ADVANCED THERMAL BARRIER COATING SYSTEMS FOR THE ATS ENGINE

Ramesh Subramanian, Stephen M. Sabol, John Goedjen and Maria Arana

Siemens Westinghouse Power Corporation
4400 Alafaya Trail
Orlando FL 32826

ABSTRACT

In order to meet the ATS operation and efficiency objectives, new thermal barrier coating systems capable of withstanding higher surface temperatures are essential. A comprehensive plan to achieve this objective was initiated by Siemens Westinghouse Power Corporation, under the Department of Energy – Oak Ridge National Laboratory Thermal Barrier Coatings Program. This paper provides an overview of the development approach adopted by Siemens Westinghouse that has culminated in the identification of a new and superior TBC system for the ATS engine.

Development efforts towards identifying new ceramic compositions, that are expected to exceed the temperature capabilities of 8 % yttria stabilized zirconia, are discussed. Results from electron beam vapor deposition (EB-PVD) of new ceramic compositions are discussed with regards to the correlation of the coating characteristics to deposition parameters. The performance of the different coatings were evaluated by cyclic furnace testing. Upon systematic failure analysis, deposition parameters were optimized to result in a significant improvement in life. The improved deposition parameters resulted in the identification of a new ceramic as a thermal barrier coating. Thus, Siemens Westinghouse has met the objectives set for the program by identifying an advanced thermal barrier coating system for the ATS engine.

INTRODUCTION

The Siemens Westinghouse Advanced Turbine System is designed to achieve a 60 % thermal efficiency, less than 10 ppm NOx emissions and a reliability-availability-maintainability (RAM) equivalent to the current advanced power generation systems. One of the many approaches to increase efficiency and reduce NOx emissions is by increasing rotor inlet temperatures at lower burner outlet temperatures. This can be achieved by utilization of a closed loop steam cooled Row 1 vane, with no thin film cooling air. This increases the rotor inlet temperatures, while maintaining a low burner outlet temperature without compromising the efficiency. Consequently, without film cooling, the TBC surface temperatures are now significantly higher than the current advanced engines (See Fig. 1). The bond coat temperatures can vary depending upon the TBC thickness, however, the average bond coat temperatures are expected to be higher than those for the F and G engines. The higher bond coat and TBC surface temperatures are challenging the limitations of the existing TBC system and new coating systems need to be identified to meet the increasing demands.
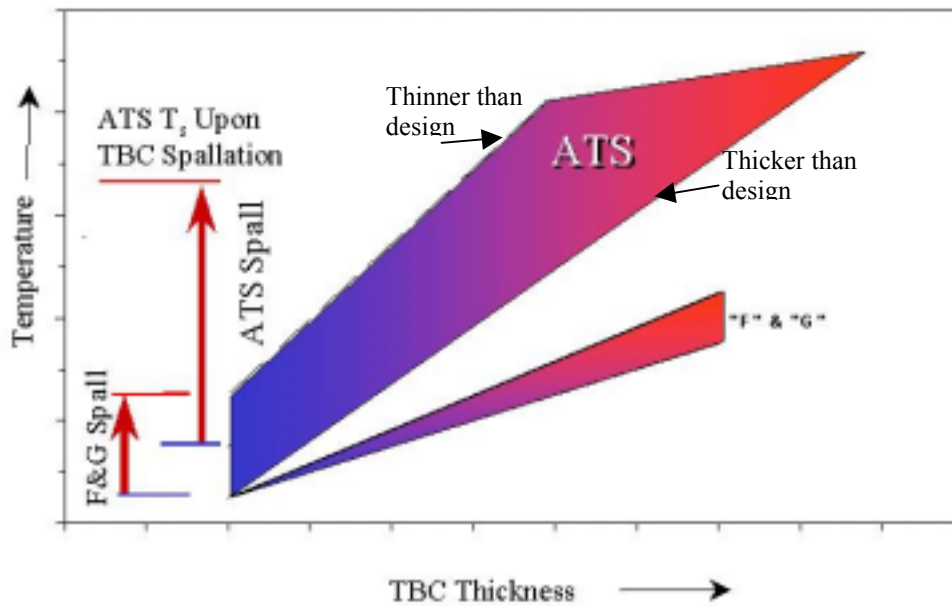

Fig. 1: Comparison of temperature gradients between the ATS and W501G (and F) engines

In addition, from Fig. 1, demands on the reliability of a TBC system can also be ascertained. In the event of a TBC spallation in the G (and F) engines, the increase in component metal temperatures would still be within the design temperatures. However, a similar spallation in the ATS engine would result in component temperatures well in excess of the design temperatures. This can, consequently, result in a rapid and severe degradation of the component properties. To realize the objective of maintaining reliability of an ATS engine equivalent to existing advanced engines, new TBC systems should be very dependable, so that a component can be designed with a guaranteed protection of the TBC system. This was attempted by adopting a complete coatings development approach which included the identification of an advanced thermal barrier coating system, a development of an

analytical model to predict its life, identification of innovative NDE techniques to monitor the performance of the TBC system and development of a reliable, robust manufacturing process. This paper focusses only on the development work performed in the fiscal year 1999 towards identifying an advanced thermal barrier coating system.

