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Thermal Barrier Coatings for Aircraft Engines: History and Directions

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Thin thermal barrier coatings (TBCs) for protecting aircraft turbine section airfoils are examined. The discussion focuses on those advances that led first to TBC use for component life extension and more recently as an integral part of airfoil design. Development has been driven by laboratory rig and furnace testing, corroborated by engine testing and engine field experience. The technology has also been supported by performance modeling to demonstrate benefits and life modeling for mission analysis. Factors that have led to the selection of current state-of-the-art plasma-sprayed and physical-vapor-deposited zirconia-yttria/MCrAlX TBCs are emphasized, as are observations fundamentally related to their behavior. Current directions in research into TBCs and recent progress at NASA are also noted.

Keywords historical review, thermal barrier coatings, zirconia

1. Introduction

THERMAL BARRIER COATINGS (TBCs) were first successfully tested in the turbine section of a research gas turbine engine in the mid-1970s. By the early 1980s they had entered revenue service on the vane platforms of aircraft gas turbine engines, and today they are flying in revenue service on vane and blade surfaces. Advanced engines, for the foreseeable future, may be expected to rely even more heavily on these coatings (Ref 1).

Two processes are used to apply today's TBCs. Plasma-sprayed coatings were brought into service first and currently remain in service. By the 1990s, a second type of TBC deposition process—physical vapor deposition (PVD)—was successfully brought into commercial service. The success of both types of coatings in commercial aircraft gas turbine applications, especially the PVD coatings, has played a pivotal role in the acceptance of this technology. However, with this acceptance comes ever-increasing demands on these coatings to perform for longer hot times under increasingly severe conditions. This paper will focus primarily on the critical steps that led to the relatively rapid advancement of this technology.

2. Early Ceramic Coatings for Aerospace Applications

The earliest ceramic coatings for aerospace applications were frit enamels. The first of these frit coatings were developed by the National Advisory Committee for Aeronautics (NACA) and the National Bureau of Standards (NBS) (Ref 2, 3). Frit enamels were used in aircraft engines throughout the 1950s (Ref 4). Later, flame-sprayed ceramic coatings were developed (Ref 5-10). Of the various early ceramic materials that were evaluated for thermal barrier applications, alumina and zirconia-calcia were the most successful. The bond coat material for these early applications, if one was used at all, was typically nichrome or molybdenum for nonoxidizing environments. Early applications included the protection of sheet metal in jet engines and in rocket engine thrust chambers. The most visible coatings during this period were the flame-sprayed zirconia-calcia coatings on the regeneratively cooled XLR99 thrust chambers for the X-15 experimental rocket planes (Ref 8, 9). A portion of this coating is visible in Fig. 1. With the subsequent development of plasma spray processing—which evolved from research into low-thrust plasma arc engines for spacecraft and from plasma arc test facilities developed for reentry simulation (Ref 11)—the utility of using the very-high-temperature plasmas for spraying ceramics was soon recognized (Ref 7, 10, 12, 13). In 1970, plasma-sprayed TBCs began to be used on hot-section transition ducts and other hot-section sheet metal components in commercial gas turbine engines (Ref 14).

Alumina and zirconia-calcia did not prove to be viable materials for the more advanced thermal barrier applications. In the case of alumina, this is primarily because its thermal conductivity is relatively high (Ref 15). Also, alumina forms nonequilibrium phases, which are variously described as gamma, eta, or delta; these nonequilibrium phases shrink when they convert to the equilibrium alpha phase upon high-temperature exposure. This shrinkage and the associated cracking would have a detrimental effect on coating life. The phase transformation to alpha

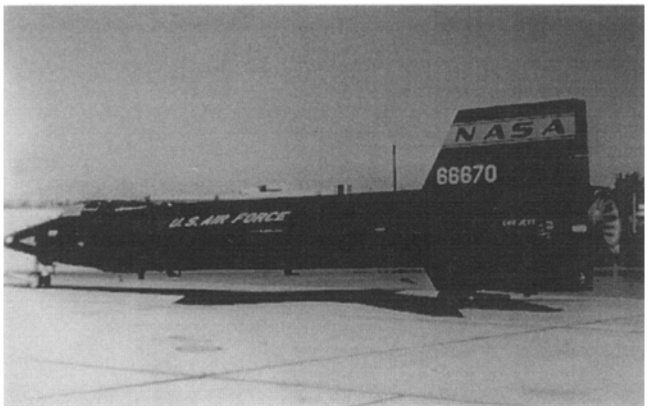

Fig. 1 Zirconia-calcia/NiCr TBC visible on the exhaust nozzle of the X-15 manned rocket plane. This is believed to be the first use of TBCs in manned flight.

