{\text{cubic}} = 0.012 \text{ mg}^3/\text{cm}^6\text{h}$ , lower than the TGA and HP-BRT results of 0.200 and  $0.024 \text{ mg}^3/\text{cm}^6\text{h}$ , respectively.

This implies that the Mach 0.3 burner test exhibited less scale growth due to three factors: 1) reduced temperature due to thermal gradients from the central hot TBC impingement face to the bare backside and cooler ends; volatility of  $TiO_2$  and  $Al_2O_3$  scales from the bare backside from high velocity water vapor (via  $TiO(OH)_2$  and  $Al(OH)_3$ , in that order); and 3) reduced transient  $TiO_2$  formed due to low pressure PS-PVD deposition.

Precise quantitative assessments of weight change are complicated for these Mach 0.3 results. The bare backside was measured as  $1216^{\circ} C$  ( $2220^{\circ} F$ ). (Heat transfer calculations arrived at  $1204^{\circ}C$  uncoated backside and  $1244^{\circ}C$  for the front side interface temperatures, D. Zhu, unpublished research at NASA GRC). From the cross-sections, the TGO under the coating at the grip end was found to be  $\sim 1/2$  that in the hot zone. It can then be shown, using cubic oxidation kinetics, that  $k_{\text{hot}} \approx 8k_{\text{grip}}$ . The interface temperature at the hot zone was estimated to be

~1244°C. Using the Arrhenius relation for Ti<sub>2</sub>AlC cubic kinetics,[39] it can be surmised that this corresponds to 1134°C, or about 100°C cooler at this section just above (~1 mm) the grip end.

For the uncoated backside, the high velocity of the atmospheric Mach 0.3 test (1 atm., 100 m/s) may be as important as the high-pressure environment of the HP-BRT. Note that volatility losses vary as  $v^{1/2}$ . Thus a 2x increased volatility rate is projected for the Mach 0.3 test due to the 4x increased velocity (100 m/s vs 25 m/s). Volatility should also vary as  $p_{\text{H}_2\text{O}}/p_{\text{tot}}^{1/2}$  for TiO<sub>2</sub>,  $p_{\text{H}_2\text{O}}^{3/2}/p_{\text{tot}}^{1/2}$  for Al<sub>2</sub>O<sub>3</sub>, and  $p_{\text{H}_2\text{O}}^2/p_{\text{tot}}^{1/2}$  for SiO<sub>2</sub> scales, predicated on the expected TiO(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, and Si(OH)<sub>4</sub> volatile species[8]–[10]. Given that the moisture content of combusted jet fuel is ~10%, the predicted loss rate, relative to the HP-BRT, can be projected

( $v^{1/2} \times (p_{\text{H}_2\text{O}})^2 / p_{\text{tot}}^{1/2}$ ) as 0.82, 0.33, and 0.14 for TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> scales, respectively, **Table**

**3.** The similarity of Mach 0.3 to HP-BRT data is consistent with primarily TiO<sub>2</sub> losses, i.e., a volatility loss ratio near unity. The microstructural results indicated substantial removal of surface TiO<sub>2</sub>, with etching of Al<sub>2</sub>O<sub>3</sub> grains.

**Figure 3** also presents similar Mach 0.3 tests of a ‘Hexoloy’ monolithic sintered SiC standard baseline material for nominally duplicate atmospheric BRT runs a, b, c, showing weight losses of -1.2, -2.8, and -6.6 mg/cm<sup>2</sup>, respectively, after 200 h [20], [and unpublished data from Smialek/Opila/Cuy, NASA GRC]. The weight loss for SiO<sub>2</sub> scales is from Si(OH)<sub>4</sub>, where the relative Mach 0.3 BRT loss rate is projected as 0.14 that for the HP-BRT volatility rates (i.e., according to  $v^{1/2} \times (p_{\text{H}_2\text{O}})^2 / p_{\text{tot}}^{1/2}$ ). Thus, pressure effects are emphasized for SiC substrates, while velocity is relatively more important for TiO<sub>2</sub>. High pressure water vapor was shown in HP-BRT to be particularly more detrimental for SiC[20]. The HP-BRT curve shown in **Figure 3** was interpolated from eqn. 2 in ref.[40] The relative SiC loss rate calculated for the Mach 0.3

BRT relative to the HP-BRT was 0.14, yielding  $-1.1 \text{ mg/cm}^2$  after 100 h. This was close to the actual  $-1.0 \text{ mg/cm}^2$  given by experimental curve 'b'.

