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Ceramic Thermal Barrier Coatings for Electric Utility Gas Turbine Engines

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CERAMIC THERMAL BARRIER COATINGS FOR ELECTRIC UTILITY GAS TURBINE ENGINES

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SUMMARY

Research and development into thermal barrier coatings for electric utility gas turbine engines is reviewed critically. The type of coating systems developed for aircraft applications are found to be preferred for clean fuel electric utility applications. These coating systems consist of a layer of plasma sprayed zirconia-yttria ceramic over a layer of MCrAlY bond coat. They are not recommended for use when molten salts are present. Efforts to understand coating degradation in "dirty" environments and to develop corrosion resistant thermal barrier coatings are discussed.

INTRODUCTION

There are considerable incentives to improve the efficiency and to lower the operating costs of heat engines used for electric power generation. Ceramic thermal barrier coatings will help to make these goals attainable. The coatings may be used to thermally insulate blades, vanes, and other components in electric utility gas turbine engines. They may also be used to insulate components in other alternative engines such as diesel engines. This paper will primarily emphasize the electric utility gas turbine applications. Developments in this area have been guided by the aircraft applications. However there are differences between the two types of gas turbine engines, for example electric utility engines tend to operate at lower gas and metal temperatures and may burn less pure fuels. Also the electric utility engines may be cycled less frequently and may operate for long periods of time between inspections. Diesel engines operate at even lower temperatures and lower heat fluxes. The temperature gradient across a coating is less when it is exposed to more moderate environments. As a result thicker coatings would be required to achieve adequate protection in a diesel engine.

The development of thermal barrier coatings for aircraft applications has been summarized in several recent review papers (refs. 1 to 3) and so those efforts will be only briefly discussed in this paper. The remainder of the paper will emphasize the performance of thermal barrier coatings in alternate applications, primarily for electric utility gas turbine engines.

THERMAL BARRIER COATINGS FOR AIRCRAFT GAS TURBINE APPLICATIONS

The current state-of-the-art coating developed for aircraft turbine blades and vanes is a two layer system consisting of an outer layer of ceramic and an inner layer of metallic bond coat (refs. 1 to 3) as shown in figure 1. The ceramic is ZrO_2 (6 to 8) percent Y_2O_3 (weight percent) and the bond coat is a MCrAlY alloy. Both layers are prepared by the plasma spray process (ref. 3). The plasma sprayed ceramic is highly porous and microcracked. This

structure imparts strain tolerance to the ceramic and also lowers its thermal conductivity because of decreased conduction. However the porosity is interconnected so it is permeable to the atmospheric gases or to liquids such as molten salt condensates. The plasma sprayed bond coat is rough and irregular which is necessary for the initial attachment of the ceramic but which may later play a role in coating failure as the bond coat oxidizes. The bond coat in figure 1 is quite dense because it has been sprayed in a reduced pressure chamber. Greater amounts of porosity are observed when bond coats are sprayed in an atmospheric pressure environment.

Current evidence indicates that correctly prepared thermal barrier coatings are very tolerant to thermal stresses. However life is severely degraded by environmental effects such as bond coat oxidation.

POTENTIAL BENEFITS AND CONCERNS

The benefits associated with using thermal barrier coatings in electric utility gas turbine engines have been analyzed by Amos (ref. 4), Carlson and Stoner (ref. 5), Nainiger (ref. 6), Vogan and Stetson (ref. 7), and Andersson et al. (ref. 8). Clark, Nainiger, and Hyland (ref. 9) have critically reviewed the studies of Amos and of Carlson and Stoner. These studies show that thermal barrier coatings effectively insulate metallic components, and this allows cooling schemes to be simplified and cooling airflows to be reduced. This in turn allows increased gas temperature and/or lowered metal temperatures. The result is decreased cost of electricity. Clark, Nainiger, and Hyland report that increasing gas temperatures to increase efficiency results in much greater savings than those obtained by reducing metal temperatures or reducing cooling airflows.

