

Surface Modification Technologies XIV

Surface Modification Technologies XIV

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T. S. Sudarshan

Materials Modification Inc.
2721-D, Merrilee Drive
Fairfax, VA 22031

M. Jeandin

Ecole des Mines de Paris
Centre des Matériaux P.M. FOURT
B.P. 87, 91003 Evry Cedex, France



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Foreword

The Fourteenth International Conference on Surface Modification Technologies was hosted by “SF2M” and held in Paris France, between September 11-14th, 2000. Over 25 countries were represented at this meeting and this proceedings is a complete compilation of all the papers that were presented. The meeting was cosponsored by ASM and IOM and the proceedings is co published by the two societies

Being the start of a new millennium, this conference had some new formats. First we had a very successful session on “Arts and Surfaces” which was not only well attended but astounding in terms of the details that have been unknown to most practicing engineers of the tremendous innovations and knowledge of our predecessors. The ability to clean statues with new techniques, the ability to make materials that were able to withstand hundreds of years of adverse exposure to the environment and the ability to recover the original features of the art forms using surface modification techniques were captivating to say the least. There were also many papers that focused on the applications of surface modification technologies and their relevance to manufacturing. The meeting was very well attended and was the largest meeting in terms of papers and attendance in the “smt” series so far. The papers included in these proceedings were peer reviewed and corrected prior to publication. We would like to thank the numerous reviewers for their time, patience and assistance.

As in the past meetings the papers presented in this proceedings cover a broad spectrum of topics and represent the diverse nature of the field. We would like to thank the authors, and the session chairmen for holding participative discussions with the audience and their cooperation during the meeting.

For the first time, we attempted to use modern technology and requested submission of all papers and abstracts via the web. Our initial experiences were less than satisfying due to the different technologies and skills available in relationship to computers and languages in the different countries. We had tremendous confusion due to the uploading of many versions by the authors, which resulted in delays beyond our control. As editors, we apologize for this delay but hope that we have learnt from our experience in the pursuit of modern technology and progress.

Finally, we would like to acknowledge the generous use of the communication facilities and the time released by our employers in the compilation of this volume that ensured its publication.

T.S. Sudarshan
Materials Modification, Inc.
2721-D, Merrilee Drive
Fairfax, VA 22031

M. Jeandin
Ecole des Mines de Paris
Centre des Matériaux P.M. FOURT
B.P. 87, 91003 Evry Cedex, France

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Organizing Committee

T.S. Sudarshan
Materials Modification Inc.
2721-D, Merrilee Drive
Fairfax, VA 22031

M. Jeandin
Ecole Nationale Supérieure des Mines de Paris
Centre des Matériaux P.M. Fourt
B.P. 87, 91003 Evry Cedex, France

Y. Franchot
SF2M
Les Fontenelles - 1, rue de Craïova
F 92024 Nanterre Cedex, France

Conference Secretariat

Chantal Iannarelli
C2S, 2, Rue des Villarmains, B.P. 124
92210 Saint-Cloud Cedex, France

Organized by

SF2M
Société Française de Métallurgie et de Matériaux
Les Fontenelles, 1, rue de Craïova, F-92024 Nanterre Cedex, France

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Technical Sessions

Thermal Spraying I:

C. Coddet
LERMPS, Université de Technologie de Belfort-Montéaliard
Belfort, France

Thermal Spraying II:

R. Rigney
R.M. Rigney & Associates
Ringgold, USA

Thermal Spraying III:

Bu-Qian Wang
FBE Technology Center, Metalspray United Inc.
2713 Oak Lake Blvd., VA 23112

Thermal Spraying IV:

K.A. Khor
School of Mechanical & production Engineering
Nanyang Technological University
50, Nanyang Avenue, Singapore 639798

High Performance Coatings I:

Y. Watanabe
Department of Materials Science and Engineering
National Defense Academy, 1-10-20 Hashirimizu
Yokosuka, Kanagawa 239-8686, Japan

High Performance Coatings II:

H. Gassot
Institut de Physique Nucléaire d'Orsay
91406, Orsay, France

Bio Materials I:

N. Llorca-Isern
Universitat de Barcelona, C/Marti I Franquès 1
08028 Barcelona, Spain

A. Agüero
Instituto Nacional de Técnica Aeroespacial (INTA)
Ctra. Ajalvir Km. 4, 28850 Torrejón de Ardoz (Madrid)
Spain

Testing and Analysis I:

C.N. Elias
Universidade Federal Fluminense
Av dos Trabalhadores 420
27260 740 Volta Redonda, RJ – Brazil

PVD and CVD:

K.L. Lin
Department of Materials Science and Engineering
National Cheng Kung University, Tainan, Taiwan 701

Wear I:

D. Pantelis
National Technical University of Athens
Dept. of Naval Architecture and Marine Engineering
9 av. Iroon Polytechniou str, 157 80, Zografou, Greece

Wear II:

W. Kaysser
German Aerospace Center, 51147 Koeln (Cologne), Germany

Wear III:

C. Richard
Laboratoire Roberval (associated CNRS)
Université de Technologie de Compiègne
60205 Compiègne Cedex, France

Laser I:

