High-Temperature Resistant Coatings for Strategic Aero-space Applications

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ABSTRACT

The aerospace components operating in hot sections of aero-engines and combustors experience extreme environments. Typically, the components are subjected to high service temperatures exceeding 1100°C and oxidizing conditions. Protective coatings are essential for preventing oxidation-induced dimensional degradation of the components and enhancing their high temperature capability as well as durability. Defence Metallurgical Research Laboratory (DMRL) has developed a variety of metallic and ceramic Thermal Barrier Coating (TBC) systems for Ni-base superalloys, and refractory Nb-alloys for strategic aerospace applications involving ultra-high temperatures and high flow velocities. These coatings have demonstrated significant effectiveness against thermal degradation at temperatures as high as 2000 °C during oxidation in static air as well as in dynamic conditions involving high flow velocities (Mach > 2). The present article provides an overview of the advanced oxidation resistant and thermal barrier coatings developed in DMRL. The effectiveness of the TBCs in preventing dimensional degradation of the metallic and composite substrate materials has been evaluated at the laboratory scale. The developed TBCs have the potential for use in aero-engines and propulsion systems of hypervelocity vehicles.

Keywords: Thermal barrier coating (TBC); Ni-superalloys; Niobium alloys; Oxidation; Aero-engines; Hypervelocity systems

1. INTRODUCTION

The engine components propelling aircrafts and hypervelocity systems operate under extreme environments, i.e. (i) ultra-high temperatures in the range of 1000-2000°C, (ii) high flow velocities in the range of 0.5-10 Mach, and (iii) oxidizing and corrosive atmospheres. Notable among these are the turbine components used in the hot-sections of aero-engines and combustor walls of air breathing engines (Fig. 1). Protective thermal barrier coatings are indispensable for enhancing the durability of components, which otherwise undergo extensive degradation during high temperature exposure. The coatings offer a first line of defense against hostile environs, and the protection is achieved by the formation of a superficial oxide layer, which is regenerative, self-healing and stable at high temperatures. The protective oxide layer acts as a diffusion barrier against ingress of oxygen and retards the overall oxidation damage of the coated component significantly. An overlay deposition of thermal barrier over the oxidation resistant coating provides further advantage of thermal insulation, i.e. the component surface experiences lower temperature than that of the relatively higher hot gas temperature. Therefore, the temperature capability and durability of the components can be enhanced by engineered development of suitable multi-layered Thermal Barrier Coating (TBC) systems1-7.

Several scientific aspects are to be considered while selecting the coating system, namely high-phase stability of the coating and superficial oxide scale, moderate kinetics of oxide growth, enhanced spallation resistance of the oxide, and reduced interdiffusion/reaction between the coating and substrate8. While deposition of multilayered TBC systems, the compatibility between thermo-physical properties of the coating constituents is another vital consideration for ensuring adhesion of the TBC ensemble over the substrate. All the above factors play crucial role for the sustained effectiveness of coatings during service.

DMRL has established several coatings for leveraging the high temperature applications of strategic Ni-superalloys and refractory Nb-alloys. The present report provides an overview of the coatings developed and their effectiveness at high temperatures. For better comprehension, the coatings are categorized into two sections based on their engineering
Figure 2. (a) Cross-section microstructure showing the various constituents of thermal barrier coating (TBC) ensemble, and (b) cyclic oxidation behavior of CMSX-4 superalloy applied with various coatings. The superior oxidation resistance of Pt-aluminide coating is evident from its low and steady weight gain over prolonged durations exceeding 700 h. The oxidation tests were carried out at 1100 °C in air and each cycle comprised 45 min. heating followed by 15 min. cooling.

Figure 3. Processing sequence and microstructure evolution of Pt-aluminide (Pt-Al) bond coat.

applications, i.e. (i) coatings for aero-turbine engines and (ii) coatings for combustor walls of hypervelocity engines.

