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EDITORIAL

Thermal Spray for Extreme Environments

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Thermal spray coating processes are versatile techniques that can be used to protect or modify the surface of a substrate material in a variety of industrial settings. Many industries worldwide use this technology for various critical applications including corrosion and oxidation prevention; wear control against mechanisms such as abrasion, erosion and scuffing; heat insulation or conduction; electrical conductors or insulators; near-net-shape manufacturing; engineered emissivity; component repair; and other functional properties (Ref 1-5). The technological road map behind using a thermal spray coating technology is often a compelling one. For instance, the so-called sunset date for hazardous hard chrome plating (HCP) process through the implementations of EU directives such as 1999/13/EC (VOC), 2011/65/EU (RoHS), 2012/19/EU (WEEE), and EU regulation EC 1907/2006 (REACH) have pushed the market to seek alternative coating technologies, capable of replacing HCP. In particular, HVOF and HVAF thermal spraying and laser material deposition (LMD) have emerged as strong substitutes for wear applications, in which carbide composites impart high wear resistance at a relatively low investment cost (Ref 6).

This special issue of JTST relates to these key industrial applications for extreme environments, many of which were presented at the International Conference on "Advancements and Futuristic Trends in Mechanical and Materials Engineering" (AFTMME), organized by the Society of Materials and Mechanical Engineers (SOMME) at Panjab University, SSG Regional Centre, Hoshiarpur (India), November 15–17, 2018.

Next Generation Thermal Barrier Coatings (TBCs)

Aerospace and industrial gas turbine (IGT) applications account for about 60% of the overall global thermal spray market (Ref 7). Progress in both aircraft and stationary modern gas turbines is greatly dependent on the progress of heat and creep resistant materials, protective coatings, and thermal barrier coatings (TBC), See Fig. 1 (Ref 8). This market push will account for continued research and development (R&D) into a multitude of surface engineering programs.

In particular, the push for higher engine efficiency means requirements of higher turbine operating temperatures. Overlay TBC coatings are the most commonly used coatings in gas turbines. Since the mid-1970s, a two layer TBC consisting of an yttria-stabilized zirconia (YSZ) coating over a metal bond coating has practically been employed for many applications up to 1200 °C. Figure 2 presents a timeline for TBC development (Ref 9). There have been many R&D programs to improve TBCs; such as the selection of the zirconia-based ceramic, material development for the bond coat, as well as the deposition technology employed.

TBCs used in rotating elements of aircraft engines (i.e., turbine blades) must possess very high durability in complex thermomechanical loading conditions. The two methods, namely (1) atmospheric plasma spray (APS), and (2) electron beam-physical vapor deposition (EB-PVD), are well-established deposition methods for the ceramic top coat (Ref 10); the latter imparts better performance, but is costly (Ref 11). Another important progress is to employ the EB-PVD YSZ topcoat with a low-pressure plasma-sprayed bond coat, i.e., NiCrAlY bond coats on Inconel-617 superalloy. These are known as second generation TBCs (i.e., GEN 2 TBCs) and have existed since the 1980s. The most significant are new technologies that combine plasma spray and PVD/CVD; Low Pressure Plasma Spraying-Thin Film (LPPS-TF) as well as Plasma Spray Physical Vapor Deposition (PS-PVD) (Ref 12) make it possible to form a homogeneous ceramic top coat of TBC with desirable columnar structure (Ref 13).

Newly developed bond coats like aluminide and silicon, as well as top coat ceramic material such as rare-earth doped zirconia, zirconates, mullite, and perovskites, have improved the high temperature performance and resistance against calcium-magnesium-alumina-silicate (CMAS) attack. On the other hand, emerging thermal spray methods like suspension plasma spray (SPS) and solution precursor plasma spray (SPPS) offer exciting prospects. Yttrium aluminum garnet (YAG) coatings engineered by SPPS have exhibited properties like phase stability, sintering resistance, CMAS resistance, thermal cycle durability, thermal conductivity, and erosion resistance, offering the near-term potential of a 200 °C to benefit TBC technology (Ref 14). It is imminent that GEN 4 TBCs will incorporate new materials deposited by multi processes.