V. Zafirooulos
Foundation for Research and Technology-Hellas, (FO.R.T.H.)
Institute of Electronic Structure and Laser
Vasilika Vouton, P.O. Box 1527, 71110 Heraklion, Crete,
Greece

Laser II:

P. Laurens
CLFA, 16 bis av. Prieur de la Côte d'Or
94114 Arcueil Cedex, France

Corrosion and Fatigue:

R. Urao
School of Engineering, Ibaraki University
Hitachi, Ibaraki, 316-8511, Japan

Arts and Surfaces I:

M. Guttman
IRSID, Groupe Usinor, Voie Romaine - BP 30320
F - 57283 Maiziere-les-Metz Cedex, France

Arts and Surfaces II:

A. Giunlia-Mair
Dipartimento di Storia e Tutela dei Beni Culturali
Università di Udine, Centro Polifunzionale di Gorizia
Palazzo Alvarez, via A. Diaz 5, 34170 Gorizia, Italy

Plasma-Assisted and Advanced Processes:

A.V. Byeli
Physical-Technical Institute, Minsk, Republic of Belarus

Modelling:

M.H. Staia
School of Metallurgy and Materials Science
Central University of Venezuela
Apartado 49141, Caracas 1042-A, Venezuela

Surface Modifications in Aerospace Applications

W. Kaysser

German Aerospace Center (DLR)
51147 Koeln (Cologne)
Germany
E-mail: wolfgang.kaysser@dlr.de

1.0 Introduction

Aerospace applications include numerous surface modifications for a broad variety of functions. Main drivers are the long service life time of civil aircraft and some space structures, the often harsh environmental conditions during service and the cyclic nature of most of the loading conditions.¹ Civil aircraft vehicles with an expected life time in the order of 30 years are critical in respect to corrosion and high cycle fatigue. Many surface modifications are therefore related to these issues. Aeroengines and rocket engines are both operated close to materials performance limits. High temperatures and oxidizing atmospheres require protective coatings against oxidation and hot corrosion and coatings which act as thermal barriers. Similar surface modifications of ceramic composites containing carbon fibers allow their use for service times up to several hours at temperatures up to 1800°C. In addition to these more traditional surface modifications advanced coatings with physical functional properties such as electromagnetic absorption to minimize radar return are of increasing interest. This paper gives a short outline of some of the current developments of surface modifications in aerospace applications.

2.0 Surface Modifications at Ambient Temperatures

2.1 Surface Coatings for Corrosion Protection

Aircraft coatings and corrosion inhibitors offer significant challenges. Coatings are multifunctional, providing air vehicles with three main attributes:

1. Survivability,
2. Corrosion protection, and
3. Cosmetic appearance.²

Current coatings for aluminum skinned aircraft consist of chromated surface pretreatment, a chromated paint primer layer and paint topcoats, each of which performs several crucial functions. Here, the term “coatings” refers to the aircraft coating structure as a system and includes all the individual elements of the system from the surface treatment to the topcoat paint. The term “paint” refers to a single organic coating comprised of a binder solvent, pigment, and additives. The surface pretreatment provides passivation of the

metal surface, incorporates corrosion inhibitors, and creates a surface topography for maximum primer coating adhesion. The organic primer coating also incorporates corrosion inhibitors and serves as an adhesive layer between the metal substrate and the topcoat layers. At mechanically stressed or damaged areas such as fasteners, rivets, expansion joints, and scratches, the surface pretreatment/primer system provides active corrosion protection from exposure to environmental factors (e.g. water, acids, and solvents). The paint topcoat layers provide signature control and protection against erosion and mechanical abrasion, in addition to providing acceptable cosmetic appearance. The surface treatment/primer coatings are intended to be applied and removed as needed, based on the mission. However, current actual practices have aircraft being repaired, primer as well as topcoats, well ahead of the functional degradation cycle because of poor appearance due to degradation. Traditional coatings for aircraft include epoxy primers and polyurethane topcoats. Primers normally contain high concentrations of corrosion inhibitors, such as chromates. More recently, alternative coatings have been developed such as self-priming topcoats, flexible primers, temporary and multifunctional coatings. These new developments reflect trends in protective coatings technology, changes in aircraft operational requirements/capabilities, and most dramatically, concerns over environmental protection and worker safety. This issue has created a drive toward coatings with low (possibly zero) concentrations of volatile organic compounds and nontoxic corrosion inhibitors. Current available primers are based on 2-component high solids or waterborne epoxy systems and corrosion inhibitors such as molybdenum, nitrides, borates, silicates, and or phosphates as well as a variety of metal cation systems.³

2.2 Surface Treatments for Fatigue and Wear Improvement

Aircraft structure components which require high strength and stiffness are often fabricated from titanium alloys. Due to the high stress levels and the long service life of aircraft structures prevention of fatigue is a major issue for the titanium parts. It is accepted practice to improve titanium alloy life substantially by controlled shot (steel, stainless steel, or ceramic) or glass-bead peening along with achieving undamaged, smooth, and oxide-/alpha case-free surfaces.⁴ This treatment plastically works the surface and produces a compressive residual stress as profiled in Figure 1.⁵ The effective depth of this compressive stress layer is generally in the range of 100 – 200 μm for shot peening and 25 to 75 μm for glass bead peening. Due to the stress distribution shot peening is considered for fatigue life enhancement only when the surface layer is expected to be the dominating fatigue crack initiation site. This explains why peening is of no benefit and, in fact may be detrimental to smooth fatigue life under vacuum where titanium alloy surfaces may not be the “weak point” for initiation.⁶