2. COATINGS FOR AERO-ENGINE APPLICATIONS

The components operating in the hot sections of advanced aero-engines, such as blades and vanes, are fabricated using directionally solidified (DS) and single crystal (SX) Ni-base superalloys. The components experience gas temperatures of 1200 °C for prolonged service durations in excess of 500 h. In the absence of protective coatings, the components undergo oxidation and corrosion damage causing depletion of alloying elements and consequent weakening of the superalloy. Progressive oxidation of the bare superalloy components results in loss of their section thickness due to the formation of loose oxide powders of NiO.Al2O3 (nickel-alumina spinel). The temperature heterogeneity in the turbine can also cause localized hot spots and incipient melting of the
surface of bare components. The reduction in section-thickness and formation of re-cast surface microstructure induce localized overstressing and failure of the components. Therefore, for protection against heat loads and enhancing the durability of hot-section components, Thermal Barrier Coatings (TBCs) are applied.

A typical TBC system comprises two coating layers: (i) an inner oxidation resistant bond coat, and (ii) an outer ceramic insulating top coat Fig. 2(a)\textsuperscript{2-7}. The bond coat is constituted of NiAl intermetallic phase, which has the inherent ability to form sustained regenerative layer of alumina (Al\textsubscript{2}O\textsubscript{3}) scale on the surface during thermal exposure in air. The alumina layer, which is couple of micron-meters in thickness, reduces the inward diffusion of O from the ambience and lowers the overall oxidation damage of the coated superalloy.

Alloying of the NiAl phase constituting the bond coat with \textasciitilde5 at.% of Pt moderates the rate of growth of alumina and further enhances the spallation resistance of the superficial oxide scale\textsuperscript{1-7}. The outer insulating coating comprises a low thermal conductivity material such as that of 7-8 wt.% yttria stabilized zirconia (YSZ)\textsuperscript{2,7}.

DMRL has established the process for indigenous development of advanced TBC systems. A processing sequence comprising Pt-electroplating, diffusion heat treatments and vapor phase aluminization has been established for the deposition of diffusion Pt-aluminide (PtAl) bond coat on Ni-superalloy components. Scientific aspects pertaining to the processing-microstructure-performance of the PtAl coatings have been investigated (Fig. 3)\textsuperscript{5,13}. The PtAl coating has a thickness of 75-100 µm and constituted of NiAl phase containing Pt in solid solution, as evident from the microstructure (Fig. 2(a) and 3). Results of thermogravimetric tests carried out in air at 1100°C confirm the superior thermal cycling life of Pt-aluminide bond coated superalloy in comparison to other coatings over long durations exceeding 700 h Fig. 2(b). Diffusion Pt-aluminide (PtAl) bond coat has been deposited on several batches of DS CM-247 Ni-superalloy components such as Low Pressure Turbine Blades (LPTBs), High Pressure Turbine Blades (HPTBs), Low Pressure Turbine Vanes (LPTVs), High Pressure Turbine Vanes (HPTVs), as shown in Fig. 4.

As mentioned earlier, a ceramic insulating coating is deposited over the bond coat. In the erstwhile engine components, the ceramic coating is deposited by conventional thermal spraying technique such as Air Plasma Spray. However, the conventional thermal spray coatings exhibit splat-type morphology and concomitant low spallation resistance\textsuperscript{2,14-16}. Therefore, Electron-Beam Physical Vapor Deposition (EB-PVD) technique has been adopted for the deposition of ceramic coatings on advanced aero-engine components. Unlike the conventional splat-type ceramic coatings deposited by thermal spray techniques, the EB-PVD coatings exhibit superior strain tolerance due to their columnar morphology, as shown in Fig. 2(a)\textsuperscript{2,14-16}. The feasibility for the deposition of columnar ceramic YSZ coating on HPTB and HPTV components by electron-beam physical vapor deposition (EB-PVD) has been demonstrated by HTCG/DMRL in collaboration with ARCI, Hyderabad (Fig. 5). Simultaneously, diffusion aluminide coatings are also being developed for γ-TiAl alloy components envisaged for use in the downstream sections of aero-engines.
The flight envelope for hypervelocity systems involves hypersonic velocities (>6 Mach) and high altitudes (>30 km). The materials used in the construction of such systems shall experience the harshest of operating conditions: (i) high temperatures exceeding 1400 °C, (ii) high aero-dynamic shear stresses, (iii) oxidation, and (iv) rapid rates of heating, to name a few. Material systems possessing good ultra-high temperature strength, low vapour pressures and sublimation rates, good oxidation and erosion resistance, and resistance against thermal shock are essential for the successful realization of hypersonic vehicles\(^8,17-23\). World-wide, the successful realization of hypersonic systems has been limited by the non-availability of strategic material systems and protective coatings. Published reports on materials and coatings for hypersonic applications are scarce in the open literature\(^8\). While coatings based on silicide and rhenium provide good oxidation resistance to refractory metals and alloys based on Nb, Mo and W\(^8,24-30\), there is not much information on the processing and characterization of ceramic thermal barrier coatings (TBCs) for hypersonic applications.

