Integrated Gasification Combined Cycle (IGCC) power plants are attractive alternatives to current pulverized coal technologies in large-scale stationary applications. IGCC systems are very efficient, with efficiencies ranging from 35 to 45 percent (depending on system configuration and size). For further increasing the IGCC efficiency, the gas turbine inlet temperature needs to be higher (> 1200°C). At higher operating temperatures, besides improved efficiency, less fuel is consumed resulting in reduced operating costs and fewer undesirable combustion by-products. At higher inlet temperature, the durability of the metallic components would be a concern.

The durability of turbine engine components is achieved by the use of a thermal barrier coating (TBC) system and/or by internal/external cooling [1,2]. Current TBC system consists of yttria stabilized (6-8 wt.% yttria) zirconia (YSZ) as the insulating top coat. YSZ works very well up to a temperature range of 1100-1200°C. In this temperature range YSZ has the desired attributes viz. relatively low thermal conductivity, relatively high thermal expansion coefficient, and high fracture toughness which yield the necessary erosion resistance for such applications. YSZ possess a metastable tetragonal-prime (t') zirconia phase which is the key to its long-term structural stability and resistance to transformation to the monoclinic or cubic phase. The t' structure of the YSZ TBC provides enhanced toughness and hence very high durability. Another key attribute of the YSZ composition is that it is in thermo-chemical equilibrium with the TGO (aluminum oxide) formed at the bond coat-YSZ interface.

For higher temperature applications, YSZ is inadequate due to phase instability, increased sintering rate and inadequate thermal conductivity. At higher temperature, sintering induced densification of YSZ is another concern. Densification increases the elastic modulus and thereby decreases strain compliance of the TBC coating. Densification also decreases the volume fraction of porosity resulting in increased thermal conductivity. Thus, the standard YSZ is unlikely to be usable at elevated temperatures and therefore new materials and/or processes are needed to be explored.

TBC materials having high temperature stability, lower thermal conductivity and lower sintering rate do exist. For example, pyrochlore oxides of the rare earth (RE) zirconates (RE$_2$Zr$_2$O$_7$ – where RE is a rare earth) are promising substitutes for YSZ. Specifically, gadolinium zirconate (GZO – Gd$_2$Zr$_2$O$_7$) has been studied by several authors due to its high thermal stability ceiling, low thermal conductivity, relatively large coefficient of thermal expansion and reduced propensity for sintering. Drawbacks of GZO and other rare earth zirconates are very low toughness and thereby very poor erosion performance of the cubic structure as well as the thermochemical instability with the alumina TGO. It has been suggested that the latter can be circumvented by first depositing an YSZ interface layer prior to GZO deposition, thus preventing reaction between GZO and the alumina TGO layer.

Doping of divalent RE oxides such as Gd$_2$O$_3$ and Yb$_2$O$_3$ has been shown to create immobile defect clusters within the structure of YSZ. These defect clusters serve to reduce thermal
conductivity, provide sintering resistance, increase toughness and phase stability. Below approximately 6 mole% of total RE oxide dopant, the YSZ maintains the t’ structure (henceforth t’ low k: ZrO$_2$-1.7mole%Y$_2$O$_3$-1.1mole%Gd$_2$O$_3$-1.2mole%Yb$_2$O$_3$) thus higher toughness, while above 6 mol%, the cubic structure (henceforth cubic low k: ZrO$_2$-6mol%Y$_2$O$_3$-2mole%Gd$_2$O$_3$-2mole%Yb$_2$O$_3$) is stable. This is important, as increasing the dopant concentration is favorable in terms of reducing thermal conductivity, but reduces the toughness and therefore erosion resistance.

In order to develop high temperature TBCs having high thermal insulation (low thermal conductivity) and enhanced erosion resistance without sacrificing strain tolerance for application in IGCC power plants, there appears to be a distinct need to develop technologies to impart toughness to materials such as GZO and cubic low k for higher temperature TBC applications.

2.0 OBJECTIVE/TECHNICAL APPROACH

The overall goal of the Phase I/initial Phase II STTR project was to develop novel TBC architectures viz. multilayer/composite that provide high thermal insulation (low thermal conductivity), low sintering rate and high erosion resistance with high toughness (high strain tolerance).

To introduce toughness in the high temperature TBC materials, our technical approach in the initial Phase II STTR was to develop multilayered and composite TBC architectures of selected high temperature base TBC materials (GZO and cubic ZrO$_2$ low k) with highly tough t’ low k TBC material. The rational for such TBC architectures is to introduce toughness by providing interfacial paths for crack deflection. The developed TBC architectures were also expected to provide lower thermal conductivity through enhanced phonon scattering by the expected strain fields at the interfaces.

3.0 RESEARCH CARRIED OUT

The research involved fabrication, microstructural optimization, characterization and performance evaluation of the multilayered/composite TBCs. Electron beam physical vapor deposition (EB PVD) and atmospheric plasma spray (APS) processes were used for the fabrication of multilayered and composite TBCs. X-ray diffraction, optical and scanning electron microscope techniques were used to characterize the microstructure. Thermal conductivities of the as-fabricated TBCs were determined at NASA Glenn by a steady state heat flux (from a 3.0KW CO$_2$ laser to maintain TBC surface temperature of 1316°C for 20 hours while cooling the back side with air) technique under thermal gradient conditions. Erosion rate of the as-fabricated and annealed TBCs was also determined at various impingement angles of 30° and 90°. Thermal cycling tests were conducted to examine the durability of fabricated TBCs. For comparison purposes, monolayered TBCs of YSZ, GZO, cubic low k and t’ low k were also fabricated and evaluated.