ADVANCED THERMAL BARRIER COATING SYSTEM DEVELOPMENT

Bond coat development

New bond coats are needed to deliver higher temperatures, as shown in Fig. 1, and for a 24,000hr service requirement. To realize these goals, new bond coat chemistries and new concepts were developed to address the degradation mechanisms of the current bond coat systems. These degradation mechanisms could be a combination of oxidation, corrosion, TBC adhesion and mechanical behavior, such as fatigue and creep, of the coating/substrate system. The development efforts also focussed on being able to consider transfer of the new technology to production. Only a summary of the results regarding bond coat development is discussed in this section.

Fig. 2 shows the performance of some of the new bond coat chemistries identified in this program. These new chemistries have outperformed the current baseline bond coat by 60 to 170 %. Also, from Fig. 2, it is clear that the choice of the new bond coat chemistry depends on the substrate. For instance, bond coat chemistry B does not provide any improvement over baseline for substrate 2, however is very effective for substrate 1. On the other hand, bond coat chemistry A shows different levels of improvement for substrates 1 and 2. Clearly, a thorough understanding of the degradation mechanisms and also the interaction of the bond coat with the substrate is essential for an appropriate selection of the bond coat chemsitry.
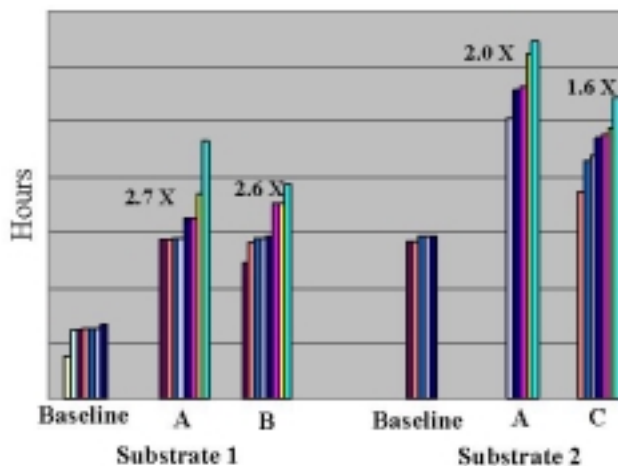

Fig. 2: Improved bond chemistry for ATS conditions

By improving the temperature capabilities of the bond coat, benefits from reduced cooling air requirements, increased reliability and extended component life are realized. However, benefits from increased temperature capability are expected to be marginal, since these temperatures are already close to the superalloy design temperature limits. Therefore, further incremental benefits can be significant

only if new TBC compositions are identified which can simultaneously withstand higher surface temperatures and provide larger thermal gradients. This would have a dual benefit of increased engine efficiency and increased realiability. With this objective, recent development efforts have focussed towards identifying new ceramic TBCs and the rest of the paper discusses the details at length.

Ceramic TBC Development

The current industrial standard for a TBC is 8 wt. % yttria stabilized zirconia and has been almost exclusively used for turbine engine thermal barrier coatings. Zirconia, ZrO_2, when stabilized by 7-8 wt % Y_2O_3 (known as 7-8YSZ) is a partially stabilized zirconia, with the high temperature tetragonal phase stabilized upon cooling to room temperature, without transformation to the equilibrium monoclinic and cubic phases. The high temperature tetragonal phase is the predominant phase of 8YSZ thermal barrier coatings, which are generally deposited by processes that rapidly quench the high temperature phase – namely, either an air plasma spray process (APS) or electron beam physical vapor deposition (EB-PVD) process. Coatings deposited by APS result in a microstructure with solidified splats and interlamellar gaps parallel to the substrate. The interlamellar gaps and splats (which have directionally solidified vertical microcracks) provide significant strain tolerance to the coating – an essential feature for the coatings to accommodate the CTE mismatch between a metallic substrate and a ceramic coating. EB-PVD processes result in a columnar microstructure with inter-columnar spaces across the complete thickness of the coating, thus providing an inherently strain tolerant microstructure. However, as the name - partially stabilized zirconia coatings - suggests, upon operation at temperatures above the stability of the quenched-in tetragonal phase, it is expected that the coatings would destabilize into the tetragonal, monoclinic and cubic phases. Also, any microstructural changes can compromise the strain tolerance of the coatings. These limitations need to be understood before establishing the requirements for new ceramic compositions to perform as effective thermal barrier coatings.

LIMITATIONS OF 8YSZ THERMAL BARRIER COATINGS

Pure zirconia undergoes a crystallographic phase transformation, which is prevented by the introduction of stabilizers such as yttrium oxide, calcium oxide, magnesium oxide and several other rare earth oxides. Of all the stabilizers, investigated so far, based on performance and an economics point of view, yttria stabilized zirconia has been the most successful in meeting the requirements of a thermal barrier coating for turbine engine components. Both APS and EB-PVD processes result in the formation of a stabilized tetragonal phase which shows no significant changes in phase composition below 1000 °C (See Fig. 3, [1]). Upon operation at temperatures above 1200 °C, this phase destabilizes upon long term exposure (greater than 100h) into a cubic phase and a tetragonal phase [see Fig. 3]. The new tetragonal phase (known as the transformable tetragonal phase), upon cooling, undergoes a phase transformation to the monoclinic phase with a volume change of about 4 % [2]. Presence of large amounts of transformable tetragonal phase can only result in formation of the monoclinic phases with significant microcracking and possible loss of mechanical integrity of the coating. Investigations attempting to correlate the relative concentrations of the monoclinic, tetragonal and cubic phases to the performance of the coating have been inconclusive [3]; however, it is well known that yttria content in APS ZrO_2 coatings can significantly change the tetragonal, monoclinic or cubic phase concentrations and consequently affect the coating performance [4]. Therefore, destabilization of the high temperature tetragonal phase increases uncertainity in the coating performance – clearly an unfavorable feature while