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alumina appears to become a factor above about 1100 °C (2010 °F) (Ref 5, 13, 17, 18). The problem with zirconia-calcia and zirconia-magnesia is related to "destabilization" from the cubic fluorite (F-ZrO_2) phase that is observed in the as-sprayed material to the monoclinic (M-ZrO_2) phase. Zirconia-base ceramics containing excessive amounts of this monoclinic phase are not usable as structural materials due to the volume change associated with a martensitic phase transformation on cooling from the higher-temperature tetragonal phase to the low-temperature monoclinic phase. Although the calcia or magnesia is added to zirconia with the intent of extending the high-temperature cubic phase field down to room temperature, it is now known that the cubic phases are actually not stable below about 1140 °C (2085 °F) for zirconia-calcia and 1400 °C (2550 °F) for zirconia-magnesia (Ref 19). Toriz et al. (Ref 20) gave 950 °C (1740 °F) as the practical upper-use temperature for zirconia-magnesia in gas turbine applications, and a similar upper-use temperature may apply for zirconia-calcia.

3. Current State of the Art

3.1 *Plasma-Sprayed TBC Development*

The current era in TBCs began in the mid-1970s with the development at the National Aeronautics and Space Administration's NASA Lewis Research Center of a two-layer TBC consisting of a porous atmospheric-pressure plasma-sprayed (APPS) zirconia-yttria (ZrO_2-Y_2O_3) ceramic over a plasma-sprayed NiCrAlY bond coat (Ref 21-23) and with the successful testing of this coating on the turbine blades in a research gas turbine engine (Ref 24). Figure 2 shows the coated J-75 turbine blades after testing.

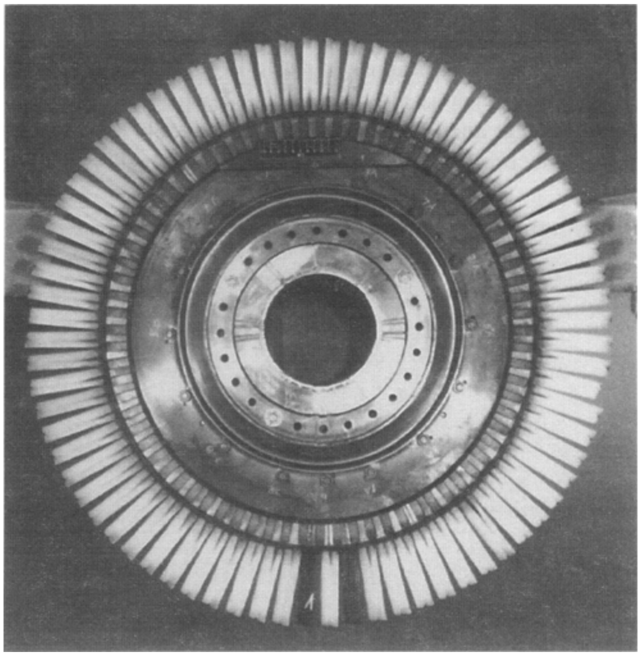

Fig. 2 ZrO_2-12Y_2O_3/NiCrAlY coated turbine J-75 blades after testing. This test marked the beginning of the modern era of TBCs.

There were three keys to the success of this new coating system. First, yttria was used to stabilize the zirconia. Second, the bond coat was an oxidation-resistant NiCrAlY alloy of the type that was then being developed for metallic overlay coatings. Finally, this new approach employed only two layers—the ceramic and the bond coat—with no intermediate layer for grading thermal expansion mismatch. Although attempts were made to include an intermediate region of mixed metal and ceramic to mitigate thermal expansion mismatch stresses, it was soon discovered that this graded expansion approach was inappropriate for temperatures high enough for oxidation to occur in the graded region (Ref 25). Later work placed an upper limit of about 800 °C (1470 °F) for the maximum temperature to which the graded region may be exposed (Ref 26, 27). Union Carbide was another early developer of zirconia-yttria/MCrAlY TBCs (Ref 28).

