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REVIEW

A Comprehensive Review of Corrosion Resistance of Thermally-Sprayed and Thermally-Diffused Protective Coatings on Steel Structures

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Abstract Protective coatings are widely utilized to promote corrosion resistance of the surfaces of steel components that are used in various industrial applications. Different surface engineering methods such as thermal spraying and thermal diffusion techniques can be used to fabricate these protective coatings. Thermal spraying processes have received significant attention due to their ability to deposit a variety of materials. Several metals such as zinc-, aluminum-, nickel, and chromium-based materials and their alloys can be deposited using thermal spraying processes to enhance the corrosion resistance and prolong the service life of steel components. On the other hand, technologies based on thermal diffusion techniques are emerging due to their unique deposition features, which alleviates the issues of cracking and delamination typical of thermal-sprayed coatings, as well as their ability to protect inaccessible and complex components such as the inner surface of long tubing and pipelines. This work is a comprehensive review on short and long-term corrosion resistance of the most effective and commonly-used coatings deposited by a variety of surface engineering techniques to protect steel structures. Moreover, the effect of the spraying process, the addition of alloying elements on the corrosion resistance of these coatings has also been reviewed in this study.

Keywords coatings · corrosion protection · steel · thermal diffusion · thermal spraying

Introduction

Carbon steel is one of the most widely used engineering materials, accounting for approximately 85% of the annual steel production worldwide. Although carbon steel alloys possess relatively high strength, they have limited corrosion resistance, which demands further surface treatment such as coatings to protect the surfaces when they are exposed to harsh environments. Coatings have historically been developed to protect surfaces from adverse chemical and physical interactions with the environments and mitigate damages caused by corrosion and other mechanical damages. Developing a coating with good quality has been a major goal for industrial applications because coating degradation is typically followed by failure of the components and system (Ref 1). Various technologies have been used to develop suitable protective layers on the steel surface, with the type of layer depending on the environmental condition from which protection is sought. Earlier coating methods have mainly included electroplating, electro-less plating, and hot-dip galvanizing. The next generation of coating technologies has involved physical and chemical vapor deposition, brazing, weld overlays, thermal spraying, and thermal diffusion techniques.

This review article presents a comprehensive review of the most recently published studies dealing with the corrosion mechanisms of thermal-sprayed and thermal-diffused coatings that were deposited on steel substrates. Different types of thermal-sprayed coatings and their corrosion mechanisms were investigated, evaluated, and compared. Thus, the potential areas and the knowledge

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gaps that demand future research are identified based on the previous findings in this area. To this end, the corrosion behavior of zinc, aluminum, and their alloys deposited by arc spraying, cold spraying, flame spraying, and high velocity air fuel (HVAF) techniques for room temperature applications have been studied here. The corrosion mechanisms of these alloys after long-term and short-term exposure to various corrosive environments, and the effect of alloying elements and spraying parameters on their corrosion behavior were thoroughly investigated in this study. The high temperature corrosion mechanism of thermally sprayed nickel, chrome, tungsten carbide, and their alloys have also been profoundly studied in the present work. Moreover, the corrosion resistance of thermal-sprayed ceramics-based coatings such as partially-stabilized zirconia and ceria against molten salt corrosive attack was studied. Finally, the corrosion resistance of protective coatings fabricated by thermal diffusion techniques was investigated. In this regard, low- and high-temperature corrosion resistance of thermal-diffused boronized, aluminized, and chromized steel substrates that were exposed to various corrosive environments was studied.

Surface Engineering Techniques

Thermal Spraying Technologies

There has been a growing interest in using thermal spray techniques due to their ability to produce coatings with superior bonding strength, high density, and low oxide contents. Thermal spray is a generic term for a group of processes in which metallic, ceramic, cermet, and some polymeric materials in the form of wire, rod, or powder are fed into a chamber, torch, or gun to be heated near or above their melting points and then accelerate toward a substrate to deposit a coating (Ref 2). The schematic of thermal spray process has been illustrated in Fig. 1. The major thermal spraying techniques are air or vacuum plasma spraying (APS, VPS) by direct current (D.C), radio frequency (R.F.) discharge-generated plasma, plasma transferred arc (PTA), wire (electric) arc spraying, flame spraying, high velocity oxy-fuel (HVOF), high velocity air-fuel (HVAF), denotation gun (D-gun), and cold gas-dynamic spraying (CS). Among these methods, flame spraying, electric arc spray, and plasma arc spray have been the most commonly used techniques to deposit corrosion resistant coatings on steel substrates in recent years (Ref 2-4).