Hot Corrosion Resistance Applications

Hot corrosion prevention is another major application domain of thermal spray processes. Hot corrosion occurs from the combined effects of oxidation and reactions with contaminants, such as sulfur, sodium, and vanadium, to form a molten salt flux on the metal at elevated temperature. This accelerated metal surface corrosion destroys or disrupts any protective oxide. Rate of hot corrosion varies depending on temperature and environment, and several thermal coatings have been investigated to reduce the rate successfully. In this context, almost all the thermal spray generations including plasma spraying, detonation gun spraying, HVOF, and cold spraying have been used successfully depending upon the type of the component properties and geometry, chemistry and physical conditions of the environment of use, and economy. For instance, Bala et al. (Ref 15, 16) investigated the hot corrosion behavior of cold sprayed Ni–Cr coatings on SA–213–T22 and SA 516 boiler steels in a simulated boiler environment. It was observed that the uncoated boiler steels suffered intensive spallation in the form of removal of their oxide scales,

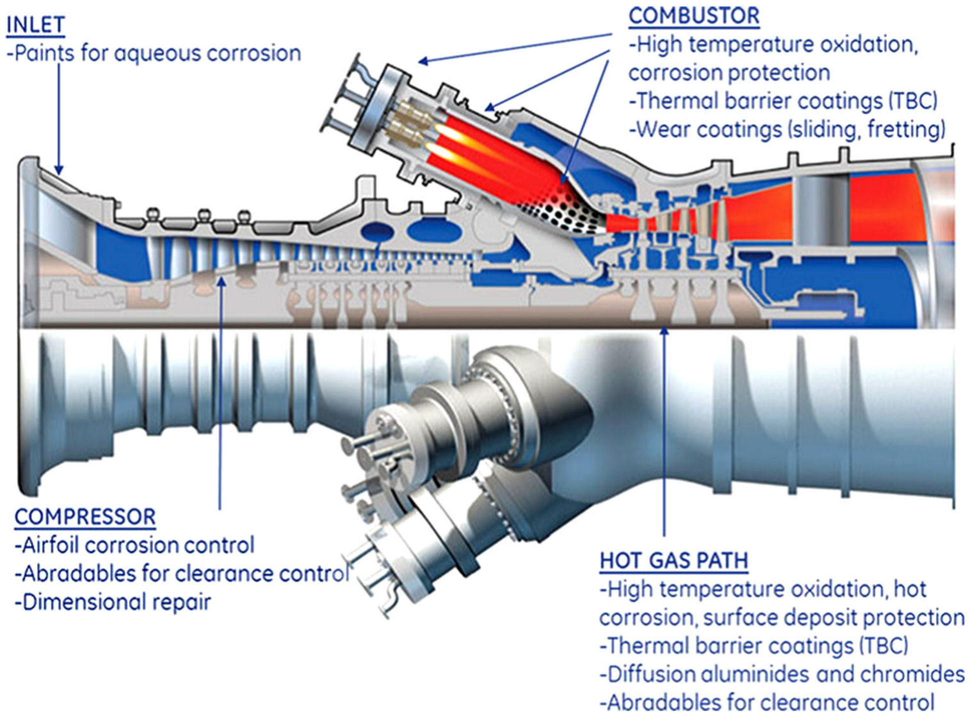

Fig. 1 Challenges in traditional gas turbine applications for thermal spray coatings with respect to turbine locations (Ref 8)