The other competing method for generating compressive residual stresses is laser shock peening recently developed. The LSP process is similar to shot peening in that it relies on an impact event to generate the compressive residual field. The difference is that the LSP process uses a high intensity, short pulse duration laser to create the impact event.⁷ When the laser beam strikes the impact site, a sequence of events occurs. The laser beam first passes through a water overlay transparent to the beam, then strikes a paint layer which is coated on the titanium to be shock treated. A thin layer of the paint is immediately vaporized and rapidly thermally expands by absorbing energy from the incoming beam. In addition a plasma forms in the rapidly heating, expanding gas. The gas and plasma are confined against the surface of the titanium by the water overlay, creating a rapid, local increase in pressure against the titanium piece. This confinement increases the attainable pressure by much more

than an order of magnitude, ranging from 1 to 7 or more GPa. The confined pressure is transmitted both into the titanium and out through the water as high amplitude shock waves. When the peak pressure of the shock wave is above the dynamic yield strength of the titanium it plastically deforms the material and creates relatively deep compressive residual stress. As in shot peening, to cover areas larger than the single spot size of the impact, the processes must be repeated with overlapped spots. Major limitations of laser shock peening are throughput and cost.

2.3 Surface Coatings for Enhanced Physical Properties

Most modern military aircraft combine conventional and state-of-the-art technology, such as special shaping and radar-absorbing materials to achieve low-observability characteristics and high aerodynamic efficiency. Novel coatings for electromagnetic absorption and shielding employ chiral materials, nonlinear metal oxides, ferroelectric tunable materials, voltage controllable dielectric and conducting polymers.⁸ It is the principal objective of recent developments to obtain both passive and active (smart) coatings with fast control architecture using neural networks, to control electromagnetic radiation over a very wide band range from very low frequencies to very high frequencies that go up to more than 100 GHz. Advanced coatings on simple planar samples and model targets show absorption in the order of -25 to -30 dB and shielding effectiveness in the order of -60 to -110 dB for a wide range of frequency. The primary focus of the smart coatings is to employ electroactive polymeric materials that would interact with the electromagnetic radiation, and perform a signature modification and evasion operation that has applications in radar stealth technology, electronic warfare, electronic countermeasures, communication, navigation, identification etc.

3.0 Surface Modifications at Higher Temperatures

3.1 Oxidation Resistant Coatings for Titanium Alloys and Aluminides

Considerable interest has been placed on conventional titanium alloys as well as titanium aluminides for high-temperature applications in aeroengines, for example, as compressor components or in the low pressure turbine. For some of these applications a high temperature capability of about 800°C will be required in order to meet advanced engine design goals. The uppermost temperature limit of current conventional high temperature titanium alloys, usually from the class of near- α alloys,⁹ is 600°C, whereas titanium aluminides are expected to operate at maximum 800°C. Since conventional titanium alloys do not form protective oxide scales during high temperature exposure to oxidizing atmospheres, components are limited to service temperatures far below 600°C, typically 520°C, and even lower for critical rotating parts.¹⁰ Despite higher oxidation resistance compared to conventional titanium alloys, environmental durability of γ -TiAl based aluminides is still a concern,¹¹ especially with respect to mechanical properties. The inability of gamma aluminides to form protective oxide scales with sufficient long-term stability limits their application to temperatures below their anticipated service temperatures.

In the past, numerous attempts to effectively improve the environmental resistance of titanium alloys and titanium aluminides by alloying additions and various surface treatments have been

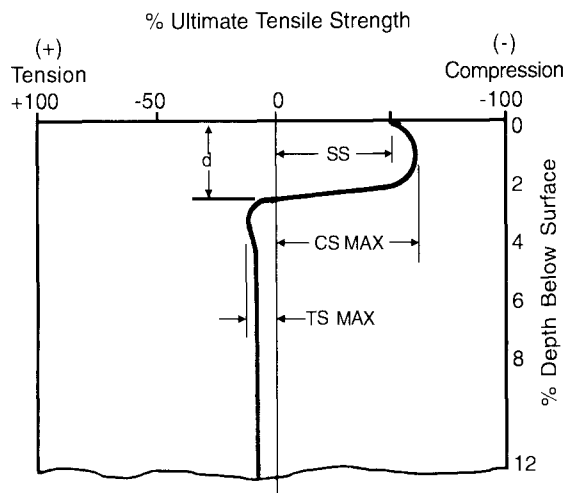


Fig. 1: Typical profile of residual compressive and tensile stresses induced in titanium component surfaces when shot-peened.^{4,5}