trying to realize the goal of a TBC with improved reliability and performance. It is, therefore, imperative to identify a phase stable ceramic and consequently eliminate the uncertainty of phase instability resulting in any performance or reliability loss.
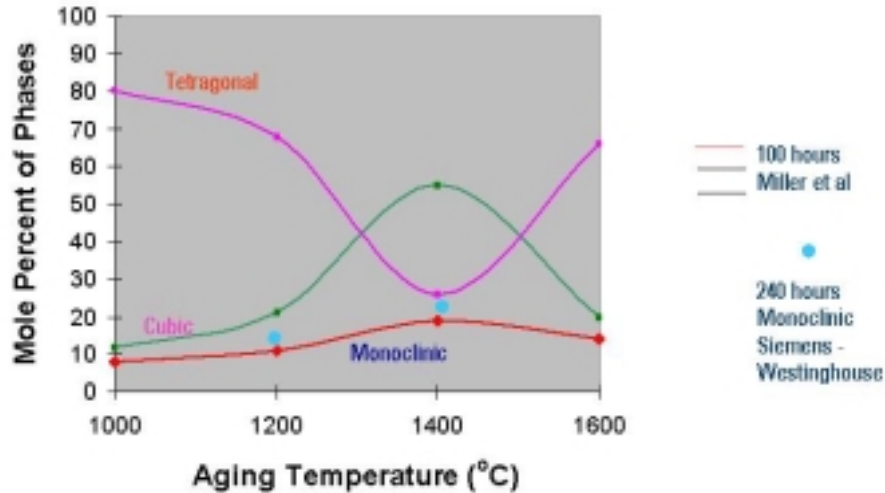

Fig. 3: 8YSZ destabilizes upon exposure to temperatures higher than 1200 C [1]

In addition, as the temperature increases another degradation mechanism, namely sintering, comes into play. Higher temperatures result in increased diffusion and consequently, elimination of pores and cracks. Densification of the coating leads to an increase of the elastic modulus and, therefore reduces the strain tolerance of the coating.

For APS coatings, several investigations have focussed on the correlation of sintering behavior to the thermal cyclic life of the coatings. These investigations clearly show a detrimental effect due to the sintering of the coatings, during operation above a critical time and temperature limit. This is supported effectively by results obtained at from the high heat flux rig assembled at Waltz Mill, PA, through this program. The rig is one-of-a-kind facility which can establish ATS surface temperatures and thermal gradients resulting from heat flux equivalent to that of the ATS row 1 vane design. Upon subjecting samples with APS TBC to ATS surface temperatures, the cyclic life is extremely poor. Fig. 4 shows a typical set of results from the Waltz Mill rig, where the number of cycles to fail is plotted versus the surface temperature, at a specific thermal gradient across the thickness. A fitted line is shown for samples maintained at their respective surface temperatures for 10 minutes during each cycle. Clearly, at the lower surface temperatures, the cycles to failure are significantly higher than at the higher surface temperatures. The plot also shows the effect of maintaining the samples at high temperature for extended periods of time, typical of industrial gas turbine engine operations. The number of cycles to failure of the APS coatings decrease further, with increasing hold time.

Failure analysis of the samples show that spallation of the APS coatings occurred layer-by-layer as shown in Fig. 5. Each of these layers are significantly denser than the as-deposited coatings. This
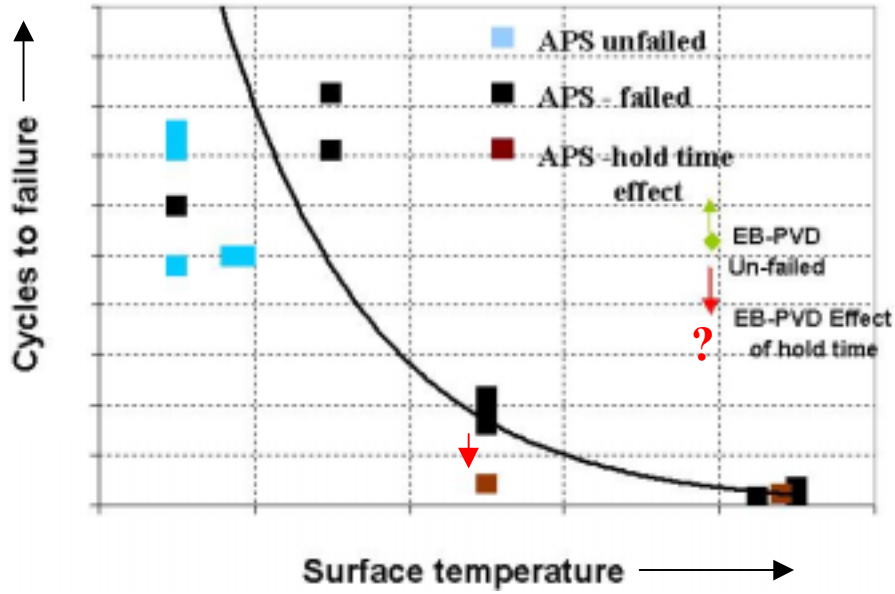
FIG. 4: EB-PVD outperforms APS by at ATS surface temperatures

results in an increased elastic modulus and, consequently a loss in strain tolerance. Upon further exposure to the ATS temperatures, the next layer sinters and spalls off. This clearly demonstrates a severe degradation in performance due to sintering of the coating.