The initial Phase II work has demonstrated that the multilayered coatings with optimal microstructure can provide lower thermal conductivity at higher temperature (>1300°C) and maintain much lower sintering rate compared to YSZ and improved erosion resistance as compared to GZO.

4.0 RESEARCH FINDINGS

Figure 1 shows the initial and sintered thermal conductivities of the as fabricated EB PVD TBCs. As shown in Figure 1, monolayered YSZ (Matrix 1) exhibited the highest initial or "as deposited" thermal conductivity of ~1.45 W/m-K, along with the highest "sintered" thermal conductivity of 2.2 W/m-K after a full 20 hours of high heat flux testing at 1316°C. The t’ low k (Matrix 2) and
GZO (Matrix 3) monolayered TBCs have initial thermal conductivities much lower than YSZ with values of 1.25 W/mK and 1.13 W/mK, respectively. The sintered thermal conductivity values of t’ low k (1.66 W/mK) and GZO (1.43 W/mK) were also significantly lower than YSZ (2.2 W/mK). Thus, among the monolayered TBCs, GZO exhibited lowest initial and sintered thermal conductivities. The initial and sintered thermal conductivities of the two multilayers viz. Matrix 5 and Matrix 6 were found to be much lower compared to YSZ and closer to that of GZO. For example, the initial and sintered thermal conductivities of Matrix 5 were measured to be 1.14 W/mK and 1.22 W/mK. The increase in thermal conductivities of YSZ (Matrix 1) and multilayer (Matrix 5) after 20 hours was ~52% and 7% respectively, showing a significant reduction. As shown in Figure 2, sintering induced cracking in the multilayer TBC (Matrix 5) is minimal compared to YSZ. Thermal cycling life of multilayers was found to be close to that of YSZ. It should be emphasized that due to the intrinsically high toughness of YSZ, it exhibits very high durability.

**Figure 1.** Plot of initial and sintered thermal conductivities of EB PVD TBCs: Matrix 1 (YSZ), Matrix 2 (t’ low k), Matrix 3 (GZO) and Matrix 5-6 (multilayers)

**Figure 2.** X-SEM micrographs of (a) Matrix 1: YSZ and (b) Matrix 5: multilayer after thermal conductivity tests
Figure 3 represents the erosion rate data of YSZ, t' low k, GZO and a multilayer TBCs at two different impact angles viz. 30 and 90 degrees. It is clear that GZO exhibits the highest erosion rate whereas the YSZ and t' low k showed very low erosion rates. The very low erosion rates of YSZ and t' low k are due to their tougher t' structure. The multilayered TBCs, compared to GZO, exhibited roughly 3x times and 2.4x times lower erosion rates, respectively, at 30 and 90° impact angle.

![Erosion rate data for EB-PVD TBCs](image)

**Figure 3. Erosion rate data for EB-PVD TBCs**

The combined data of Figures 1-3 demonstrate that the multilayered EB PVD TBCs can provide substantially lower erosion rate compared to GZO while maintaining thermal conductivity close to that of GZO. The sintering rate of the multilayered TBCs was also found to be much lower than that of YSZ. Thermal cyclic life of the optimized multilayered TBC was found to be close to that of YSZ.

Although cubic low k exhibits lower thermal conductivity and lower sintering rate, its toughness is very low. Due to lower toughness, cubic low k exhibits much higher erosion rate and lower durability. In that sense, characteristics of cubic low k are similar to that of GZO. Thus, in the initial Phase II program efforts were directed to lower the erosion rate and to increase durability of cubic low k by compositing with tougher t' low k while maintaining lower thermal conductivity.

In the initial Phase II program various composite TBCs viz. were fabricated by atmospheric plasma spray (APS) technique. Three different composite TBCs were fabricated, Matrix 3, 4 and 5, having different ratios of t' low k and cubic low k. For comparison purpose APS monolayered TBCs of YSZ (Matrix 6), cubic low k (Matrix 2) and t' low k (Matrix 1) were also fabricated. The thermal conductivity, erosion rate and thermal cycling life of the fabricated TBCs were evaluated and shown in Figure 4, 5 and 6 respectively.

The thermal conductivity data (Figure 4) showed that the composite TBCs can provide initial thermal conductivity and the sintered thermal conductivity much lower than YSZ and closer to that of cubic low k. The erosion data (Figure 5) exhibited that the composite coatings can have much lower erosion rate compared to cubic low k. The thermal cycling data (Figure 6) indicated that the composite coatings provide higher durability (cyclic life) than cubic low k.
Figure 4. Plot of initial and sintered thermal conductivities of APS TBCs; composite (Matrix 3-5), YSZ (Matrix 6), cubic low k (Matrix 2) and t' low k (Matrix 1).

Figure 5. Erosion data of APS TBCs.
The combined data of Figures 4-6 demonstrate that the composite APS TBC design architectures can provide substantially lower erosion rates and enhanced durability (higher cyclic life) compared to cubic low k while maintaining thermal conductivity close to that of cubic low k.

The initial Phase II objectives were met in that the UES-PSU team has successfully fabricated multilayered/composite TBC architectures with reduced thermal conductivity and sintering rate as well as with improved erosion resistance.

5.0 THE PHASE IIB PROJECT

In the initial Phase II program, two distinct TBC architectures, viz. multilayer and composite, were developed to provide desired characteristics for high temperature applications. However, the processing of these architectures can be considered as time consuming and therefore expensive.

In the Phase IIB program we are working to develop a novel approach to fabricate tougher high temperature TBCs. This approach involves making sprayable high temperature TBC powders to fabricate multilayered and/or composite TBCs by utilizing cost effective APS process. It is believed that the APS processing of such powders to fabricate TBCs for higher temperature applications will be much more conducive with respect to commercialization of the proposed technology.

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