The resistance of YSZ and  $\text{Ti}_2\text{AlC}$  to oxide volatility compared to SiC is clearly shown in **Figure 3**. Comparison of the rig and furnace  $\text{Ti}_2\text{AlC}$  data indicate lower weight gains produced by burner tests due in part to volatility losses. The similarity of HP-BRT and Mach 0.3 results are consistent with  $\text{TiO}_2$  losses. However, Jacobson predicted higher vapor pressures and loss rates for  $\text{Al}_2\text{O}_3$  than  $\text{TiO}_2$  in water vapor using thermodynamic data.[11]  $\text{SiO}_2$  scales, on the other hand, were rapidly removed, showing substantial losses in both tests and more pronounced pressure sensitivity compared to velocity as predicted.[8]  $\text{SiO}_2$  scales have been shown to oxidize by parabolic kinetics in water vapor[17]. There has been some suggestion that the  $\text{Ti}_2\text{AlC}$  oxidation kinetics in BRT can be treated by an analogous cubic-linear law.[41] The same behavior appears to apply to this test, but the present configuration with thermal gradients complicates detailed analyses.

Backside Ca and Mg contaminants, not present in the starting material, may arise from dissolved minerals in cooling tower water supplies or from air supply line calcium-magnesium-alumino-silicate (CMAS) contaminants. No Si was observed on this BRT sample. No Ca, Mg phases were identified by xrd and little solubility exists within alumina. The faceted  $\text{Al}_2\text{O}_3$  (near  $\text{TiAl}_2\text{O}_5$ ) laminar structure is believed to be a vestige of water vapor etching via  $\text{TiO}(\text{OH})_2$  or  $\text{Al}(\text{OH})_3$  volatile hydroxide formation. The incorporation of impurities may indicate a role in reformation or growth of the scale here.

The improved lifetime durability of YSZ/MAX phases compared to superalloys had been presented as scale thickness vs temperature, where TGO scales upwards of 30-40  $\mu\text{m}$  were sustained compared to 5-10  $\mu\text{m}$  for single crystal superalloys.[14] Alternatively, the life duration

can be tabulated as a function of temperature, **Table 4**. It can be seen that TBCs on MAX phases survive to higher temperatures and at hundreds of hours above 1200°C. There is an overall time advantage for Ti<sub>2</sub>AlC substrates compared to Cr<sub>2</sub>AlC. For example, TBCs on superalloys survive, on average, only 30 h at 1300°C, or, alternatively, 500 h at 1150°C[30], vs 500 h at 1300°C for Ti<sub>2</sub>AlC. Very long term (2500 h) YSZ TBC/Ti<sub>2</sub>AlC compatibility had been shown in successive 1100°-1300°C interrupted furnace tests [42]. Based on TGO scale thickness, it was shown that this was equivalent to a TBC oxidative life of 25-50x that determined for conventional single crystal superalloys. Even an advanced two-layer Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>-YSZ coating on a superalloy survived only 588 1-h cycles at 1100°C or 42 hot hours with a surface temperature of 1400°C in a gradient burner test.[43]

Commercial purity Cr<sub>2</sub>AlC (Kanthal) MAX phase substrates exhibited PS-PVD YSZ failure in stepped, interrupted furnace tests beginning at 400 h at 1150°C, and complete after 100 h at 1200°C.[44][45] On a high purity Cr<sub>2</sub>AlC MAX phase (Jülich), APS YSZ coatings have been shown to survive 500 h up to 1200°C or to fail at 268 h at 1300°C.[14] While Cr<sub>7</sub>C<sub>3</sub> depletion layers and impurities have generally been associated with scale/TBC spallation for Cr<sub>2</sub>AlC, interfacial delamination was also observed. (Ti<sub>2</sub>AlC MAX phase exhibits no depletion zone or scale adherence issues). A high gradient BRT test using Cr<sub>2</sub>AlC as a bond coat survived 745 fast heating cycles (5 min.), with a high TBC surface temperature of 1400°C and TGO interface temperature of 1050°C.[25]. Again, a porous Cr<sub>7</sub>C<sub>3</sub> depletion layer, now exacerbated by Al interdiffusional losses for Cr<sub>2</sub>AlC employed as a bond coat, was detrimental to the coating system. The use of Al-MAX phases as thin bond coats remains problematic.