An additional debit due to the sintering of the coating, is the increase in thermal conductivity. This necessitates increased cooling air to maintain the metal temperatures within design – a direct impact on engine efficiency. However, if the cooling air is not increased, metal temperatures are likely to increase, leading to an increase in the thickness of the thermally grown oxide (TGO). This can further increase the probability of initiating failure at the bond coat/TBC interface leading to complete spallation of the coating. All these factors, in combination result in a drastic reduction in thermal barrier coating life.
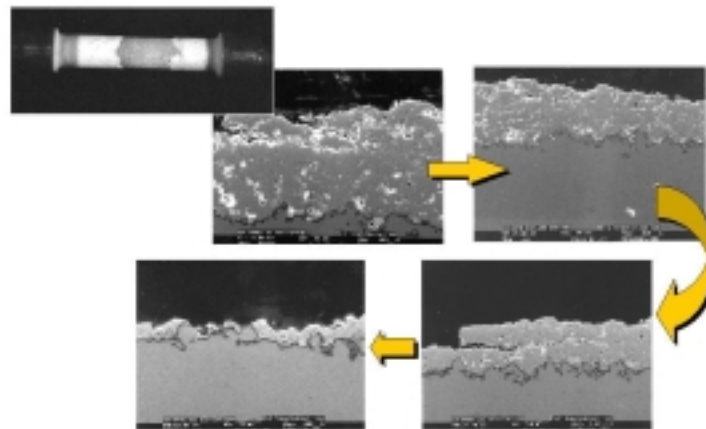

FIG. 5: Upon exposure of APS 8YSZ to ATS temperatures, failure occurs layer-by-layer.

It is well known that the sintering tendency of a solid is a function of the inherent sintering resistance (governed by defect populations) and porosity level, including pore size, shape and distribution [5]. The obvious difference between APS and EB-PVD 8YSZ coatings is the porosity level, pore size, shape and distribution. Therefore, the sintering resistance of the APS and EB-PVD 8YSZ coatings are expected to differ from each other primarily due to differences in the pore morphology and distribution. This is evident in Fig. 4, where EB-PVD coatings outperform APS coatings at ATS temperatures. EB-PVD coatings obtain their superior strain tolerance from the presence of vertical cracks or inter columnar spacings. However, when EB-PVD coatings are maintained at ATS surface temperatures for durations typical of IGT operation times, these spacings also sinter (see Fig. 6). Fig. 6A clearly shows the bridging of columns upon an isothermal exposure of the complete TBC coating to ATS surface temperatures. The loss of intercolumnar spaces will result in an increase in elastic modulus of the coating and consequently spallation of the coating. Sintering of EB-PVD coatings has also been observed in samples tested in the Waltz Mill rig under ATS thermal gradients and during thermal cycling (See Fig. 6B). The columns show a tendency to sinter by formation of bridges as shown in Fig. 6A. In addition, a bundling of the columns is observed due to the sintering of groups of columns – clearly a loss in strain tolerance relative to the as-deposited columnar microstructure. Further investigations are underway to quantify the effect of increasing duration of time and therefore, sintering of PVD columns on the thermal fatigue life of the coatings.
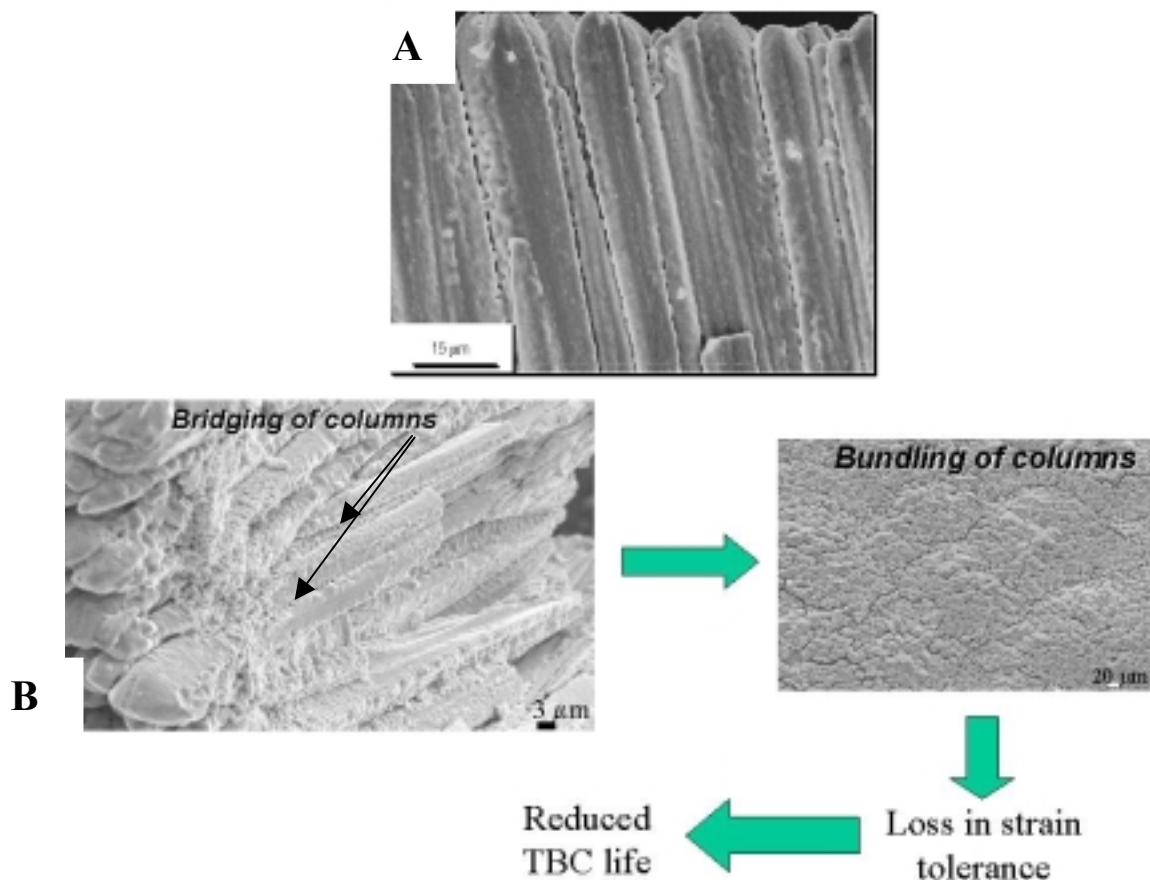