DMRL has successfully established critical technologies pertaining to development and advanced characterization of high-temperature resistant metallic and ceramic coatings for refractory Nb-based alloys. Brief overview of ultra-high temperature coatings developed and their characterization are provided in the subsequent text.

Thermal barrier coating (TBC) systems, comprising diffusion silicide and ceramic coatings have been developed for providing oxidation resistance and thermal insulation to Nb-alloys (C-103/Cb-752) (Fig. 6). The coatings are developed...
Figure 7. Photographs corresponding to the uncoated C-103 sample: (a) configuration of the sample during the test, (b) tip/leading edge before the test, (c) severe degradation of the leading edge after 100 sec., and (d) side view showing erosion and crater formation at the tip/leading edge profile.

Figure 8. Photographs corresponding to the 300 µm thick silicide coated Nb-alloy samples after 10 min. of IPEC testing at higher heat flux of 200 W/cm². The surface temperature was 1450°C during the tests. Coated C-103: (a) before test, (b) after test and (c) coated Cb-752 after test. There is no visible erosion of the tip profile for either of the samples, as typically shown in Fig. 3(d).
Figure 9. (a,b) Surface morphology of the coated Nb-alloys after IPEC testing and (c,d) their corresponding EDS spectra showing the formation of superficial silicate scale. The cross-section views at various locations of impact of the plasma arc with the tip profile are shown in (e-h). The combination of legends (e-1, f) denotes the sample tip cross-section at the region of direct impact of the plasma arc; likewise (e-2, g) and (e-3, h) indicate the cross-section at increasing farther regions along the tip/leading edge.
using a combination of diffusion slurry and thermal spray processes. The 250-300 µm thick silicide coating is constituted of an outer layer (OL) of NbSi2, intermediate layer (IL) of Nb-Fe-Cr-complex silicides, and the interdiffusion zone (IDZ) comprising lower silicides of Nb (Fig. 6(a)). The silicide coating provides oxidation resistance by the formation of protective silica scale, which has the inherent ability to spread on the surface and heal the cracks formed in the coating during rapid thermal heating21-27. The ceramic insulating coating, which has been developed to a thickness of 1 mm, provides effective ultra-high temperature resistance against heat loads exceeding 2000 °C in temperature.

The performance of the coated samples has been evaluated by carrying out dynamic oxidation tests in an IPEC (Induction Plasma Erosion & Coating) test system involving conditions of high heat flux (160-200 W/cm²) and high flow rates (Mach. 2 and above), as shown in Fig. 7-10. The surface temperature of the samples was in the range of 1400-1500°C during the test. In the absence of coatings, the bare Nb-alloy undergoes rapid oxidation-induced deterioration and profile erosion during the initial 30-100 sec. of the test (Fig. 7).

The high profile erosion of about 5 mm can be ascribed to rapid oxidation of the bare Nb-alloy and simultaneous erosion of the oxide layer31. The porous nature of Nb-oxide and poor interfacial adhesion of the oxide with the base metal surface promotes rapid dimensional degradation. On the other hand, the coating is effective in preventing dimensional degradation and surface recession of coated Nb-alloys over the entire 10 min. of test duration (Fig. 8).

The maximum extent of erosion was restricted to ~ 200 µm from the surface of the coated sample (Figs 8 and 9), which was negligible compared to the erosion depth of 5 mm exhibited by the uncoated samples (Fig. 7). The oxidation resistance of the coating is derived from the in-situ formation of protective silicate scale on the coating surface and within the cracks formed in the coating during high-temperature oxidation exposure (Fig. 9).

The silicate scale (detected as the dark phase in the coating as well as within the coating in the cross-section images) effectively heals the cracks in the coating (Figs. 9(f-h)) and acts as diffusion barrier against the ingress of oxygen from the atmosphere, which prevents oxidation of the base Nb-alloy (Figs. 7 and 8). Results of IPEC tests, carried out on Nb-alloy applied with TBC system comprising 300 µm thick silicide coating and an overlay ceramic coating of 1 mm thickness, indicate that the TBC prevents degradation of the substrate alloy and there is no coating delamination (Fig. 10).