made.¹² Macro-alloying additions such as Nb, Si, W and Cr, typically of the order of a few percent, have improved oxidation resistance of conventional titanium alloys significantly and raised their service temperatures from 300°C for the classical workhorse alloy of the aerospace industry, Ti-6Al-4V, to approximately 520°C for near- α alloys. However, further improvement of environmental resistance by macro-alloying often adversely affects mechanical properties; thus alloy development always requires a proper balance of environmental resistance and mechanical properties. Micro-alloying additions such as Cl and P, typically of the order of a few ppm, have recently been considered a useful way to improve long-term oxidation resistance of gamma titanium aluminides without sacrifice to mechanical properties. However, the micro-alloying effect has not yet been demonstrated for conventional titanium alloys. Surface treatments, first and foremost various types of coatings, have been investigated for more than 30 years now. One major problem of coating development has been that, although reasonable oxidation resistance was achieved in many cases, most of these coatings tended to be inherently brittle or formed brittle phases with the substrate material, thus degrading its mechanical properties, especially fatigue behavior. Since the embrittlement problem has never been acceptably solved and therefore benefits obtained from coating usage have remained small or questionable, none of the coatings investigated has been brought into service so far.

As part of an extensive research effort devoted to the development of fiber-reinforced titanium matrix composites (TMCs) for advanced compressor components in aeroengines,¹³ DLR has initiated a program focused on development of oxidation resistant coatings for titanium alloys and aluminides. Components such as so called blings (bladed rings) comprise a fiber-reinforced ring and monolithic compressor blades welded to the ring.¹⁴ Enormous weight savings of the order of 70% are being predicted with such a design but still technical and economic hurdles have to be cleared before these composites will become established in aeroengines. In order to fully utilize the high temperature capability of TMCs, protection of the matrix and the monolithic material against environmental attack is required.

In the initial stages of this study, binary TiAl coatings deposited onto conventional titanium alloys such as IMI 834 and TIMETAL

1100 were investigated. The basic concept was to provide mechanical and chemical compatibility between the substrate and the alloy and achieve reasonable environmental protection. Therefore, two types of TiAl-coatings were investigated: a) gradient Ti-Al coatings with increasing Al content towards the outermost surface (marked "G") and b) Ti-Al multilayer coatings consisting of three single layers (marked "ML"); their nominal chemical compositions corresponded to Ti_3Al , TiAl, and $TiAl_3$. Overall coating thicknesses for G and ML-TiAl coatings were 4 and 16 μm .

Although, in general, providing oxidation resistance to the base alloy was the driver for coating development, it was not the key issue of this study. Rather, the impact of the coatings on the mechanical properties of the substrate materials was of prime interest. The magnetron-sputtered TiAl coatings improved oxidation resistance by approximately one order of magnitude in the temperature range between 600 and 750°C, however, since only binary coatings were studied, maximum oxidation resistance was not anticipated. From a standpoint of environmental protection, the coatings did not only increase oxidation resistance of the base material but also effectively hindered dissolution of oxygen and nitrogen in the subsurface zone. Essentially no increase of microhardness was measured for the Ti-Al-coated base alloy after long-term exposure to air.¹⁵ The protection against embrittlement had significant impact on the mechanical properties. Even a thin embrittlement zone was reported to facilitate crack formation and thus deteriorate ductility.¹⁶ On the other hand, avoiding embrittlement of the subsurface zone resulted in a high level of ductility maintained even after long-term exposure.¹⁷ After 100 h exposure at 600°C, ML-TiAl-coated material maintained 95% of its initial ductility compared to only 74% for the uncoated material.

In creep tests at 600°C, TiAl coatings demonstrated potential to improve lifetime of the substrate by 20%, however, the benefits obtained from the coatings appeared to be somewhat dependent on the stress level applied during the tests, with lower levels providing more improvement.¹⁸ The most striking result from the creep tests was the ability of the coating to survive significant plastic deformation without notable crack formation (Figure 2). Whereas the uncoated substrate material was heavily cracked in the outer part of the specimen, no cracks were visible on the coated sample.

The impact of ML-TiAl coatings on the fatigue behavior of the base material depended on the maximum strain during testing (Figure 3). When strain exceeded 1.5%, ML-TiAl coatings somewhat beneficially influenced fatigue life of the system. However, for lower strain, 16 μm ML-TiAl coatings slightly decreased the fatigue limit under repeated strain to $c_1 = 0.6\%$ and also reduced fatigue life. However, 4 μm ML-TiAl coatings had an identical fatigue limit relative to the uncoated material and showed no detrimental effect on the fatigue properties of the base material.¹⁹ This very important result clearly demonstrated that once a suitable coating chemistry and processing method is available, protective coatings can be applied to conventional titanium alloys without sacrifice to their fatigue properties. Furthermore, it has encouraged ongoing research and development efforts towards *improvement* of the fatigue behavior of titanium alloys via coating usage.

Cr additions seem to be a promising way to further improve oxidation resistance of Ti-Al coatings. Initial work on a near- α alloy as well as on a gamma titanium aluminide demonstrate significant potential of Ti-Al-Cr coatings for coating applications in aeroengines. Future work is being directed towards optimization of coating compatibility to titanium aluminides and improvement of the thermo-mechanical properties of the coated materials system. Long-term durability of the coatings has yet to be determined. Furthermore, coating processing itself offers further potential for improvements.