Figure 2 from reference 5 illustrates the temperature reductions obtained by applying a 0.038 cm ceramic thermal barrier coating to the first stage vanes in a Pratt and Whitney electric utility engine. The figure shows the cooling airflows required to maintain a maximum metal temperature of 815 or 870 °C as a function of rotor inlet temperature. Curves are plotted for both coated and uncoated blades. The uncoated blade employs transpiration cooling of the leading edge while a simpler impingement cooling scheme is used for the coated blade. The design maximum metal temperature was 870° at an inlet temperature of 1180 °C and a cooling requirement of 3.1 percent of the total airflow. The coated blade could be cooled to a metal temperature of 870 °C with only 1.3 percent of total airflow or to 815 °C with a 2.0 percent airflow. A significant increase in rotor inlet temperature of 50 °C required only 1.6 percent of total flow to achieve 870° maximum metal temperature.

The benefits from using thermal barrier coatings in diesel engines are analogous to the benefits from other engines. Diesel engines range in size from a few horsepower to about 50 000 hp (37 0000 KW) with the larger ones in use for ship propulsion or electric power generation (ref. 10). Components which may benefit from the application of thermal barrier coatings include exhaust valves, piston liners, and cylinder heads (ref. 11). Heat fluxes and maximum metal temperatures in diesel engines tend to be much lower than those in gas turbine engines. Also, metallic components are typically lower temperature materials such as iron or aluminum based alloys. Relatively thick ceramic coatings are generally required for such applications and some method of strain accommodation at the interface may be required. Thermal barrier

coatings may play an especially important role in the adiabatic diesel engine (ref. 12). According to this concept cooling water is removed and the engine is allowed to run hotter to improve efficiency. Improvements of up to 6 percent have been calculated for adiabatic diesel engine designs employing 0.15 cm thick zirconia-yttria thermal barrier coatings (ref. 13).

An additional approach to lowering the costs of operating electric utility or other alternative gas turbine or diesel engines is to burn "dirty" or "heavy" fuel. Clark, Nainiger, and Hyland (ref. 9) have indicated that the savings from burning dirty fuels could potentially exceed those obtainable from improving the efficiency. However, gas path components may be subjected to significant corrosion from the molten salts which may condense. Thus the performance of ceramic coatings in dirty environments becomes an issue. Salt condensates are a comparatively minor problem in aircraft gas turbine engines. This is because aircraft fuels are highly refined and the only major contaminant is sulfur. Although, under certain conditions this sulfur can react with ingested salts to form condensates such as sodium sulfate. Salt ingestion may result for example from operating at low altitude near a sea coast.

Fuels for alternate gas turbine engines may contain higher levels of sulfur plus additional contaminants such as sodium, vanadium, and phosphorous. A typical "clean" fuel for alternate gas turbine applications is "gas turbine no. 2." This fuel contains higher sulfur levels than the aircraft fuels plus minor amounts of metal-ion impurities. Since the levels of sulfur are significant there is an increased potential for forming corrosive salts from ingested aerosols such as from operation near a sea coast or on board a ship. This problem is however reduced by filtering the intake air. The contaminants present in the dirty fuel may react to form salt condensates. An example of an especially dirty fuel is "residual" fuel. This fuel contains increased sulfur plus significant metallic impurities such as sodium, potassium, vanadium, phosphorous, and lead. Magnesium is usually added to tie up the vanadium. Possible condensates from residual fuel include sodium sulfate, vanadium sulfate, vanadium pentoxide, magnesium vanadate, and phosphorous pentoxide.

Molten salt deposits accelerate coating failure by a mechanism involving deposition onto the surface and wicking into the pores and microcracks of the coating (refs. 14 to 20). The presence of condensates in the pores and crack tips severely degrades the strain tolerance of the coating and leads to premature failure. In cases where the salt reacts chemically with the ceramic, failure may be accelerated even further. Molten salts will deposit on a coating if the surface temperature is below the thermodynamic dew point of the condensate and above its melting point. The salt will only penetrate into regions of the coating which are above the melting point. Figure 3 illustrates this concept. Case A in the figure is the most damaging because salts may penetrate throughout the entire coating. Failure is expected near the interface where stresses are highest. In case B the condensate does not penetrate entirely to the interface and failure is expected closer to the surface. Case C is not generally harmful to the coating since the deposit is solid. A thick solid deposit may cause other problems however such as cooling hole plugging or increased aerodynamic drag. In case D no deposits would form on the coating at that location. However deposits may be possible at a cooler location on the component. These observations were confirmed in general (ref. 15) based on an analysis of experiments reported by Hodge et al. (ref. 21). Evidence supporting case D was first reported by Dapkunas (ref. 22).