The initial zirconia-yttria TBCs contained from 12 to 20% of yttria, which was added to fully stabilize the cubic phase. Later, Stecura showed that better performance could be achieved by lowering the yttria level to between 6 and 8% (Ref 29); a portion of these data is shown in Fig. 3. The TBC literature, in general, now supports the view that ZrO_2/6-8Y_2O_3 is superior to ZrO_2/12-20Y_2O_3 for advanced gas turbine applications and that zirconia-yttria TBCs are in turn superior to zirconia-magnesia and zirconia-calcia (Ref 20, 26, 27, 30, 31). It also has been shown that residual stress control via substrate cooling is required for optimum ceramic coating life (Ref 32). In addition, there is general agreement that low-pressure plasma-sprayed (LPPS) bond coats (Ref 33, 34) (or shrouded bond coats, Ref 35) are superior to APPS bond coats. A cross-sectional micrograph of the current optimum zirconia-yttria/MCrAlX TBC is shown in Fig. 4.

3.2 *Physical Vapor Deposited TBC Development*

Electron beam/physical vapor deposited (EB-PVD) zirconia-yttria coatings were first developed at Pratt & Whitney in the late 1970s (Ref 32, 36-38). Other early players were Airco-Temescal (Ref 39) and Chromalloy (Ref 40). The burner rig lives of the early PVD coatings were reported to have been far better than those of the early dense plasma-sprayed, fully stabi-

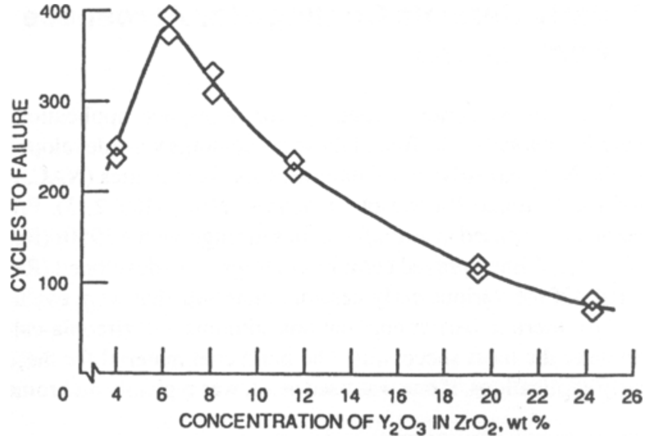

Fig. 3 Laboratory test results showing that the optimum TBC composition occurs in the ZrO_2/6-8Y_2O_3 range

lized zirconia-yttria coatings and comparable to the lives achieved for optimized plasma-sprayed, fully stabilized zirconia-yttria (Ref 32). By the early 1980s, lives of the best PVD zirconia-yttria coatings were exceeding the lives of the modern partially stabilized zirconia-yttria coatings (Ref 34, 36). However, early PVD coatings suffered from poor reproduciblity, which was attributed to small differences in the coating microstructure caused by subtle differences in processing parameters (Ref 36). By mid-decade the reproducibility problems had been solved (Ref 37, 38, 41) and laboratory tests and, more importantly, engine tests indicated that this type of coating was well suited for protecting airfoils in subsonic engines. Among the advances were the replacement of the earlier ZrO_2-$20Y_2O_3$ compositions with $ZrO_2/6$-$8Y_2O_3$. Also, the earlier work tended to be limited to PVD MCrAlX bond coats, whereas currently it is recognized that PVD zirconia-yttria coatings may be applied to LPPS MCrAlX bond coats as well as to aluminide coatings.

The columnar microstructure characteristic of PVD coatings (Fig. 5) imparts excellent strain tolerance to the material. As a result, PVD coatings are favored for more demanding applications that involve frequent cycling. Other characteristics of PVD ceramic coatings are excellent adherence to smooth surfaces, a relatively smooth surface finish, and the ability not to clog fine cooling holes when deposited. However, PVD TBCs do not insulate as well as APPS TBCs and may be less durable in missions requiring very infrequent cycling, as shown by their rather poor performance when subjected to relatively rapid cooling after 10 to 20 h cycling. (Ref 42).

4. Supporting Developments

The advances that have led to the acceptance of TBCs in gas turbine engines are not limited to materials optimization. Advances in life prediction modeling and performance benefit modeling have played key roles, as has TBC durability testing.

4.1 *Life Prediction*

In the mid-1970s, TBCs had successfully entered service in the turbine section of certain advanced gas turbine engines. While the early application was one of relatively low risk, it was recognized that the full potential of this technology could only be achieved if the coatings were placed in higher-risk locations. Establishment of an engine life prediction methodology was therefore needed for further advancement.