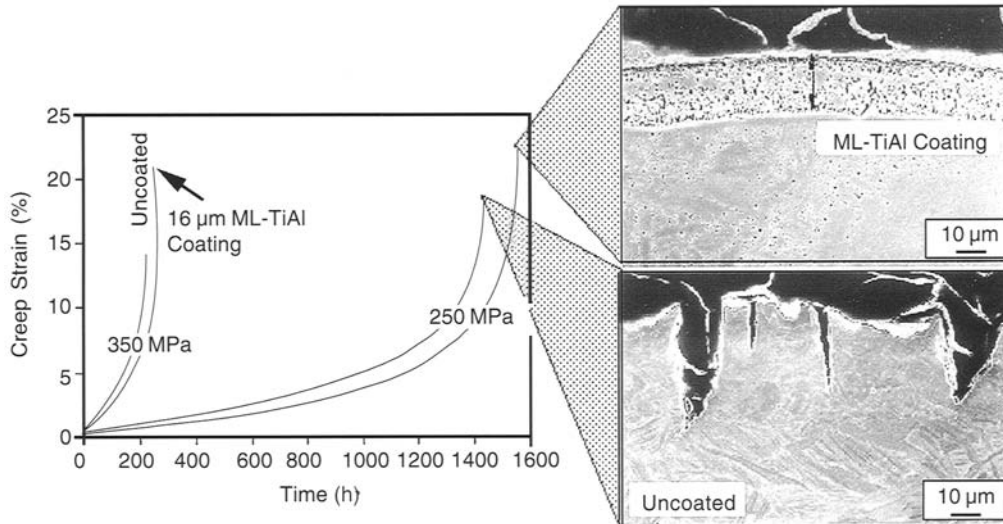


Fig. 2: Creep strain vs. time curves and SEM cross-section micrographs of uncoated and Ti-Al-coated TIMETAL 1100 tested at 600°C in air at different constant load levels. Significant crack formation of the uncoated material was caused by oxygen/nitrogen embrittlement.

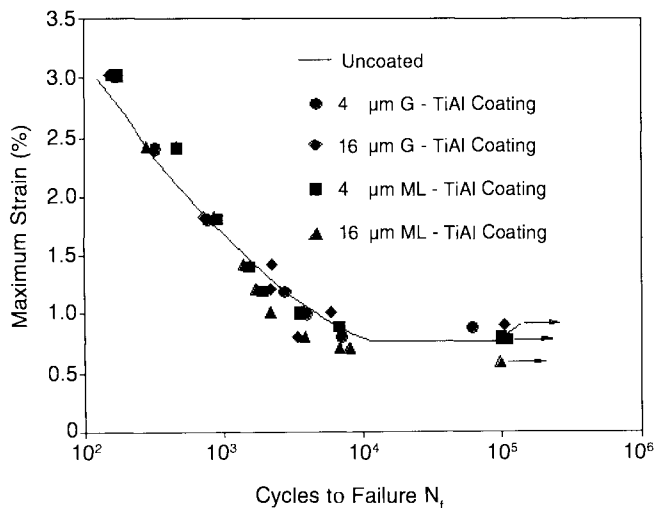


Fig. 3: Maximum strain vs. cycles to failure for uncoated and Ti-Al-coated TIMETAL 1100 at 600°C in air. Data revealed essentially no adverse effect of the coatings on the fatigue behavior of the substrate material.

3.2 Ceramic Oxidation Protective Coatings

The C/C composites provide best property combinations for high temperature applications. Extreme strength to weight ratio, resistance to extreme thermal shocks, good heat conductivity, low coefficient of thermal expansion, strength retention and creep resistance up to extremely high temperature. Unfortunately the poor oxidation resistance at high temperatures limits their service range. The development of oxide protection for carbon/carbon and carbon/SiC composites started more than two decades ago to develop thermal

protection for the shuttle orbiter vehicles. The coating system for the carbon/carbon composites used for the shuttle nose cap and wing leading edges is composed of a SiC inner layer and an outer silicate glaze coating filled with SiC powder.²⁰ A pack process in which the surface of the substrate reacts with silicon vapor and SiO vapor is used to form the SiC layer. Glazing is performed with a commercial liquid silicate. The process also involves sealing cracks in the coating system with silicon ethoxide.²¹ There are many issues which must be considered in the development of a successful oxidation-protection system for carbon based materials. Externally, the coating must provide an effective barrier to inward diffusion of oxygen. In addition, it must possess low volatility to prevent excessive erosion in the high velocity gas streams. From an internal viewpoint, good adherence to the substrate must be achieved without excessive substrate penetration. The internal layers must also prevent outward carbon diffusion at least to the extent of preventing carbothermic reduction of oxides in the external layers. The development of thermal stresses is a major time limiting factor. The carbon-carbon composite has a substantially lower thermal expansion coefficient than any ceramic exhibiting a symmetric crystal structure. The intrinsic protective temperature range of the coating is defined by the microcracking temperature and the coating limiting-use temperature. In this range the cracks are mechanically closed and sealed by oxidation products. It is clear that an additional technology to seal cracks below the microcracking temperature must be employed.