THE PERFORMANCE OF THERMAL BARRIER COATINGS IN ELECTRIC UTILITY AND OTHER ALTERNATE APPLICATIONS

Behavior of Current Thermal Barrier Coatings

The current optimum thermal barrier coating system developed for aircraft gas turbine engines consists of a layer of porous, plasma sprayed zirconia - 6 to 8 percent yttria applied over a layer of low pressure plasma sprayed MCrAlY (ref. 3). This coating system was designed for use in a high temperature, high heat flux, clean, and oxidizing environment.

Alternative applications currently tend to involve lower temperatures and lower heat fluxes. The current state-of-the-art aircraft type of coating system can be expected to perform well in alternate applications where clean fuel is being fired (refs. 8, 18 to 20, 23 and 24). The coating systems described in the above studies have differed from the aircraft coatings only to the extent that the bond coats were air plasma sprayed rather than low pressure plasma sprayed. The lower temperatures encountered in current electric utility engines may allow the use of air plasma sprayed bond coats. However, since very long lives will be required, low pressure plasma sprayed bond coating still may be preferred.

The aircraft type of coating cannot be recommended for all applications. For example tests have shown that the current system performs poorly when it is exposed to dirty fuels (refs. 14, 17 to 21, 25 to 34). The tests employed in the above studies included crucible tests, furnace test of specimens sprayed with salt, salt-doped burner rig tests, and to a limited extent, engine tests. An example of a specimen which has failed after burner rig exposure to sodium and vanadium salts is shown in figure 3 from reference 21.

As discussed above, salt condensates may promote failure by a combination of mechanical and chemical processes. Sodium sulfate is the most important condensate encountered in aircraft applications and it is an important condensate for alternate applications. This salt does not react chemically with zirconia-yttria (refs. 14, 26 and 35) except under conditions of very high SO_3 partial pressure (ref. 36). Therefore if conditions are such that only small amounts of sodium sulfate are expected then the aircraft type of thermal barrier coating is recommended. If heavy deposits of sodium sulfate are expected then this coating cannot be recommended since the ceramic will quickly fail by a mechanical mechanism.

The condensates which cause the most concern in dirty fuels are those containing vanadium. Vanadium salts react chemically with the yttria in zirconia-yttria coatings. This reaction destabilizes the coating to form a significant amount of the monoclinic phase. Large amounts of this phase are undesirable because of the volume expansion associated with its transformation to a low-yttrium tetragonal phase at high temperatures. As a result ZrO_2 (6 to 8) percent Y_2O_3 thermal barrier coatings cannot be recommended when fuels containing vanadium are present (refs. 7, 16 to 21, 23, 26, 28 and 35). In addition to reactivity, vanadium salts tend to have low melting points. Magnesium is usually added to high vanadium fuels so that a solid magnesium vanadate may form. However magnesium additives do not appear to prevent attack of thermal barrier coatings by vanadium (refs. 18 to 20).

Finally, it should be noted that a small amount of ceramic generally remains attached to the bond coat after spalling and that this layer appears to protect the underlying bond coat and substrate from corrosion (refs. 19, 20 and 34).

The Performance of Other Zirconia-Based Thermal Barrier Coatings

Numerous variations to the aircraft standard ZrO_2 -(6 to 8) percent Y_2O_3 thermal barrier coating system have been evaluated in dirty fuel combustion. The variations have included altering the level of yttria, replacement of yttria by other stabilizers, controlling surface density (through plasma spray processing, infiltration, laser glazing, or sputtering), or interface treatments.