Fig. 6: Sintering of PVD columns are observed at ATS surface temperatures during
(A) isothermal exposure and also (B) thermal gradient tests

NEW CERAMIC TBC IDENTIFICATION

Based on the foregoing discussions on the limitations of 8YSZ, two important criteria for the selection of a new ceramic composition for thermal barrier coating applications have emerged – long term high temperature phase stability and superior sintering resistance.

In addition to phase stability and sintering resistance at ATS temperatures, the new compound should not show any crystallographic transformations during thermal cycling. This is essential in order to maintain the integrity of the coating during thermal cycling. The new compound should also have a high thermal expansion coefficient in order to minimize the CTE mismatch between the coating and substrate and a thermal conductivity at least equivalent to 8YSZ, if not lower. The new TBC should eventually satisfy a requirement of $\geq$ 24,000 hours at ATS surface temperatures.

Several investigations have determined means of further increasing the chemical stability of partially stabilized zirconia, by utilizing other stabilizers, for instance, Yb_2O_3 [6]. Since the developments are based on maintaining the long term stability of a metastable tetragonal phase, it is only a matter of time, before initiating the degradation of the as-deposited phase. Therefore, a detailed literature search was undertaken to identify promising compounds, that were inherently phase stable and not requiring any stabilizers.

Several compounds were selected, that were identified as phase stable compounds, capable for application as TBCs. Although the compounds were predicted to be phase stable by the literature, it was considered important to confirm it by performing systematic lab scale evaluation. The lab scale evaluation focussed on determining the phase stability upon long term exposure at ATS surface temperatures and simultaneously determining the sintering resistance of the compounds. Therefore, a simple approach was adapted to achieve the lab scale evaluation economically. The ceramic compounds were prepared by mixing the constituent powders, selecting a specific particle size range, preparing pellets and then aging them at ATS temperatures, for time periods typical of IGT applications. Comparison of the X-ray diffraction patterns allowed for determination of the long term phase stability of the compounds. In addition, microstructural evaluation showed the changes in density with increase in exposure to high temperatures. The lab scale evaluation of the ceramic compounds allowed for prioritization based on their phase stability and sintering resistance at ATS surface temperatures. The compounds that were identified as high priority were further evaluated for the feasibility of deposition by EB-PVD. EB-PVD was selected as the deposition process of the new compositions, primarily from the results shown in Fig. 4. From Fig. 4, it is evident that performance of EB-PVD 8YSZ is superior to APS 8YSZ at ATS surface temperatures. Therefore, it is expected that EB-PVD processing will provide the best opportunity to improve on the performance of 8YSZ. The next section discusses the deposition trials of the new compositions and evaluation of the furnace cyclic life and sintering resistance.

EB-PVD deposition trials:

The objective of the deposition trials was to determine the feasibility of depositing new compositions by EB-PVD. Upon successful deposition, an optimum set of processing parameters were identified to deposit the microstructure with the best thermal fatigue life. Ingots of all the new

compositions, for deposition by EB-PVD, were prepared by Transtech Inc. The deposition trials were conducted at the Operhall research center at Howmet Corporation.

As a basis for understanding the results from the deposition trials, it is important to first understand the EB-PVD process and the variables that affect the growth of the columnar features. A comprehensive article by Movchan and Demischin summarizes the effect of substrate temperature on the formation of columnar microstructures by EB-PVD of yttria stabilized zirconia [7]. The results are schematically shown in Fig. 7. There are three zones with different microstructures. Two critical temperatures T1 and T2 demarcate these zones. The critical values are 380 C and 1065-1213 C for ZrO_2. At temperatures below 380 C, there are no columnar microstructures, but primarily polycrystalline or amorphous coatings.