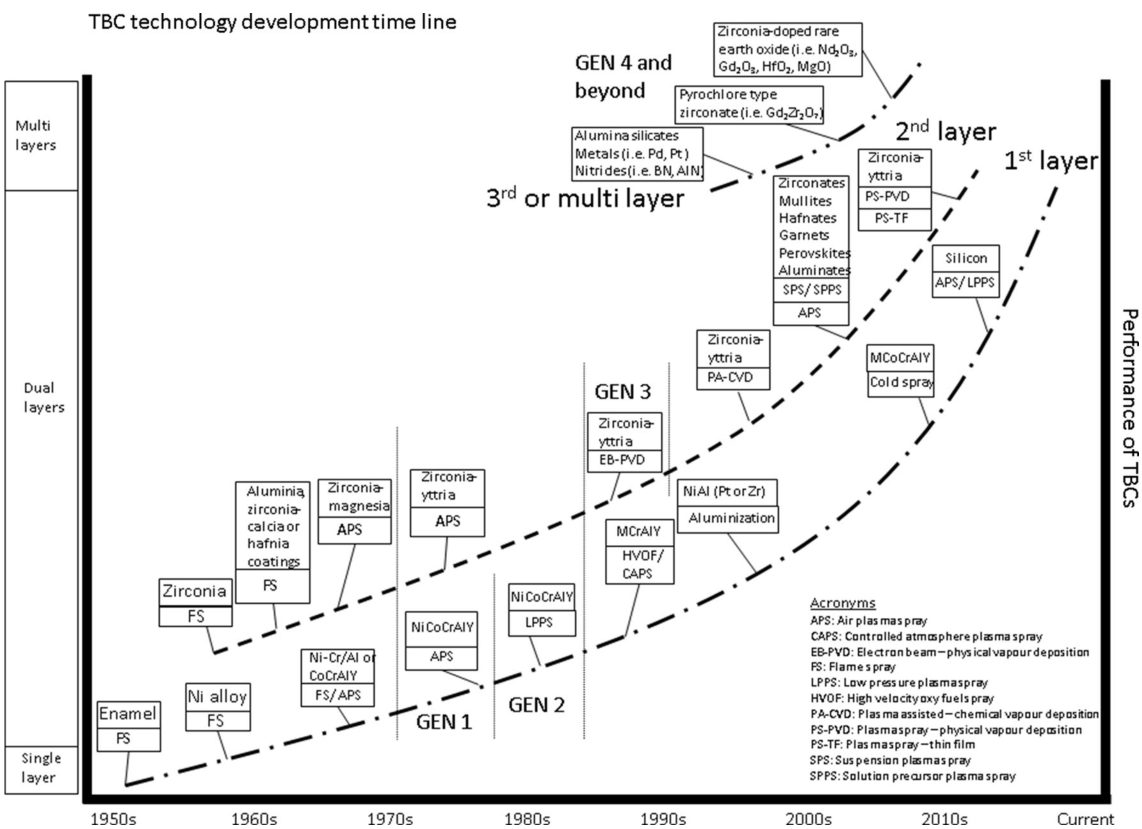

Fig. 2 TBC technology development timeline. Adapted from Ref 9

which became almost negligible after the deposition of the coating. The hot corrosion resistance in the coated steel was provided by the protective oxides and spinels of nickel and chromium. A diagram representing the hot corrosion mode for the cold sprayed Ni–50Cr coating on SA 516 steel exposed to Na_2SO_4–$60V_2O_5$ at 900 °C is presented in

Fig. 3 (Ref 15). The coated steels were also exposed to an actual environment, where they could sustain the erosion-corrosion attack successfully.

There are now plenty of similar literature and patent databases available on thermal spray coatings in the form of different *coating composition-thermal spray process-substrate* combinations, which are reported to be successful against hot corrosion. These databases could be referenced to select a suitable combination for a given application. A brief account of some of these studies is presented in Table 1; several such studies can be found in the open literature. In terms of microstructures, there are now several investigations on the development of nano-structured coatings by thermal spraying routes; for instance, Kumar et al. (Ref 17) reported the deposition of cold-spray nanostructured Ni–20Cr coatings on boiler steels, which showed exceptional erosion–corrosion (E–C) resistance in