The development of life prediction methodologies consists generally of identification of critical failure mechanisms, stress/strain modeling, and the development of mathematical expressions that define life in terms of stress state and relevant failure criteria. To be useful, the model must be able to extrapolate the life of a given coating system beyond the experimental space achievable in the laboratory and must be extendable to engine service. Related efforts at NASA in the early 1980s consisted of research to understand the failure mechanisms (Ref 43), followed by the development of a prototype laboratory mathematical model (Ref 44, 45). The NASA model focused on thermal expansion mismatch stress between the ceramic and the bond coat/substrate (which is at a maximum after cooling to room temperature) and high-temperature oxidation of the bond coat. Although NASA was conducting stress/strain modeling at the time (Ref 46), modeled stresses were not coupled to the NASA life model; rather, cyclic stress was treated as an adjustable parameter. This model was applied to laboratory life data at NASA. It was extended by Pratt & Whitney and subcontractor Southwest Research Institute to engine modeling. This included the direct incorporation of modeled strain and replacement of oxidative weight gain by oxide scale thickness (Ref 47, 48). Later, this model was extended to PVD coatings (Ref 42).

Another model, developed by General Electric (Ref 49), employed time-dependent, nonlinear finite-element modeling of the stresses and strains present in the TBC system, followed by

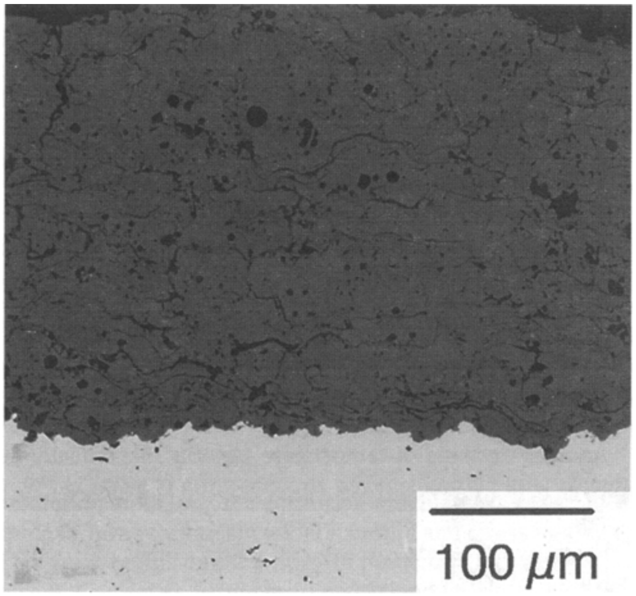

Fig. 4 Cross-sectional micrograph of a current state-of-the-art plasma-sprayed zirconia-yttria/MCrAlX TBC showing a porous and microcracked ceramic layer over a relatively dense metallic bond coat

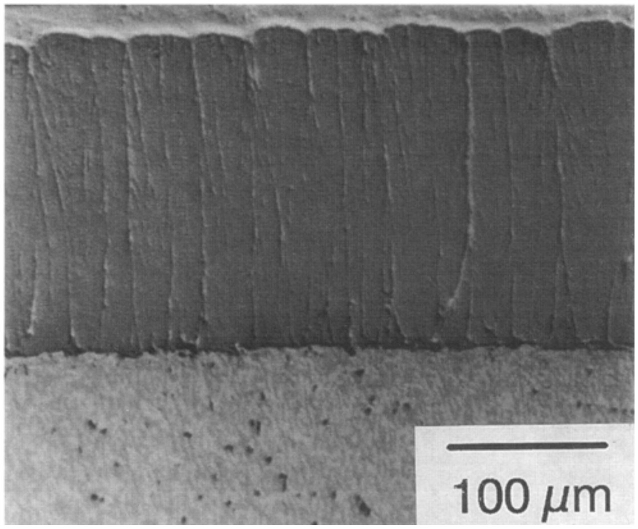

Fig. 5 Cross-sectional photomicrograph of a current state-of-the-art EB/PVD zirconia-yttria/MCrAlX TBC showing a columnar ceramic over a relatively dense bond coat

correlation of these stresses and strains with test lives. A third model, developed by Garrett Turbine Engine Company (Ref 50), involved estimated rate constants and scale factors for cycle length, oxidation life, zirconia time-at-temperature effects, and damage due to salt deposition.