$$\text{For } ZrO_2: T_1 = 0.22T_m \text{ and } T_2 = 0.45\text{-}0.5T_m$$
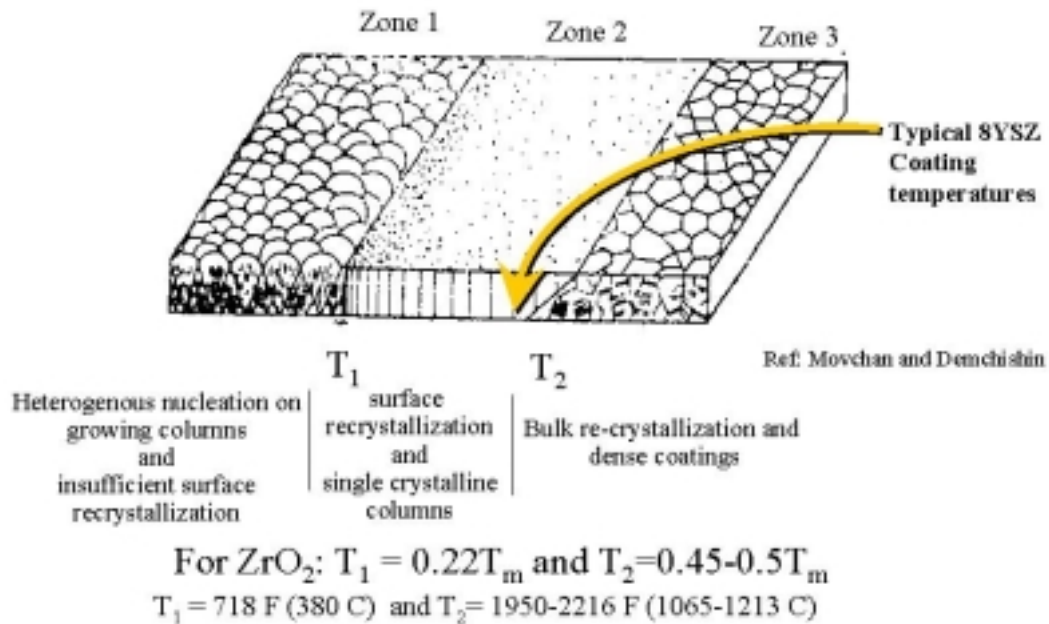$$T_1 = 718 \text{ F (380 C)} \text{ and } T_2 = 1950\text{-}2216 \text{ F (1065-1213 C)}$$

Fig. 8: Effect of substrate temperature on columnar microstructure during EB-PVD of ZrO2 (Ref. 7)

This is suggested to arise due to insuffucient recrystallisation at the surface of the substrate and also of the new molecules that are continuosly being deposited on the growing columns. Upon increasing the temperature above 380 C columns start forming, which are single crystalline and textured. With increasing temperature, the columns grow in thickness due to the larger size of the nucleii but maintain their columnar structure. Around T2 (1065 $^\circ$C) the columns start joining together, due to the increased diffusion of the atoms and above T2 only equiaxed coatings are obtained.

Typical deposition temperatures for production of 8YSZ coated blades are near T2. The critical difference to be kept in mind is that the blades are rotated and the work performed by Movchan and Demishin does not include effect of rotation. Rotation plays a critical role in the formation of the intercolumnar spacing due to the shadowing of the flux as it is being deposited onto the substrate [8]. A typical microstructure for 8YSZ shows the changes in the columnar features due to rotation. Clearly,

rotation of the parts results in a columnar microstructure with intercolumnar spacings. Changes in rotation speed, or the rpm, does not significantly change the microstructure, other than some small changes in the formation of striations at lower rpm. These striations are a result of the part moving in and out of the vapor flux. Any specific location has a higher flux of atoms condensing on to the part when it is facing the melt pool, when compared to condensing flux when facing away from the pool. Upon increasing the rpm, the differences between the "day" and "night" of the flux is minimized and therefore, columnas are deposited with no striations. (see Fig. 8).
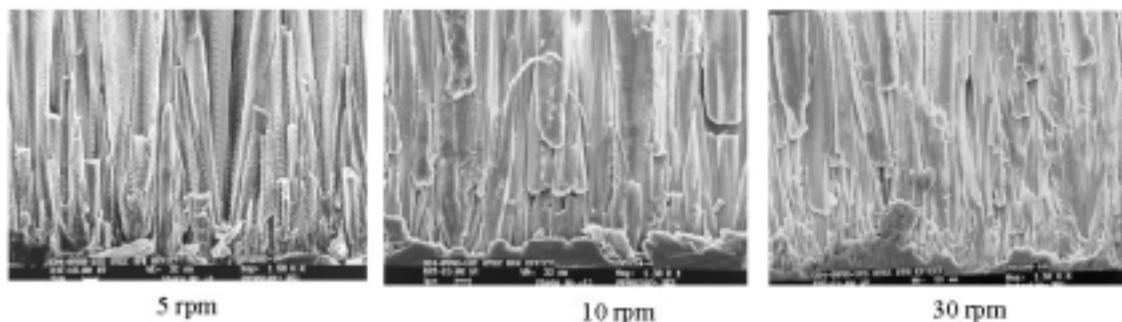

| 5 rpm | 10 rpm | 30 rpm |

Fig. 8: Effect of rotation on the columnar microstructure during EB-PVD of 8YSZ

The zones, as described in Fig. 7, are specific for the deposition of 8YSZ and no such information is available to date for different material compositions. Therefore, for the new ceramic compositions, determination of the correct temperatures to obtain a columnar microstructure is very important. In addition to the correct substrate temperature, the effect of many other parameters are inter-related to the deposition of a columnar microstructure such as – feed rate, gun power, oxygen bleed rate, total pressure and very critical for continuous operation is the ingot homogeniety.