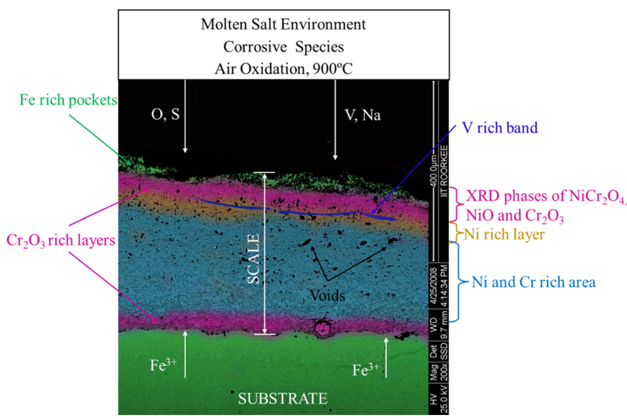

Fig. 3 Schematic diagram showing probable hot corrosion mode for cold sprayed Ni-50Cr coating on SA 516 boiler steel subjected to Na_2SO_4–60%V_2O_5 at 900 °C for 50 cycles (Ref 15)

an actual boiler environment (Ref 17). As we are moving towards super-critical and ultra-super-critical generations of boilers, the need for designing and manufacturing better and better coating systems is increasing; therefore, there is a tremendous scope for future research. In addition, there are several carbide-reinforced metallic compositions such as NiCr/Cr_3C_2 and NiCr/TiC, which are being investigated and found successful for hot corrosion applications, as discussed in the next section.

Hard Metal Carbide Composites for Extreme Environments

Hard metal or carbide composite thermal spray coatings are synonymous with the formation of hard, wear resistant coatings, across a diverse range of applications. The most widely employed composition is WC-Co, typically with 12-17 wt.% Co binder (Ref 22-25). It is used for ambient and low temperature conditions up to 500 °C (Ref 25), where wear resistance is the primary functional requirement, due to the extreme hardness and wear resistance of the WC phase. Under aggressive conditions in which corrosion becomes a significant factor, this composition is typically modified through the addition of Cr, e.g. WC-10Co-4Cr. The Cr may form alloys with the Co and thereby improve the corrosion and oxidation resistance of the metallic binder phase (Ref 23). However, in practice, Cr may also form part of the complex series of eta-phases (Co, $Cr)_XW_YC$, due to in-flight decarburization, in addition to alloying in the binder phase (Ref 22, 23), which may influence the ability to offer corrosion protection.

Under the most aggressive corrosion and/or oxidation conditions, Cr_3C_2-NiCr compositions become important.

Table 1 A comparison of cyclic hot corrosion behavior of Ni–20Cr coatings in molten salt environment at 900 °C for 50 cycles deposited by various thermal spray processes

Coating technique	Substrate	Parabolic rate constant, $K_p \times 10^{-10}$ g^2 cm^{-4} s^{-1}	Corrosion resistance multiplication factor (%) with reference to bare substrate	Protective phases	References
Cold spray	SA 516 boiler steel	52	87	NiO, Cr_2O_3	Bala et al. (Ref 15, 16)
	T22 boiler steel	140	76	NiO	
HVOF spray	347 boiler steel	0.30	76	NiO, Cr_2O_3, $NiCr_2O_4$	Kaushal et al. (Ref 18)
HVOF spray	ASTM SA210 GradeA1	11	90	NiO, $NiCr_2O_4$, Cr_2O_3	Sidhu et al. (Ref 19)
HVOF spray	Superni 75	2	69	Cr_2O_3, NiO, $NiCr_2O_4$, TiO_2	Sidhu et al. (Ref 20, 21)
	Superni 600	3	60	NiO, $NiCr_2O_4$, Cr_2O_3	

While Cr_3C_2 is not as hard as WC and, therefore, generates a lower wear resistance, the superior corrosion and oxidation resistance of Cr_3C_2, in combination with the superior oxidation resistance of the NiCr alloy binder over Co and CoCr, give this composite the best balance of properties for such extreme conditions. The ability to form a protective Cr_2O_3 oxide enables Cr_3C_2–NiCr coatings to be employed at temperatures up to 900 °C (Ref 25).

