

# Improvement of TBC Coating Resistance to Simultaneous Attacks by Sulfur and Vanadium Compounds

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Vanadium and sulfur are present in the hot section of gas turbine engines in the condensed or gaseous state due to the use of low quality or less refined fuels or operation in corrosive environments. Vanadium forms vanadium oxide  $V_2O_5$  which can react with both metals, and ceramic thermal barrier (TBC) coatings. It has been reported that  $V_2O_5$  reacts preferentially with  $Y_2O_3$  to form  $YVO_4$  compound, leaching out stabilizer from zirconia, resulting in changing YSZ chemistry and YSZ crystal structure [5-21], although another reaction between  $ZrO_2$  and  $V_2O_5$ , where  $ZrV_2O_7$  crystals are formed when the temperature ranges below  $750^\circ C$ . In either case, the non-equilibrium tetragonal phase ( $t'$ - $ZrO_2$ ) transforms to monoclinic zirconia phase ( $m$ - $ZrO_2$ ) in TBCs due to the removal of  $Y_2O_3$  caused by formation of  $YVO_4$ . This phenomenon leads to a significant volume expansion, and as a consequence, the coating delamination occurs. The reaction between  $V_2O_5$  and metal oxides has been proposed to follow a Lewis acid – base mechanism and the reactivity decreases with increasing acidity of metal oxides. For example,  $Y_2O_3$  has higher reactivity with  $V_2O_5$  than  $CeO_2$ , and  $CeO_2$  has higher reactivity than  $ZrO_2$ . Therefore, the vanadate resistance of several non- $Y_2O_3$  stabilized zirconia coatings, including  $CeO_2$ - $Y_2O_3$  co-stabilized zirconia (CeYSZ),  $TiO_2$ - $Y_2O_3$  co-stabilized zirconia (TiYSZ), and  $Ta_2O_5$ - $Y_2O_3$  co-stabilized zirconia (TaYSZ) have been investigated in the past.

300  $\mu m$  bond coat of argon gas atomized CoNiCrAlY powder (Diamalloy 4700) was sprayed on Hastelloy X buttons (1" diameter x  $\frac{1}{4}$ " thickness) and on 1020 carbon steel substrates (1 x 3 x  $\frac{1}{8}$ ") by a HVOF process (Oerlikon Metco DJ-2600). Based on the literature survey, as presented in the previous section, the top coat chemistry selection was made and is listed in table 1. For hot corrosion testing, similar salt composition was used as those were used for other studies. All the ceramic topcoats were sprayed using air plasma spray (APS) process and were of 300 $\mu m$  thickness. Metco 205 NS (CeYSZ) was not selected because the coatings synthesized by this powder have been fully investigated. The nominal oxide percentages of the powders are listed in Table 1

Table 1 Nominal oxide percentage of the top coat powders (wt.%)

Powder	$Cr_2O_3$	$TiO_2$	$Y_2O_3$	$ZrO_2$
Amdry 204NS-1	-	-	7	93
Metco 6038A	-	-	100	-
Metco 215	-	-	48	52
Metco 102	-	100	-	-
Metco 111	45	55	-	-
Metco 143	-	18	10	72

Using the powders listed in Table 1, seven different TBC systems were synthesized and are listed in Table 2, based on three considerations (1) a standard 7YSZ (Amdry 204NS-1) top coat is used as benchmark; (2) In the two layer top coats, the top layers (100  $\mu m$  thick) are designed to prevent from hot corrosion, and bottom layers (200  $\mu m$  thick Amdry 204NS-1) are employed to minimize the differences in

other performances between tested coating and benchmark coating; and (3) Samples are from the existed products, with chemistries to differentiate contents of  $Y_2O_3$  and  $TiO_2$ .

Table 2 Description of layer structure of the various coatings (A-G)\*

Coating	Top coat structure	Powder (top-bottom)	
A	Single layer	Amdry 204NS-1	
B	Bi-layer	Metco 215	Amdry 204NS-1
C	Bi-layer	Metco 6038A	Amdry 204NS-1
D	Single layer	50% Metco 143 + 50% Metco 215	
E	Bi-layer	Metco 111	Amdry 204NS-1
F	Bi-layer	Metco 102	Amdry 204NS-1
G	Bi-layer	Metco 143	Amdry204NS-1

\*Coating A to C are sprayed on Hastelloy X substrate, and Coating D-F are sprayed on the 1020 carbon steel substrate.

Hot corrosion attacks of various TBC systems by sulfur and vanadium compounds have been tested at 1050°C for 2 hours and 4 hours in the presence of 60 %  $V_2O_5$  and %  $Na_2SO_4$ , and the results are summarized as follows.

1. Sulfur and vanadium compounds at high temperature aggressively attacked the conventional 7YSZ TBC, the coating has been damaged at 1050°C for only 2 hours in the presence of 60%  $V_2O_5$  and 40%  $Na_2SO_4$ .
2. High density of coarse  $YVO_4$  crystals are quickly formed on coating surface, removal of  $Y_2O_3$  stabilizer from zirconia leads  $t'$ - $ZrO_2$  to  $m$ - $ZrO_2$  phase transformation and thus dramatic increase in volume. There is no evidence showing fair metallurgical bonds among  $YVO_4$  crystal and  $YVO_4$  crystal, and matrix, therefore, integrity of the coating is totally destroyed by sulfur and vanadium compounds. At the same time, molten salt infiltrate into entire top coat and seal splat boundaries and pores similar to molten silicate deposits to reduce strain tolerance, finally causing top coat delamination.
3. Hot corrosion resistance of  $TiO_2$  and  $Y_2O_3$  co-stabilized zirconia has doubled compared to a standard 7 YSZ TBC, while single stabilizer TBCs with high  $Y_2O_3$  ratios do not increase hot corrosion resistance in the presence of 60 %  $V_2O_5$  and 40 %  $Na_2SO_4$ .
4. TBC sprayed using mixture of 50% Metco 143 and 50% 48YSZ and Metco143/A204NS-1/bi-layer TBC had the highest resistance to simultaneous attacks by sulfur and vanadium compounds, although the microstructures on the surface and cross-section of these two TBCs are totally different.

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