While the cyclic durability of moisture-resistant YSZ on SiC was improved with specialized bond coats, it is still quite limited because of thermal expansion incompatibility.[46][47]

$\text{Yb}_2\text{Si}_2\text{O}_7$  – based EBC coatings, successfully engineered for protecting strong SiC CMC materials in high temperature water vapor, remain the most qualified class of EBC materials.  $\text{Al}_2\text{O}_3$ -containing additives can dramatically reduce moisture-assisted oxidation under the EBC.[48] These systems typically survive 1000 h furnace exposures in high water vapor contents at  $1316^\circ\text{C}$ , while also exhibiting low volatility rates in moving gases. [21]; [22], [23] The overall durability of EBCs for CMCs in aggressive turbine environments at temperatures  $\geq 1300^\circ\text{C}$  remains a topic of great importance and interest.

## 5.0 Concluding remarks

The durability of a PS-PVD YSZ coating on a  $\text{Ti}_2\text{AlC}$  MAX phase substrate has been demonstrated by cyclic, 500-h, high-velocity burner rig testing at  $1300^\circ\text{C}$ . No spalling or visible degradation of the coating occurred. This represents perhaps the longest TBC survival duration in an aggressive  $1300^\circ\text{C}$  burner rig test. Cyclic oxidative life benefited from CTE matching of substrate, TGO, and TBC. Unlike TBC/superalloy systems, protective  $\alpha\text{-Al}_2\text{O}_3$  scale growth was not life limiting. The YSZ coating face showed no evidence of oxide volatility or reactivity with moisture. Xrd indicated some as-deposited [111] texture, an increase in the amount of cubic phase with thermal exposure, but no indication of massive monoclinic destabilization products. Moderate bending of the  $\text{Ti}_2\text{AlC}$  sample, however, was indicative of creep and low strength at high temperature. Comparisons with  $1300^\circ\text{C}$  furnace and high-pressure burner oxidation data for uncoated  $\text{Ti}_2\text{AlC}$  indicate similar cubic scale growth behavior. Lower values observed for rig tests are explained by scale volatility. Surface SEM of the uncoated backside showed effective removal of  $\text{TiO}_2$  surface nodules, presumably via  $\text{TiO}(\text{OH})_2$  vapor species. Etching and  $\text{Al}_2\text{O}_3$  intergranular porosity also suggested losses by  $\text{Al}(\text{OH})_3$ . In contrast, SiC exhibited notable

weight loss from  $\text{Si(OH)}_4$  under similar Mach 0.3 burner conditions, becoming more severe at high pressures.

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**Table 1.**

Summary of surface phases for burner rig exposure of bare and YSZ coated Ti<sub>2</sub>AlC MAX phase. Rietveld estimates of wt.% phase contents. Test temperature indicates maximum surface temperature of coating in hot zone. (sample from previous furnace tests included for comparison).

**Table 2.**

Estimates of YO<sub>1.5</sub> mole % in YSZ phases according to published lattice parameter and c/a ratio calibrations.

**Table 3.**

HP-BRT and Mach 0.3 BRT comparisons. (a) typical burner conditions and (b) relative TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> scale volatility factors ( $J_{M0.3}/J_{HP-BRT}$ ) according to  $v^{1/2}p_{H_2O}^n/p_{tot}^{1/2}$

**Table 4.**

Oxidative Life Summary of YSZ TBC on MAX Phases Compared to Single Crystal Superalloys (SXSA). Black (survived); red italic (failed)

(SXSA: Smialek 2015; GZ/YSZ: University West, Mahade, 2019; FCT-1: Kanthal (K), Smialek, 2016, 2018; FCT-2: Juelich (J), Gonzalez-Julian, 2018; BRT: Juelich (J), Gonzalez-Julian 2019); BRT: Kanthal (K), this study.