Critical to maximizing the functionality of all carbide composite thermal spray coatings is the ability to minimize in-flight degradation, particularly carbon loss. This typically occurs via two mechanisms—loss of carbide through carbide rebounding, and loss of carbon through chemical decarburization reactions (Ref 22, 23, 26). The latter has additional flow-on effects in addition to reducing the overall primary carbide content. Typically carbide composite powders become susceptible to decarburization as a result of dissolution of carbide grains into the molten metallic binder phase in-flight. The dissolved carbon can diffuse to the particle periphery to react with oxygen, or water vapor in combustion based thermal spray systems, to be lost as CO/CO_2. Furthermore, upon solidification the dissolved carbide elements become trapped in the binder phase, forming an amorphous or nano-crystalline supersaturated solid solution. This transforms the originally ductile binder into a considerably harder and more brittle material, reducing the critical toughening functionality required of the metallic binder and leading to a reduction in the wear resistance. As such, considerable efforts have been made to optimize deposition techniques and associated operating parameters, as well as powder morphologies, to minimize decarburization in-flight.

It is widely known from bulk hard metal manufacturing that the wear resistance of carbide composites increases with decreasing carbide size (Ref 27). However, most thermal spray powders utilize carbide grains in the range of 1-5 µm. A contributing factor to this is the critical balance between reducing the carbide size to improve wear resistance, while minimizing the negative effects of carbide dissolution, which increase dramatically as the carbide–binder interfacial area increases with decreasing carbide size. A number of works have investigated nanostructured WC based coatings (Ref 28-35), but with mixed results. High temperature processing tended to generate extensive decarburization and binder embrittlement, while low temperature processing conditions resulted in porous and poorly bonded coatings. However, encouraging developments in the production of nanostructured carbide composite coatings are being explored through the use of bimodal carbide distributions, the use of cold spray (Ref 28), and suspension HVOF spraying (Ref 32) technologies, as well as a novel shrouded plasma and heat treatment approach (Ref 26), Fig. 4 (Ref 36).

A further characteristic that must be considered in the durability of carbide composite coatings in extreme environments is the change in functionality (both the wear and corrosion resistance) with time at high temperature, due to compositional and microstructural developments. Carbide composite thermal spray coatings are typically metastable in the as–sprayed condition due to in-flight carbide dissolution and rapid solidification upon impact. With extended duration at high temperature the coating composition transforms, tending towards the equilibrium composition for the as sprayed elemental make up, i.e., taking into account changes in the elemental composition due to in-flight oxidation and decarburization (Ref 33). Furthermore, the microstructure is also subject to change as the interfacial area between the phases is reduced via Ostwald ripening. These changes, in turn, have been shown to have a significant effect on the oxidation characteristics of the composite (Ref 34), the wear resistance, and wear mechanism (Ref 35), as well as the combined response to both wear and oxidation (Ref 37). Furthermore, a largely unexplored area of research is the interaction between the coating and substrate during long-term high temperature exposure. Recent work characterizing the interdiffusion between an HVOF Cr_3C_2-NiCr coating and an Alloy 625 substrate has highlighted the critical role that element diffusion between the systems, as well as that within each system as a result of interdiffusion of selected elements, plays in modifying the near interface composition and microstructure, and, therefore, the mechanical and oxidation resistant properties, of both the coating and substrate (Ref 36) (see Fig. 5) (Ref 36).