It is also very important to understand that for 8YSZ, we have a relatively clear idea of the preferred columnar microstructure. However, it is quite possible that the columnar features – such as width, porosity distribution, surface features and texture – that provide the best thermal fatigue life for new chemistries is completely different from that for 8YSZ. Therefore, the experimental evaluation in this program included deposition of coatings and, in addition, identification of the microstructure that provides the best furnace cyclic life.

For the deposition of new ceramic compositions, the first criteria for success is the feasibility of obtaining a stable melt pool. A stable melt pool is obtained when the heat input from the gun allows for formation of a melt pool with a composition in equilibrium with the ingot composition without any severe spitting or mechanical instability. Differences in vapor pressure of the constituents can result in formation of bubbles and can lead to spitting of liquid droplets from the melt pool onto the substrate. This results in inhomogeneity in the coating microstructure. Melt pool instability was clearly noticed for one of the chemistries shown in Fig. 9. The pictures show the solidified melt pools of two different chemistries. A stable melt pool results in no bubbles underneath the melt pool surface as in Fig. 9A. The chemistry, which formed several bubbles during the deposition process (Fig. 9B), was eliminated from the further consideration.
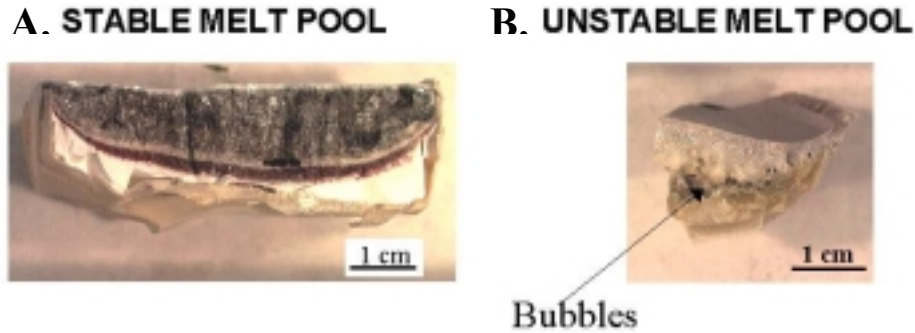
A. STABLE MELT POOL **B. UNSTABLE MELT POOL**

1 cm

1 cm

Bubbles

Fig. 9: Typical cross-sections of (A) stable melt pools and (B). unstable melt pool obtained during EB-PVD of new ceramic compositions

Upon identification of the melt pool stability of the new compositions, several microstructures were obtained (See Fig. 10). The microstructures were a function of the ceramic composition, substrate temperature, rotation rate, feed rate, total pressure, oxygen bleed rate, gun power and ingot quality. Some of the microstructures were significantly different from those typically observed for 8YSZ – dense coatings with few intercolumnar spaces, coatings with fine columns (1-2 mm) and coatings with thicker columns (5-10 mm). The microstructure and chemistry with best performance was identified after evaluation of cyclic furnace life.

6 µm

10 µm

10 µm

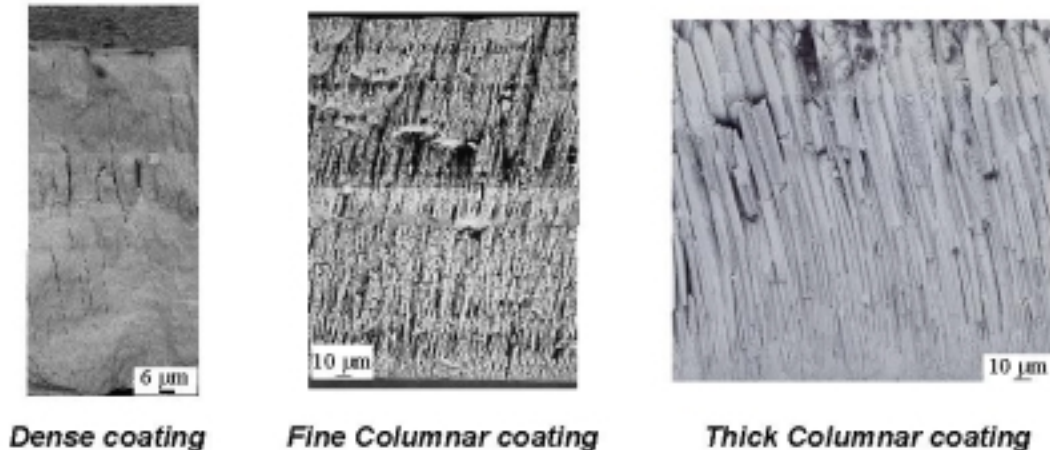**Dense coating**   **Fine Columnar coating**   **Thick Columnar coating**

Fig. 10: A variety of microstructures can be obtained by selection of an appropriate combination of deposition parameters

Fig. 11 shows the performance of new compositions after the initial deposition trials (Labels A through C). They have a much lower life compared to that of the baseline EB-PVD 8YSZ coatings. Based on the failure analysis results, the process parameters were modified in order to improve the cyclic furnace life. With the modifications, a different set of microstructures were obtained which results in some improvement of the properties, however, still poorer than the baseline 8YSZ coatings (labels C1 and C2). Further failure analysis resulted in additional changes in the deposition conditions. The final optimized conditions clearly show a significant improvement (labels B3 and A3) compared to the initial coatings that were deposited. The improvement is a result of new deposition conditions that were