4.2 *Performance Modeling*

The potential benefits provided by thermally insulating TBCs were recognized at the time of the NASA J-75 engine test (Ref 51). The benefits include considerable reduction in component temperatures and/or reduced coolant airflow requirements for a given turbine inlet temperature. Alternatively, the benefits could be taken in terms of higher allowable turbine inlet temperatures for given component temperatures and reduced coolant flows. At the same time, potential problem areas were identified; these included potential efficiency losses resulting from increased roughness and increased airfoil leading edge thickness. Performance analyses, such as that described previously and others (Ref 52-54), were important factors that helped to drive TBC development.

Although the details of these calculations may often be proprietary, the results of an early analysis were reported for a vane coated with 0.25 cm of plasma-sprayed zirconia-yttria. The benefits were expressed in terms of component temperature reductions of up to about 170 °C (300 °F), with component durability improvement of three to four times or reduced cooling airflows corresponding to a 1% specific fuel consumption savings (Ref 34, 37).

Another example of temperature benefits theoretically attainable with plasma-sprayed zirconia-yttria is given in Fig. 6 (Ref 53). Figure 6 gives coating surface, interface, and inner metal temperatures for both the pressure and suction sides of the airfoil as a function of ceramic layer thickness for a film-cooled turbine vane subjected to a very high hot-spot temperature of 2280 °C (4130 °F). For this calculation, the cooling airflow is sufficient to reduce the temperature of an uncoated blade to 1055 °C (1930 °F) on the suction side, with a similar value reached on the pressure side. The addition of just 0.0127 cm (0.005 in.) of ceramic, while maintaining the same high coolant flow, is expected to reduce the interface temperature to only about 870 °C (1600 °F). Metal temperatures are somewhat higher on the pressure side, but the reduction is still very significant. Thus, for this example, 0.0127 cm (0.005 in.) of coating has lowered the component surface (interface) temperature by about 190 °C (340 °F). Note, however, that the second 0.0127 cm (0.005 in.) of ceramic reduced the temperature less than an additional 100 °C (180 °F); that is, a decreasing benefit with increasing coating thickness is predicted.

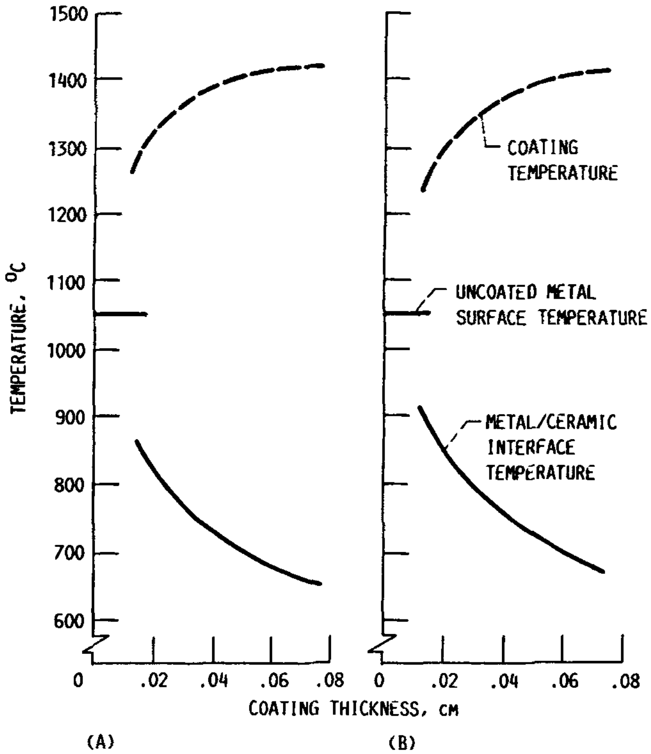

Fig. 6 Modeled temperatures for a film-cooled TBC-coated turbine blade. (a) Suction side. (b) Pressure side

Since there are coating durability and weight penalties associated with thicker coatings, turbine section ceramic coatings are typically limited to between 0.0127 and 0.0254 cm (0.005 and 0.010 in.). Another reason to limit the coating thickness is to limit the surface temperature of the ceramic. Generally, the interface temperature drop is accompanied by a comparable rise in the ceramic surface temperature. If temperatures rise too high, then sintering and phase transformations begin to occur. Phase transformations have been observed after 100 h at 1200 °C (2200 °F) (Ref 55).