Studies where the percentage of yttria was varied have generally concluded that the 6 to 8 percent level is optimum in dirty fuels just as it is in clean fuels (refs. 18 to 21 and 34). In one study the high yttria compositions survived longer in the presence of vanadium condensates (refs. 16 and 17). Higher yttria levels may help to postpone the formation of monoclinic zirconia as the vanadium attacks the yttria. However the mechanical performance of the 6 to 8 percent yttria compositions is so superior to that of higher yttria compositions that any benefits associated with increasing the yttria level appear to be minimal at best.

Magnesia-stabilized zirconia has been evaluated in dirty fuels by a number of investigations. Its performance has generally been unsatisfactory (refs. 7, 18 to 20 and 31). The MgO stabilizer appears to be quite reactive, even to the sulfur in the fuel and the coating is readily destabilized to monoclinic zirconia.

Ceria stabilized zirconia has shown promise for high vanadium fuels (refs. 8 and 37). This is because the ceria does not react with sodium vanadate. More work is required examine the durability of thermal barrier coatings formed from zirconia-ceria.

One approach towards limiting the damage done by molten salt condensates is to seal the surface of the porous ceramic layer. Laser glazing is one promising approach (refs. 38 and 39). The laser melted region of the coating is 100 percent dense, however these dense regions are enclosed within a mudflat crack network. Figure 5 from Zaplatynsky (ref. 38) shows a cross-sectional photomicrograph of a laser glazed specimen. Both the dense outer region of the ceramic and a portion of the crack network are visible in this photograph. Laser glazed coatings survive longer in the presence of salt condensates than unglazed coatings. This is true even though the mudflat crack network allows access to the interior of the coating. Rice (ref. 40) has experimented with infiltrating the surface of the coating with zirconia sols or other materials prior to laser glazing.

Andersson et al. (ref. 8) have reported some success with various methods of surface sealing. These have included infiltration by a glass, spraying of a dense coat of zirconia-yttria, and the application of a layer of sputtered

platinum or platinum-containing metallic alloys. Clarke (ref. 4) had previously reported improvements from platinum sealing layers. However platinum volatility may be a problem.

The use of a graded region at the interface or a fibrous pad for strain isolation has a temperature limitation. That is, they may only be used if interface temperatures remain below about 800 °C (refs. 8, 18 to 20). For lower temperature diesel applications these approaches may be practical.

The Performance of Alternate Ceramics

Many alternatives to zirconia-based thermal barrier coatings have been evaluated (refs. 7, 18 to 21, 23 and 24). Two promising ceramic materials have come out of this work. They are calcium silicate (refs. 18 to 21, and 34) and calcium titanate (refs. 7 and 23). Another promising material is a metal/ceramic mixture MgO/NiCrAlY (ref. 21).

Calcium silicate based thermal barrier coatings survived longer in dirty environments than zirconia-yttria coatings. There is however concern over a reaction with sulfur dioxides to produce surface layers of calcium sulfate. This sulfation reaction is protective in the sense that the reaction rate continuously decreases as the reaction proceeds (ref. 42). However Bratton and coworkers (ref. 19) reported that the calcium sulfate formed in their experiments was soft and therefore susceptible to erosive wear.

Erosion resistance was also noted as a concern for calcium titanate. However it was more tolerant to dirty fuels than zirconia-yttria. As a result, Vogan and coworkers (refs. 8 and 28) recommended calcium titanate for low velocity, dirty applications.

CONCLUSIONS

Thermal barrier coatings help to improve the operating efficiency of alternate gas turbine engines and diesel engines. For clean fuel applications and applications involving low levels of sodium sulfate condensates the type of thermal barrier coatings developed for aircraft applications are recommended. This optimum system is a plasma sprayed ZrO₂- (6 to 8) percent Y₂O₃ ceramic applied over a MCrAlY bond coat. For applications involving low temperatures and low heat fluxes - such as a diesel engine - thick coatings with interfacial strain accommodation may be required. Coatings for diesel engines are at an early stage of development, and the technology of plasma sprayed aircraft engine abradable seals will help guide this work.

Thermal barrier coatings must be avoided when residual fuels are fired. For less dirty fuels several areas deserve further attention. These include surface sealing such as laser glazing and possibly alternate materials such as zirconia-ceria, calcium silicate, or calcium titanate.