identified specifically for each chemistry. The successful identification relies on a systematic correlation of the processing parameters to the microstructures. It is clear from this invetsigation that, selection of a compound alone is insufficient; it is critical to have the optimized processing parameters to identify the complete potential of the new compositions.
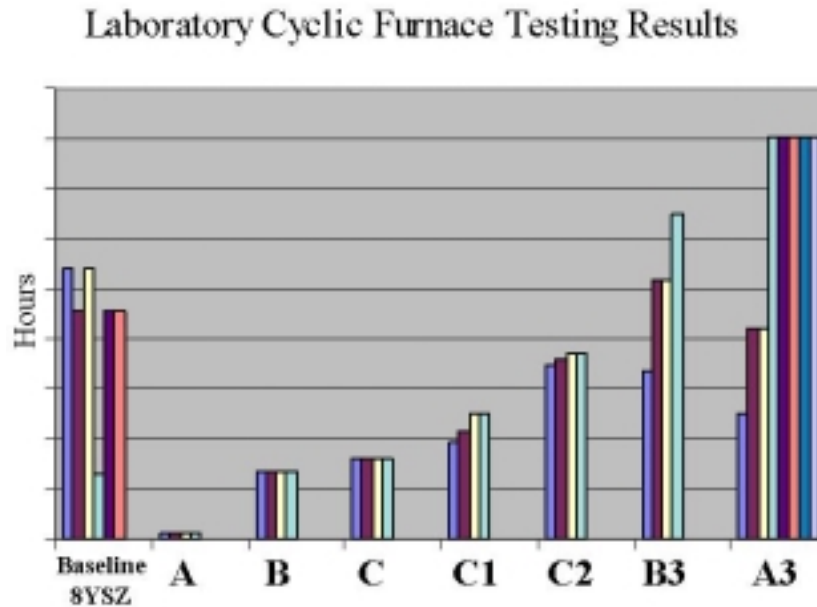

Fig. 11: Furnace cyclic life of new ceramicTBCs deposited by EB-PVD

The furnace life shows that these new coatings can be deposited on to a blade alloy with an improved life relative to that of 8YSZ. However, the isothermal test temperature are restricted by the bond coat and therefore do not fully address the sintering behavior of the coatings. Therefore, evaluation of samples annealed at ATS surface temperatures were needed to establish the sintering tendency of the coatings. Fig. 12A shows the typical PVD 8YSZ columns and the sintered columns after a long term exposure at ATS surface temperatures. The bridging of the columns lead to a reduction in strain tolerance and hence may reduce TBC life. By comparison, a new thermal barrier coating identified in
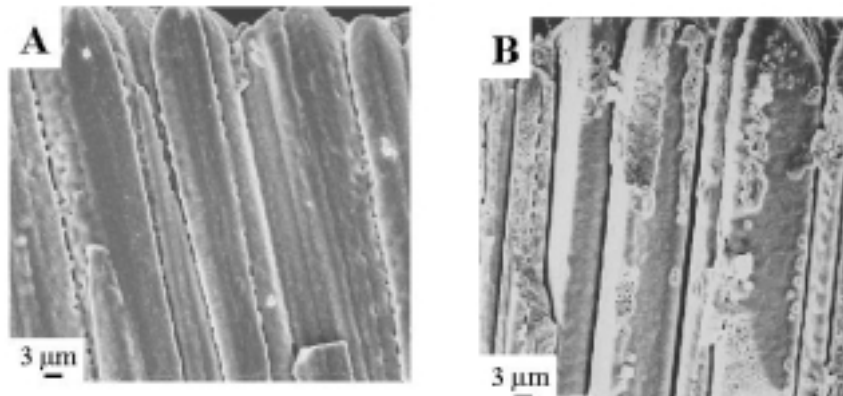

Fig. 12: Improvement of sintering resistance of (B) new TBC system over (A) current 8YSZ after long term exposure at expected ATS surface temperatures.

this program is shown in Fig. 12B. After the same duration of exposure at high temperature, the columns do not show any signs of sintering. This is a significant improvement over the baseline 8YSZ coatings. This new ceramic composition is sinter resistant and phase stable – the two key shortcomings of 8YSZ that needed to be overcome. Also, the cyclic furnace life of the new TBC shows that the requirements of minimum CTE mismatch is also satisfied. In addition, the new composition has a thermal conductivity lower than 8YSZ. The combination of good furnace life, sintering resistance and low thermal conductivity is exactly the combination desired for a potential TBC candidate for the ATS engine.

This is a significant achievement for a development program that was initiated only 3 years ago. To put this in perspective, this achievement should be compared to the development of 8YSZ coatings that took almost about 15-20 years of process optimization to achieve an acceptable thermal fatigue life. The new TBC system, with the best performing bond coat and TBC, identified above, are clearly the candidates for the future engines. However, additional work remains to evaluate the TBC system in an ATS temperature gradient at the Waltz Mill high heat flux rig facility. A successful test will be followed by a demonstration of the new system in an operational engine to test for performance of the coating system on IGT parts.

SUMMARY

Based on the results from the laboratory scale evalution, Siemens Westinghouse Power Corporation has successfully demonstrated a new TBC system for the ATS engine. New bond coat chemistries have been identified, that can be used with selected substrates and they clearly perform better than the baseline compositions. The new ceramic compositions identified as TBCs overcome the key shortcomings of the existing 8YSZ TBC – phase stability and sintering resistance. The combination of the best bond coat and a new ceramic TBC is expected to meet ATS requirements, thus achieving the objective that was set forth in the proposal. Also, several improvements in the EB-PVD process were identified that enable utilization of a wide range of thermal barrier coatings.

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