4.3 *TBC Durability Testing*

Durability testing, defined as coating life under high-temperature cyclic exposure, has tended to guide TBC development. The assessment of durability has been much more important than independent measures of the various properties that affect durability (such as mechanical properties, environmental durability, and phase stability). This reliance on durability testing follows from the complexity of TBC failure mechanisms, which involve a complicated interplay of numerous high-temperature effects. In the bond coat, these effects include oxidation, thermal expansion, phase transformations, thermal fatigue, creep/stress relaxation, and bond coat/substrate interaction. In the ceramic layer, these effects include thickness, structure, chemistry, thermal expansion, phase stability, the effect of microcracking, thermal gradient, and tensile and creep strength. Between layers there are also complex issues involving thermal expansion and adhesion strength, as well as the interaction between these properties and bond coat oxidation.

Although an understanding of these effects is necessary for life prediction, they are not independently useful for ranking durability. Nor, generally, is stress modeling useful for ranking durability. Therefore, ranking usually is first carried out in laboratory furnaces or burner rigs (or other laboratory torch rigs). These two types of durability tests each have advantages and disadvantages. Furnace tests have several advantages over burner rig tests:

- They are generally low cost.
- Temperature can be measured accurately.

- Specimen weight gains can be monitored (if all surfaces are coated).
- Contaminants are less likely to be a problem.

Burner rig tests (Fig. 7) can be used to:

- Force hot spots, thereby avoiding edge effect failures
- Allow internal cooling
- Heat specimens relatively rapidly so that short-duration cycle durability representative of subsonic engine takeoff and climb can be investigated
- Expose specimens to relatively high gas velocity, which may be important when volatility is an issue
- Expose specimens to injected salt contaminants

The burner rig also has somewhat higher heating and cooling rates than the furnace, but they are significantly less than in the engine. Generally, the greatest problem in the burner rig involves difficulties in measuring temperature, as discussed in Ref 56 and 57.

5. Current Directions in TBC Research

It is now evident that, for the foreseeable future, aircraft turbine airfoils will be fabricated from air-cooled superalloys protected by TBCs (Ref 1). The potential of advanced ceramic and metallic composites is in the more distant future. Furthermore, even when these new materials come on line they are likely to require TBCs. Therefore, more demanding requirements will be placed on this technology, and there will be a continuing need to develop coatings with increased durability. The following research areas are being investigated at or sponsored by NASA Lewis Research Center.

5.1 *Enabling Propulsion Materials Program*

One of the more demanding future applications of TBCs will be to protect airfoils in the next generation of supersonic gas turbine engines. These engines will operate at peak temperatures for several hours per cycle. This contrasts with current subsonic engines, which operate at peak temperatures for several minutes per cycle (during takeoff and climb). NASA is currently actively pursuing research in this area through the Enabling Propulsion Materials program with prime contractors Pratt & Whitney and General Electric.

5.2 *TBCs for Alternative Substrates*

Many new applications of TBCs will involve adapting the coatings to the special requirements of new substrate materials. One example of such a material is the NiAl+Zr intermetallic alloy. This material is highly oxidation resistant and may not require a bond coat. In one study at NASA (Ref 58), it was shown that zirconia-yttria can be plasma sprayed onto smooth NiAl+Zr if the first mil (0.0025 cm) or so of the ceramic is applied by LPPS. This initial layer of LPPS zirconia-yttria is then followed by a layer of conventionally air-plasma sprayed (APS) ceramic. Later, unpublished work showed that the conventional APS ceramic could be applied to grit-blasted NiAl. Very long lives of more than 800 h at 1200 °C (2190 °F) were observed in furnace tests.

Another new class of substrates comprises silicon-base ceramics. Although these materials may be used only in the distant future in the turbine section of aircraft gas turbine engines, their use in certain land-based engines may be more near-term. Also, silicon-base ceramics may be used elsewhere in advanced gas turbine engines. It appears that in many applications these new ceramics will need thermal barrier and/or environmental protection coatings. Mullite-base coatings are being developed for silicon-base ceramics (Ref 59). Mullite is attractive because of an excellent coefficient of thermal expansion match between it and silicon carbide. However, it was discovered at NASA that plasma-sprayed mullite tends to deposit as an amorphous phase that converts to crystalline mullite, with shrinkage and cracking, when heated to above 1000 °C (1830 °F). This shrinkage even begins to slowly occur at about 600 °C (1110 °F). It was discovered that it is possible to deposit mullite in a stable crystalline form if the deposition is carried out above 1000 °C (1830 °F), as shown in Fig. 8. Although this work has been promising, a considerable amount of work needs to be done, including the development of multilayered ceramics tailored for specific requirements (Ref 60) and the development of better approaches for coating silicon-nitride-base ceramics.