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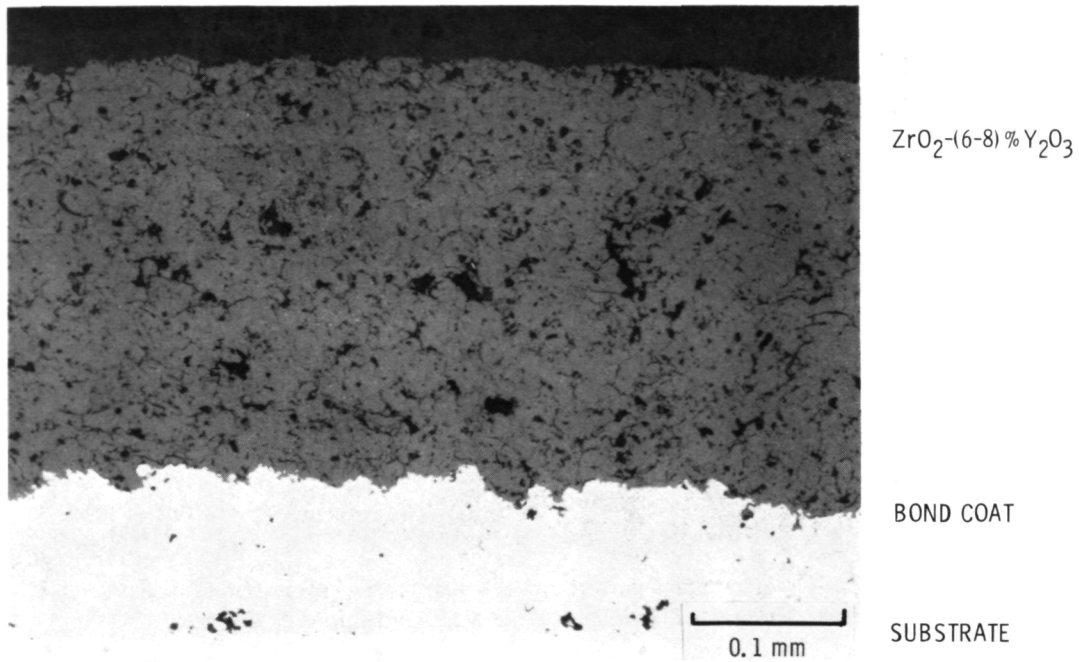


Figure 1. - State-of-the art thermal barrier coating system developed for aircraft applications.

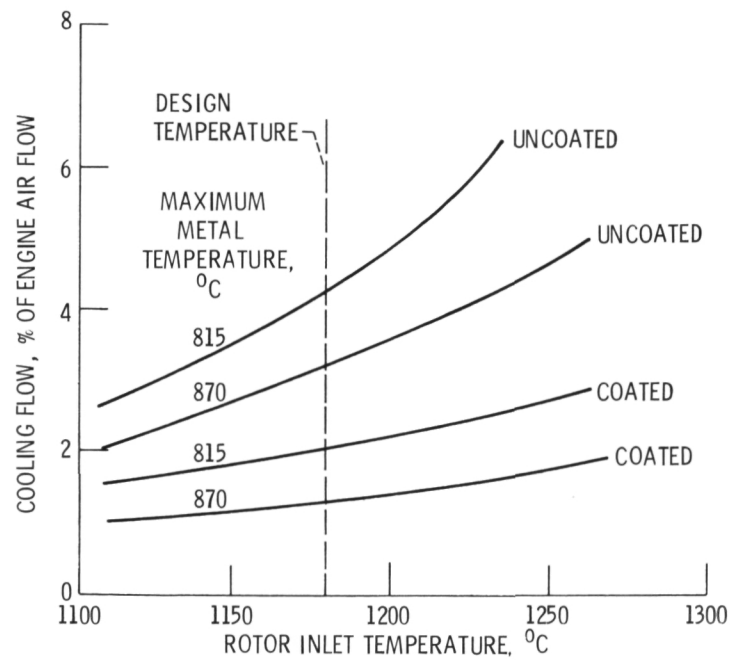
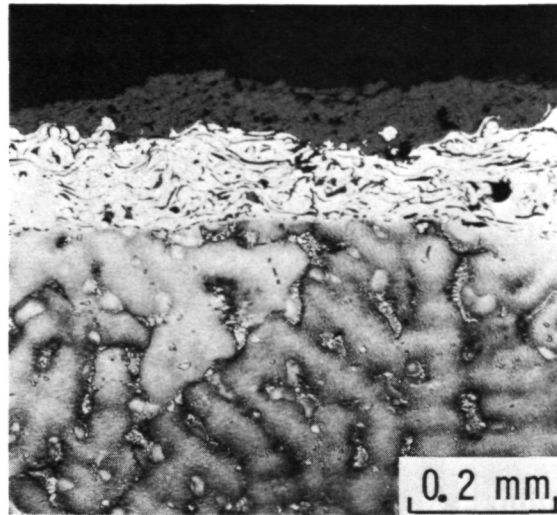