From the above observations, it is evident that the coatings are indispensible and have the potential for use in ultra-high temperature hypervelocity systems. Presently, the process for TBC development is being scaled-up for the realization of large size coated sections.

4. TBC

The increasing requirement for Higher Turbine Entry Temperatures (TET) and high efficiency air breathing engines necessitates the development of advanced TBC systems having higher temperature capability, superior oxidation resistance, and low thermal conductivity32-33. Besides, since the failure of TBC systems occurs mostly by rumpling-induced delamination of the outer ceramic coating34-35, bond coats exhibiting higher strength and creep resistance are sought after.

Figure 10. Photographs corresponding to the C-103 sample (dimensions: 50 x 50 x 4, mm) applied with the silicide & ceramic TBC system: (a) configuration of the sample during the plasma erosion test, (b) sample before the test, and (c) sample after the test duration of 10 min. The heat flux, surface temperature and flow velocity for the tests were 200 W/cm², 1450°C and ~ 3 Mach, respectively. There was no TBC delamination and degradation of the Nb-alloy during the plasma erosion test.
Alloying of the conventional Pt-aluminide bond coat with other Pt-group elements such as Pd and Rh, can enhance its high temperature strength and oxidation resistance. High entropy multicomponent metallic systems are also being explored as alternatives to the thermally sprayed MCrAIY and diffusion aluminide coatings.

Enhancement in the thermal insulation characteristics, i.e., lowering of thermal conductivity, can be achieved by the addition of rare earth dopants to the ceramic zirconia coating such as that of lanthanum, samarium and gadolinium zirconates. Rare earth ceriates and multi-component rare earth based oxide ceramics are also potential low thermal conductivity thermal barriers. However, studies on the above ceramic systems are mostly confined to their synthesis and thermophysical characterization in the bulk form, and their processing as coatings is yet to be widely explored.

A durable TBC system should have good resistance against residual stress-induced delamination. Therefore, consideration of thermo-physical and thermo-mechanical properties, such as co-efficient of thermal expansion and modulus of elasticity, of the TBC constituents is essential while developing a multi-layered TBC system. Simulation models have been proposed for predicting the durability of TBC systems based on strain energy and fracture mechanics approach. However, the successful implementation of the above models requires relevant micro-mechanical data pertaining to the coating systems. In the recent times, micro-mechanical characterization of TBC constituents has gained importance for generating representative mechanical properties for coatings, and attempts are being made to develop ICME based lifting models for TBC coated superalloys based on the concomitant failure micro-mechanisms with respect to temperature.

Modifications in the processing route of TBC systems can also generate strain tolerant coatings. Suspension plasma spraying (SPS) and Solution precursor plasma spraying (SPPS) have been devised as alternates to conventional plasma spraying. The inherent through-thickness vertical cracks in the SPS- and SPPS-deposited dense coatings are reported to induce enhanced thermal cycling life. The SPS and SPPS thermal spray processes, being economical than that of the expensive EB-PVD process, are subjects for further research in the TBC community and gaining prominence at the industrial scale for the development of columnar strain-tolerant TBCs.

5. CONCLUSIONS
   - The High Temperature Coatings Group (HTCG) at DMRL, Hyderabad has established several indispensable Thermal Barrier Coating (TBC) systems for strategic applications in gas-turbine engines and hypervelocity combustors
   - The effectiveness of the coatings in providing thermal protection to the Ni-superalloy and Nb-alloy substrates at high temperatures has been demonstrated
   - Thermal barrier coating (TBC) ensemble, comprising 75-100 µm thick diffusion Pt-aluminide bond coat and 150-200 µm thick zirconia coating, has been developed for Ni-superalloy aero-engine components
   - Ultra-high temperature resistant diffusion silicide coating and thick ceramic thermal barrier coatings have been developed for refractory Nb-alloys for combustor walls of hypervelocity systems
   - The protective coatings, i.e. the diffusion silicide and the ceramic TBC, are effective in preventing the dimensional degradation and erosion of the Nb alloys (C-103/Cb-752) during dynamic oxidation conditions involving high-heat flux and high flow velocity conditions. In the absence of coatings, the bare Nb-alloy undergoes extensive oxidation, melting and erosion.

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