For CVD-deposited coatings based on SiC and Si₃N₄ the upper use temperature is usually defined by reactions at the interface between the SiO₂ scale and the underlying ceramic. Only if the silicon activity is maintained at unity, SiO₂ films are stable on SiC or Si₃N₄, up to 1800°C. It was noted during the past years, however, that the presence of flowing water vapor could dramatically reduce the stability of the SiO₂ films even below 1200°C. The microcracking temperature limits the intrinsic protective range of the Si₃N₄ coating to the temperature range between 1200 and 1760°C. At lower temperatures crack sealing is often achieved by sealants based on B₂O₃ which, however, provide protection for limited time only (i.e. < 10 h at 1300°C), due to volatilization.

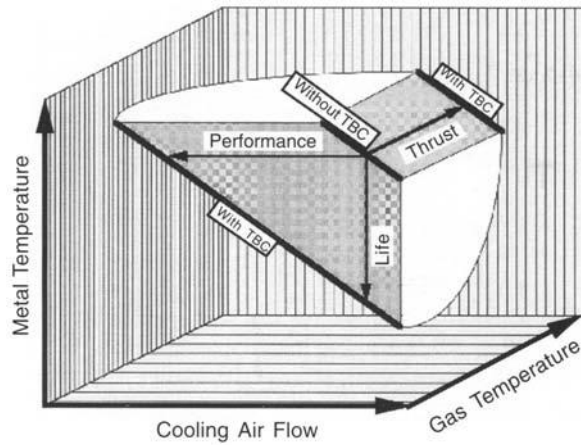


Fig. 4: Potential benefits in gas turbines for the use of TBCs: depending on operating conditions and requirements, TBCs can improve engine performance and thrust as well as component life.

3.3 Thermal Barrier Coatings

Thermal barrier coating (TBC) systems have been developed to fulfill the demands placed on current high-temperature Ni-base superalloys for gas turbine applications in both aeroengines and land based gas turbines.²²⁻²⁵ TBC systems typically consist of an yttria-stabilized zirconia (YSZ) top layer, which has low thermal conductivity, which is chemically inert in combustion atmospheres, and has a relatively high coefficient of thermal expansion which is reasonably compatible with Ni-base superalloys. As zirconia is essentially transparent to oxygen at high temperatures, the metallic substrate is usually protected by an oxidation-resistant metallic coating in order to limit the environmental attack to a technically acceptable level. However, for safe component operation, this coating must not only protect against oxidation but must also provide sufficient bonding of the ceramic top layer to the substrate. Usually in gas turbine applications bond coats rely on the formation of a slow-growing alumina scale (also designated as TGO = thermally grown oxide) between the bond coat and the ceramic top coat. Today most bond coats are based either on MCrAlY-type compositions or on aluminides (simple or Pt-modified) with sufficiently high levels of aluminum to provide a reservoir of scale-forming aluminum over a long service period without depleting the substrate alloy.

The potential benefits of TBC application on turbine blades in aeroengines are schematically outlined in Figure 4.²⁶ The insulating properties of these coatings may lead to performance improvements by allowing a reduced cooling air flow at a given metal temperature or may improve lifetime of the components by reducing the metal temperature at a given cooling air flow. Higher engine thrust can be achieved by allowing higher gas temperatures at a given cooling air flow.²⁷ Currently, engine design primarily relies on lifetime extension benefits of TBCs. It is, however, obvious that prime reliant TBCs with predictable lifetime performance are required to implement TBCs as designed-in components and in this way fully exploit their potential for significant performance improvements.

Among various coating processes which are industrially available, plasma spraying (PS) of overlay coatings and chemical vapor deposition processes, including pack aluminizing, are the most common bond coat deposition techniques. For YSZ deposition, PS

and electron beam physical vapor deposition (EB-PVD) are widely used, the latter process being considered to exhibit inherent advantages over plasma sprayed coatings.^{28,29} One of the most favorable features of an EB-PVD TBC is its strain-tolerant columnar microstructure (Figure 5); these coatings also retain an aerodynamically-favorable smooth surface, and usually exhibit longer lifetimes than PS YSZ coatings.

Although it is expected that over 50% of aeroengines will be specifying EB-PVD TBCs in the year 2000,³⁰ and despite the fact that currently TBC technology is being introduced into stationary gas turbines for power generation, a lot of research issues have to be addressed until TBCs qualify to become an integral part of the turbine blades and vanes. Critical R&D needs of TBCs in future gas turbines have been described (in random order)³¹ as follows. Some of them will be briefly addressed below.

- Reduced thermal conductivity,
- Higher temperature capability,
- Improved hot corrosion resistance,
- Long-term thermal cycle testing in thermal gradient,
- Lifetime prediction modeling,
- Nondestructive inspection technique development,
- Coatings on ceramics,
- Process modeling/validation, and
- Modeling of long-term TBC system stability.