5.3 *Second-Generation Life Prediction Modeling*

One important direction for future research involves life prediction modeling, the definition of which has grown to include failure mechanism understanding and stress modeling. This work builds on the prior life prediction work described earlier. Current experiments to understand failure mechanisms include an exploration of the role of time-dependent bond coat properties and the bond coat thermal expansion coefficient on TBC life (see the paper by W.J. Brindley in this issue). This work grew out of studies to understand why high-chromium bond coat

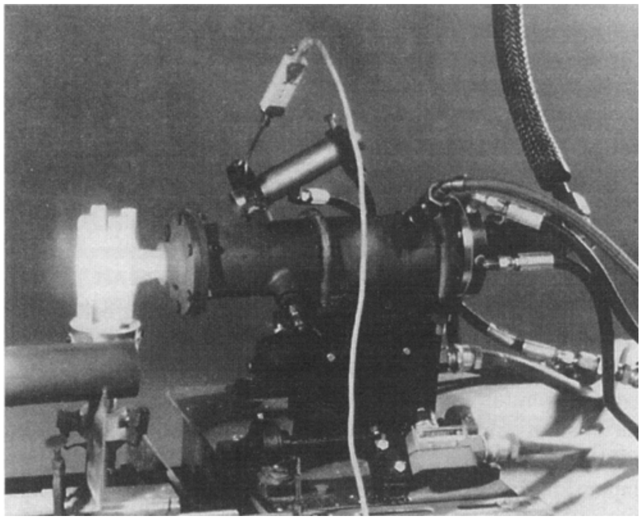

Fig. 7 Mach 0.3 burner rig test of four cylindrical, TBC-coated specimens in a rotating carousel

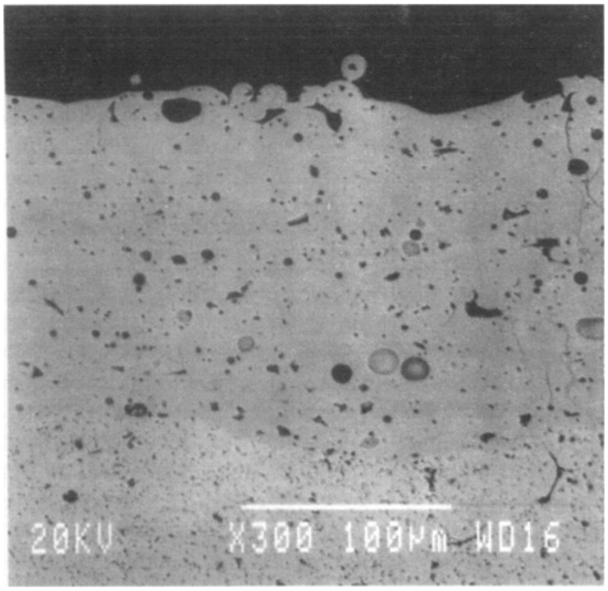

Fig. 8 Cross-sectional micrograph of plasma-sprayed mullite over silicon carbide

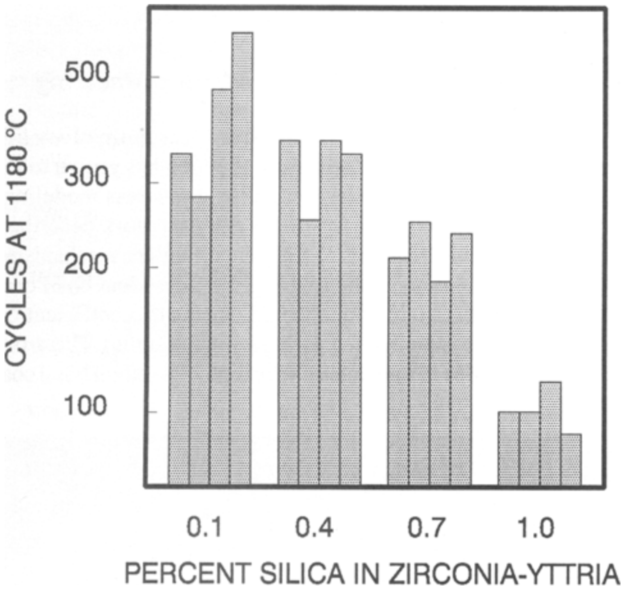

Fig. 9 Effect of silica level in sol-gel-processed ZrO_2-$8Y_2O_3$ on the burner rig life of TBC-coated specimens.