## Figure Captions

**Figure 1.** Photographs of burner rig and YSZ coated  $Ti_2AlC$  MAX phase sample in operation. a) upper angled view showing flame, sample and mounting base; b) short exposure indicating temperature gradients along sample length.

**Figure 2.** Mach 0.3 1300°C BRT of YSZ TBC on  $Ti_2AlC$ . a) Specific weight gain and degree of bending. Deflection rate is slightly moderated with time as subtended sample area decreases. b) Cubic oxidation kinetics (without spalling) is suggested by plotting transient corrected weight vs  $t^{1/3}$ .

**Figure 3.** Comparison of YSZ-MAX sample BRT oxidation data with other 1300°C exposures in similar tests. (HPBR at 6 atm. and 20-25 m/s, TGA dry air, and ambient air furnace tests. and Sintered ‘Hexoloy’ SiC curve (a) Opila, et al., 1316°C, (a,b) pyrometer sighted on edge; (c) sighted on face).

**Figure 4.** Visual appearance of the YSZ-MAX strip sample before and after test. YSZ coating shows rust discoloration due to Fe transfer from Kanthal A1 FeCrAl mounting sheet. (Coating ground off in mounting area to avoid abrasion losses).

**Figure 5.** YSZ/ $Ti_2AlC$  sample deflection due to creep from face-on, Mach 0.3 BRT flame impingement. (2.3 mm delta over 6.8 cm sample length. Lower ~1.5 cm gripped).

**Figure 6.** SEM of YSZ coating surface after 1300°C/500 h BRT, hot zone. a) craze crack pattern; b,c) columnar PS-PVD deposition; d) pristine individual 1-3  $\mu m$  YSZ grains on column surface.

**Figure 7.** SEM/BSE images of the coating cross-section after 500 h BRT at 1300°C. (Ni plated) YSZ/TGO/ $Ti_2AlC$  matrix: a, c, at the hot zone; b, d, at the grip end. Clean interfacial structures; 22.2/20.7  $\mu m$  and 12.4  $\mu m$  alumina scale thickness, respectively.

**Figure 8.** SEM/BSE images of the uncoated backside cross-section after 500 h BRT. (Ni Plated) TGO/ $Ti_2AlC$  matrix: a, c, at the hot zone; b, d, at the grip end. Clean interfacial structures with moisture attack of external scale; 12.8/13.8  $\mu m$  and 9.0  $\mu m$  alumina scale thickness, respectively.

**Figure 9.** SEM/BSE images of the uncoated  $Ti_2AlC$  backside surface at the hot zone after BRT. a) textured open scale structure; b) higher magnification showing individual laminar ~1 x 5  $\mu m$  platelets (P); corresponding EDS spectra showing: c) high Al, O intensity for granular particles (G); and d) small Mg, Ca, Ti peaks corresponding to platelets (P).

**Figure 10.** SEM/BSE images of uncoated  $Ti_2AlC$  backside surface at the lower grip end after BRT. a) finely peppered nodules dispersed on textured dense scale structure; b) higher magnification showing individual equiaxed ~1  $\mu m$  grains (G) and bright nodules (N); corresponding EDS spectra showing c) high Al, O intensity for granular particles (G); and d) additional Ca, Ti peaks corresponding to bright nodules (N).

**Figure 11.** XRD scans for uncoated (back) and YSZ coated (front) sides for the  $\text{Ti}_2\text{AlC}$  burner sample tested at  $926^\circ\text{C}$  for 10 m (S1) or at  $1300^\circ\text{C}$  for 500 h (S2). Top end, hot zone, and grip end positions. Primary peaks for (A)  $\alpha\text{-Al}_2\text{O}_3$ , (R)  $\text{TiO}_2$  rutile, (M)  $\text{Ti}_2\text{AlC}$  MAX phase, (Y) cubic/tetragonal YSZ, and (F)  $\text{Fe}_2\text{O}_3$  hematite.

**Figure 12.** Pole figure from YSZ columns showing primarily  $(111)_{\text{cubic}}$  fiber texture ( $926^\circ\text{C}/10$  m exposure). B-G-Y-R color scale corresponds to 200-450 relative intensity range.