Figure 2. - Calculated benefits of applying a thermal barrier coating to a first stage turbine blade in an electric utility gas turbine engine.⁵



THERMAL
BARRIER
BOND
COATING

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Figure 3. - Cross sectional photomicrograph of a thermal barrier coating which spalled upon exposure to sodium-and vanadium-containing condensates²¹.

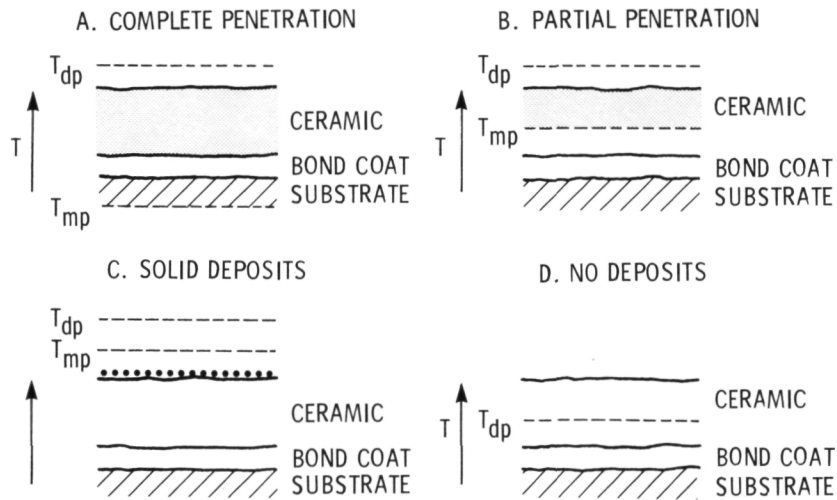


Figure 4. - Regions where molten salt condensates may penetrate a thermal barrier coating as a function of condensate melting points and dew points. 15

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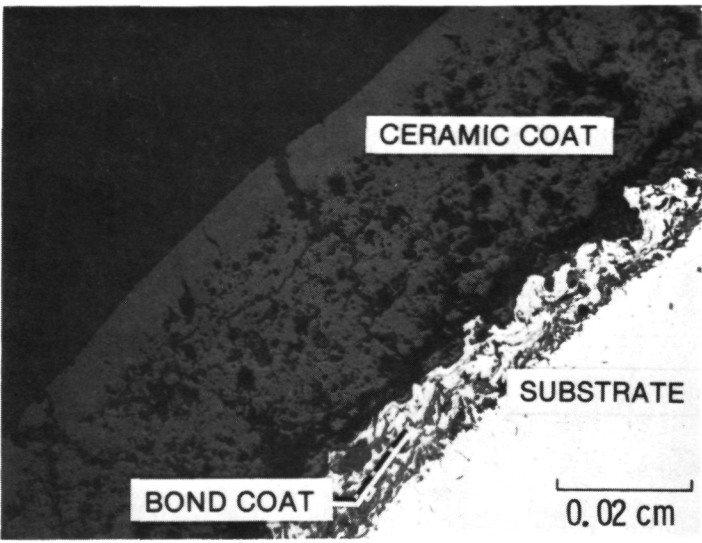


Figure 5. - Cross section photomicrographs of a laser glazed thermal barrier coating³⁸.

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