compositions such as Ni-35Cr-6Al-1Y perform better than lower-chromium, higher-aluminum bond coats such as Ni-18Cr-12Al-0.3Y (Ref 61, 62). This is true even though the lower-chromium, higher-aluminum compositions would be superior as an oxidation-resistant overlay coating. This surprising behavior was found to be related to a comparatively low thermal expansion for the high-chromium bond coat at lower temperatures (Ref 63, 64), combined with greater stress relaxation for the higher-chromium bond coat at higher temperatures. Initial approximate stress modeling (see Brindley) and ongoing finite-element modeling are quantifying these effects. Although this analysis suggests that bond coat stress relaxation can be beneficial, an alternative approach involving high-strength bond coats has also been advocated (Ref 65).

5.4 *Alternative Compositions*

No clearly superior successor to yttria as a stabilizer for zirconia has been developed over the past two decades. One promising material is zirconia-ytterbia, which has performed well in furnace tests. The optimum composition tested was 12% (by weight) or 4 mol% (Ref 66). This composition appears to be in the same position relative to the equilibrium phase diagram (Ref 67) as zirconia-yttria in the 6 to 8% range. In more recent unpublished work, Yb_2O_3, Er_2O_3, and Dy_2O_3 were evaluated in furnace tests. All three materials performed well, but none was clearly superior to a reference ZrO_2-$8Y_2O_3$ coating.

In contrast, the level of silica in sol-gel-prepared ZrO_2-$8Y_2O_3$ (Fig. 9) was found to greatly influence performance. Recent work at NASA has shown a strong correlation between TBC durability and the level of silica impurity in plasma-sprayed zirconia-yttria coatings produced from sol-gel-processed powders. Increasing the silica level from 0.1 to 1.0% caused a fivefold decrease in burner rig life (Ref 68), apparently due to increased stress relaxation in the higher-silica coating. This work is continuing. The effect of silica on the sintering of the plasma-sprayed material is being evaluated by dilatometry, and the durability of TBCs prepared from sintered and crushed powders is being determined.

Recently at NASA hafnia-yttria-base coatings have been evaluated (Ref 69). Hafnia is an element that is chemically similar to zirconia, and plasma-sprayed HfO_2-Y_2O_3 TBCs have performed well in laboratory tests. However, the best-performing hafnia-base coatings appear to be no better than zirconia-base coatings. Interestingly, the best hafnia-yttria coatings contain high levels of yttria stabilizer, up to and including 27%, and are fully cubic. Therefore, they may be more stable at very high surface temperatures that would cause destabilization of the optimum, partially stabilized zirconia-yttria compositions. However, this has not been demonstrated experimentally.

Metal/ceramic composite bond coats are also being considered for their ability to lower the thermal expansion mismatch between the ceramic and metal layers (Ref 70). This is similar to the intermediate layers produced in graded coatings. However, a major difference is that these composite coatings are produced by LPPS. Results in this area have not been definitive, and further work is under way.

5.5 *Programs Sponsored by Other Organizations*

An important area of research at NASA involves thick coatings for diesel engines. This effort, sponsored by the Army Research Laboratory, is primarily designed to develop laboratory tests that can be used to screen new concepts in diesel TBCs. Also, U.S. Department of Energy (DOE) funding has been used to sponsor a Cooperative Agreement with Vanderbilt University to evaluate the mechanical high-cycle fatigue behavior of thick TBCs and to develop tests to measure and understand the role of the tensile and shear strengths of these coatings.

NASA also expects to become more involved in the near future in the area of TBCs for electric utility engines. This is in response to new DOE programs and represents a return to an area in which NASA was once active. However, unlike past efforts, the new efforts will not emphasize fuels with high impurity levels.

6. Concluding Remarks

In summary, TBCs have evolved from the laboratory to low-risk turbine section applications and then on to an integral part of engine design. These coatings applied to advanced, air-cooled, superalloy components will be the materials systems of choice in advanced engines for the foreseeable future. Even as nonsuperalloy components gradually come into service, these new materials will still require the protection of a TBC.

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