The key physical property of TBCs is their thermal conductivity, which characterizes the heat flow through the coating. A reduced thermal conductivity of the insulating ceramic increases the surface temperature of the turbine blades thus effectively improving the performance of the engine. Alternatively, a thinner coating would yield the same insulating effect. This directly translates into reduced weight which is particularly desirable for highly rotating components like turbine blades, because the extra weight reduction reduces creep rates and thus ultimately increases the maximum operation temperature of the component. Both considerations explain the strong efforts presently being placed on reduction of thermal conductivity of TBCs.³²⁻³⁴

With increasing maximum temperature requirements the thermal stability of the top coating becomes a concern. Today's state-of-the-art material suffers from both phase transformation and sintering, even at temperatures as low as 1100°C with a considerable increase of these effects at 1200°C and above. For instance, YPSZ TBCs produced by EB-PVD show decomposition of the metastable tetragonal t' phase into monoclinic and cubic phase upon cooling already after 200 h at 1200°C³⁵ which is a common temperature level for the outer layer of current TBCs in flight engines during. Since these transformations are associated with a volume change of about 4 to 5% they must be avoided in order to maintain the long-term integrity of the TBC system.

Knowledge of the interplay between properties and processing parameters is essential to optimize TBC lifetime. For EB-PVD coatings, the microstructure is primarily influenced by four basic processes: shadowing, surface diffusion, volume diffusion and desorption. The microstructural evolution of these coatings is roughly predicted in structural zone diagrams.^{36,37} Furthermore rotation of substrates during deposition adds another degree of freedom to the structural design.³⁸ This is of particular importance since coatings on 3-D parts like turbine vanes and blades necessitate substrate rotation during deposition.

Elevated substrate temperatures during EB-PVD processing cause higher density of the TBCs and higher hardness as well.³⁹ In addition the stabilizer type and content, degree of ionization of the vapor cloud, gas pressure, surface roughness, deposition rate and vapor impact angle are other parameters that influence the columnar microstructure of EB-PVD thermal barrier coatings.⁴⁰

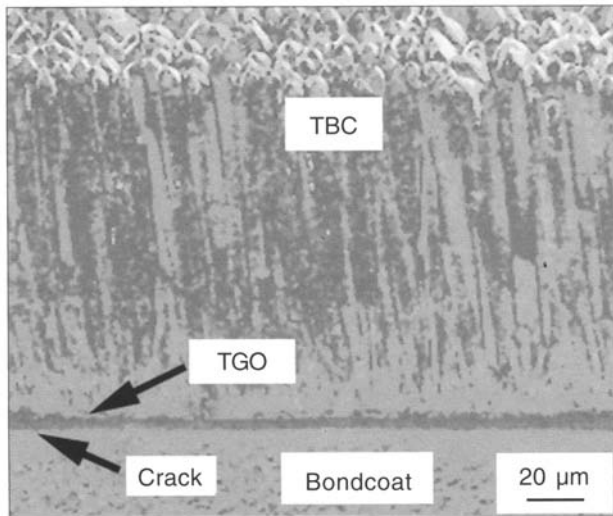


Fig. 5: Yttria partially stabilized zirconia TBC with strain-tolerant columnar microstructure fabricated by EB-PVD.

A more detailed TEM study gave insight on the evolution of the typical columnar EB-PVD structure. The first zirconia layers on top of the Al_2O_3 TGO nucleate and grow in an equiaxed manner which then turns into a small-diameter “c-shaped” structure as shown in Figure 6.⁴¹ The beaded c-shaped structure of the columns is formed due to the continuous change of vapor impact angle and amount of vapor particles that adhere on the surface during each revolution.^{42,43} At this point the layered structure develops as a result of the rotation during EB-PVD processing. Finally, in a growth selection process few columns develop into the favorable columnar-type structure as can be seen in the upper part of Figure 6. It is worth mentioning that the columns are highly textured,⁴¹ which might affect the on lifetime of TBCs on highly anisotropic single crystal Ni-base superalloys.

The environmental resistance of the bond coat plays a crucial role with regard to TBC lifetime and/or service temperature limitations. Due to high operating temperatures in aeroengines, oxidation rather than hot corrosion is a concern for TBC-coated airfoils, however, cooler parts of a component are potentially threatened by hot corrosion attack.^{44,45} In contrast to conventional applications, TBC systems cannot tolerate any spallation of the protective oxide scale during service, since scale spallation immediately leads to loss of the ceramic top coating. Therefore, for demanding applications in future generation aeroengines with further increased gas temperatures, advanced bond coats have to be developed to overcome the, under these conditions, insufficient spallation resistance of state-of-the-art bond coats.⁴⁶

From an oxidation standpoint, nickel aluminides doped with reactive elements such as Hf provide excellent oxidation resistance.⁴⁷ In the temperature range between 1000 and 1200°C their resistance against oxide scale spallation is significantly higher than that of conventional MCrAlY-type coatings. Platinum additions, usually used in practical applications for high performance state-of-the-art aluminide bond coats, beneficially influence spallation resistance of conventional nickel aluminide coatings but are less effective than reactive element doping, especially with Hf.⁴⁸ However, at present, there is no suitable technique available to reproducibly dope technical coatings with reactive elements. In terms of improved hot corrosion resistance, Cr seems to be the only element that effectively protects nickel aluminides against rapid attack. As low as 2 at.% Cr significantly reduces hot corrosion attack of NiAl. However, at oxidation temperatures beyond 1150°C, Cr additions decidedly accelerate oxide