While WC-Co, WC-10Co-4Cr, and Cr_3C_2-NiCr have become well-qualified composite coating compositions industrially, work continues to expand the portfolio of deposition techniques and compositions within the sector. Novel compositions incorporating mixed carbide, such as

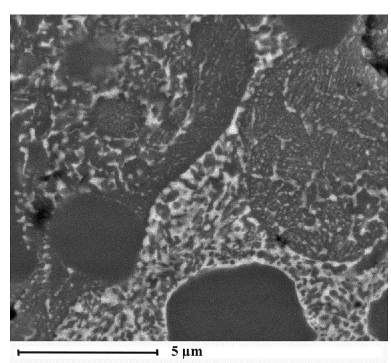

Fig. 4 Novel carbide composite microstructure formed after high power plasma spraying to generate large degrees of carbide dissolution, followed by heat treatment at 780 °C for 1 h to precipitate the Cr_3C_2 carbide grains (dark contrast phase) within the NiCr binder (bright contrast phase) (Ref 36)

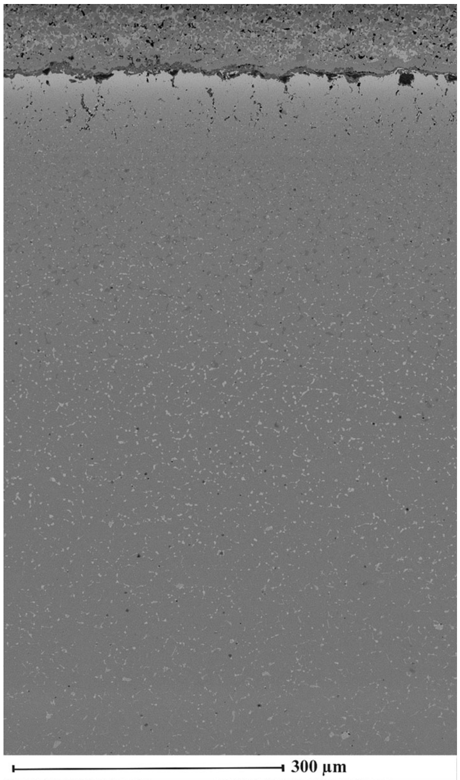

Fig. 5 Back scattered electron image of the interface zone between an HVOF sprayed Cr_3C_2-NiCr coating (top) and an alloy 625 substrate (bottom). Cr diffusion from the substrate to the coating generated a continuous interfacial carbide layer within the coating (continuous light grey contrast band along the coating side of the interface). Diffusion of carbon from the coating, combined with back diffusion of carbon within the substrate, led to precipitation of mixed Mo and Nb carbides within the substrate to depths of more than 300 µm (Ref 36)

WC-Cr_3C_2-Ni and WC-W_2C-Ni (Ref 23, 25), as well as (Ti, Mo)(C, N)-NiCo (Ref 23), are being explored. Similarly, bespoke binder compositions for selected industrial applications are moving beyond Co, CoCr, and NiCr to consider CoNiCrAlY, NiMoCr, and Alloy 625 binders (Ref 25, 38), together with the revision of interest in multiphase "atomized" composites incorporating chromium carbides and both Cr-rich and Ni-rich binder phases.

Concluding Remarks

Thermal spraying is a group of promising technologies used to develop high performance coatings for several extreme environments, some of which are highlighted in this editorial note. However, there are several other extreme environment sectors in which thermal spray coatings can be used, such as in defense, space, hydropower, chemical process plants, and nuclear applications. There are ever-increasing and compelling demands for improvement in efficiency of several engineering systems for which the limits of process parameters such as temperature, pressure, and environmental severity are increasing; therefore, the demand for high-performance materials are increasing. In such applications, thermal spraying can provide the possibility of deposition of newer materials with high quality, along with high production rates and flexibility of on-site applicability. Therefore, research and the business of thermal spraying show great potential for further growth in surface engineering and additive manufacturing spaces. This special issue of JTST concentrates on Thermal Spray Applications for Extreme Environments. The selection of manuscripts within this issue covers a broad spectrum of interests, most notably applications, thermal spray processing, and new materials development. This special issue has 14 contributions addressing the fundamental needs of industrial sectors that operate in extreme environments. The issue presents a balanced mixture of different aspects of thermal spraying, including characterization, fundamental research studies, post-treatments, and performance evaluation for various applications such as boilers, hydro-turbines, gas turbines, and hydrogen storage. We hope that the issue will add value to the knowledge base of readers of JTST.

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