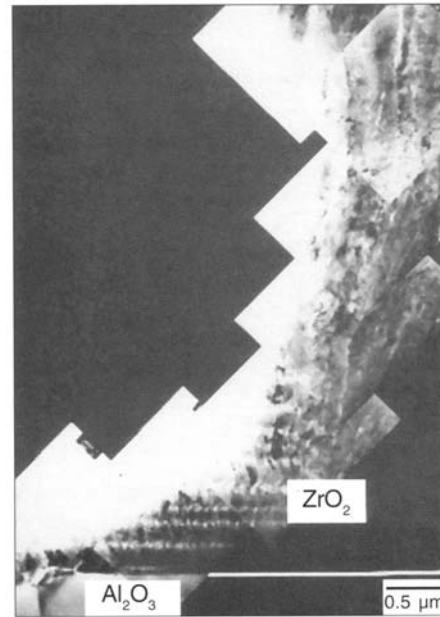


Fig. 6: TEM micrograph of the bond coat-TBC interface documenting the evolution of the columnar structure of EB-PVD thermal barriers.

scale formation rate and increase susceptibility to scale spallation.⁴⁹ Obviously, oxide scale adherence is essential for coatings. However, the data on nickel aluminides suggest that rather oxide scale adhesion and Cr are needed to provide both oxidation and hot corrosion resistance. At this time, it appears that combined hot corrosion resistance and exceptional scale spallation resistance is an unattainable goal for nickel aluminide coating performance. Future generations of aluminide bond coats will require careful compositional control to meet significant performance improvement requirements.

4.0 Conclusions

Surface modification plays an ever increasing role in aerospace applications. It leads to the reduction of production and maintenance costs, such as coatings for the corrosion protection of aluminum skinned aircraft. The increasing consciousness of environmental issues leads to significant additional developments. One example is the replacement of the current chromated coatings for aluminum skinned aircraft by coatings with low (possibly zero) concentrations of volatile organic compounds and nontoxic corrosion inhibitors. The service life time of civil and military aircraft and space structures (e.g. the Mir station) is continuously increasing mostly due to cost considerations. Surface modifications improving fatigue behavior will therefore be of remaining interest. Higher performance aerospace propulsion systems are based on weight reduction and increasing operation temperatures. Replacement of Ni superalloys by Ti alloys and titanium matrix composites for components operating at temperatures above 520°C reduces weight but depends on the successful development of oxidation protective coatings. Similar improvements of protective bond coats are required for the application of higher gas temperatures in the high pressure turbine section. Coatings and other surface treatments which give smart active response to changing mission targets are just at the early beginning of their development.

5.0 Acknowledgment

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In Situ Formation of Titanium Carbide by Reactive Plasma Spraying with Elemental Titanium Powder

Y. Tsunekawa, M. Okumiya, and A. Kogure
Toyota Technological Institute
2-12 Hisakata, Tempaku
Nagoya 468-8511, Japan
E-mail: tsunekawa@toyota-ti.ac.jp

Abstract

In situ composite coatings with titanium carbide (TiC) precipitates were synthesized by reactive RF plasma spraying using elemental titanium powder. The influence of methane (CH_4) concentration in the plasma gas on the TiC formation was examined at each processing step. The absorption of decomposed carbon into molten titanium droplets occurs during their flight in the plasma flame. Hence fine TiC precipitates which increase in volume with mixed CH_4 are recognized in sprayed titanium particles. The flattening ratio of splats impinged on a stainless steel substrate decreases with increasing premixed CH_4 concentration. The volume fraction of TiC precipitates in the titanium matrix composite coatings is approximately five times larger than that in sprayed particles, regardless of premixed CH_4 concentration. Hence, TiC formation is mainly determined by the splat deposition step, because the period exposed to the CH_4 mixed plasma flame is much longer than the flight time of droplets. The maximum volume fraction of TiC precipitates is approximately 30 vol.% in the coatings sprayed with the CH_4 mixed plasma.

1.0 Introduction

Plasma spraying is a surface modification process used to deposit hard coatings such as ceramics and their composites. Plasma spraying is characterized by (a) the formation of deposits with the same composition as spray material and (b) the rapid synthesis of coatings formed by the reaction of newly formed constituents with the operating gas. In the case of reactive DC plasma spraying, in situ reinforcements such as TiN ,¹ Ti_2AlN^2 and CrN^3 are formed during the spray process. The size and the volume fraction of in situ reinforcements affect the mechanical properties of coatings and can be controlled by changing the process parameters. However, the operating plasma gas as a reactant is limited to nitrogen in conventional DC plasma spray apparatus, because of the optimum gap distance for the generation of a discharged arc. Besides nitrides, in situ composite coatings containing carbides are formed by using CH_4 as a carrier gas for powder feeding,⁴ although the formation of carbides is limited to a small amount. In contrast, in the case of RF