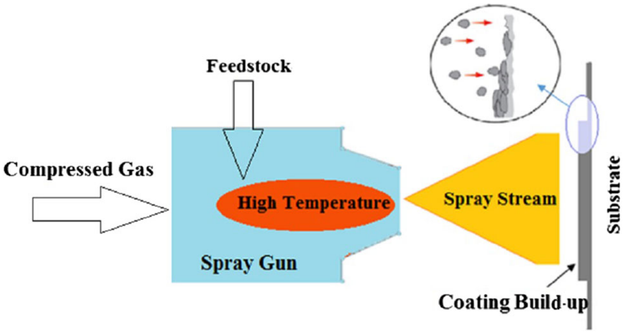

Fig. 1 Schematic of the thermal spraying process

Flame spraying is one of the oldest thermal spraying techniques with high deposition rates and at high efficiency (Ref 5). This technique uses combustible gases as the heat source to melt the coating materials in the form of wire, rod, or powder. Acetylene, propane, methyl-acetylene-propadiene, and hydrogen, along with oxygen are the most well-known gases used in this technique. Flame spraying can be conducted in low velocity condition which is capable of spraying metals and alloys using both powder and wire feedstock. Compressed air will help to accelerate molten materials in flame spraying technique (Ref 2). Flame spraying can also be conducted at high velocity and HVOF is the most well-known technique in this category. HVOF uses a combination of oxygen with various fuel gases including hydrogen, propane, propylene, and kerosene. The powder particles are heated in a temperature range of 2500-3200 °C inside a combustion chamber and consequently soften and turn to molten particles which are accelerated toward the substrate with very high velocity 1500-1800 m/s (Ref 3). HVOF is capable of depositing coatings with high density and high bonding strength due to evolution of mechanical bonding between the coating and the substrate.

Electric arc spraying, which is also known as twin-wire arc, arc spray, or wire arc spraying has been commercially introduced to the industry in early 1960s (Ref 3, 4). Unlike the other thermal spraying techniques, in which feedstock particles were indirectly heated by hot gas jet, in electric arc spraying process, direct current (DC) is used to strike between two consumable electrode wires to effect direct melting. An electric arc is formed in the gap between the wire tips as the two wires are continuously fed together into the system. There is a high velocity air jet located behind the intersection of the wires which shears away the molten particles and propels them toward the substrate. The velocity of in-flight particles in arc spraying technique could range within 0.8-1.8 m/min which is much lower than that of HVOF.

Plasma arc spraying is one of the most convoluted and versatile thermal spraying techniques using DC electric power to generate a stream of high temperature ionized plasma gas to heat, melt, and carry particles toward substrate (Ref 6, 7). The temperature range provided by this method is within 6000-15,000 °C, which is above the melting point of any known material (Ref 3).

Cold gas-dynamic spraying (cold spray) is a process in which powders are accelerated by a supersonic gas jet (300-1200 m/s) towards the substrate. This is the only thermal spraying technique which does not involve extreme high temperature and melting of the feedstock materials and the spraying is performed in temperature ranges below the melting point of the powders. Thus, this method is only suitable for deposition of deformable and ductile materials. Cold spraying systems are available for operation at low and high pressures ranging from approximately 650 kPa to 4 MPa (Ref 8-10). Therefore, by using the cold spray technique, the detrimental effects inherent in high temperature deposition such as melting, oxidation, evaporation, build-up of residual stress during solidification, and recrystallization is expected to be minimized (Ref 11).

Thermal Diffusion Technologies

Thermal diffusion technology is an innovative surface engineering process that can be utilized to modify surfaces to provide protection to industrial components with different sizes and shapes, especially pipelines and tubing with a high length-to-diameter ratio, against harsh environmental conditions (Ref 12, 13). Thermal diffusion technology has been successfully employed to fabricate thin, hard, and corrosion and wear resistant layers of carbides, borides, aluminides, and chromides on the surface of steel substrates (Ref 14, 15). In this regard, study and review of the corrosion and wear resistance of thermal diffusion coatings can pave the way for further developments in providing reliable and long-lasting protective surfaces for the steel substrates in waste-to-energy plants and in the Oil and Gas industry.

The thermal diffusion process, which is primarily based on chemical vapor deposition (CVD) principles, comprises the chemical modification of steel substrates by exposing them to the vaporized form of certain atoms and species (e.g., boron) at elevated temperatures of approximately 800-1100 °C, which consequently leads to formation of new inorganic hard substances through the diffusion of these active gaseous species into the preheated substrates (Ref 12). In other words, thermal diffusion coatings are formed by exposing preheated steel substrates to specially selected powder mixes (usually boron-rich species) and with diffusion of the vaporized phases of these atoms into the metal substrate at high temperatures. As a result, high-temperature interaction of these diffused atoms with the metal substrate produces new consolidated phases (Ref 13, 16, 17). Consequently, depending on the deposited active vapor atoms, new compounds such as borides or intermetallides (e.g., aluminides and chromides) are formed on the surfaces of the steel substrates. Thermal diffusion technology is based to diffusion processes; therefore, the diffusion laws are applicable to the formation of the coating. For instance, the boronizing process is primarily formed through two major mechanisms, namely, diffusion of the boron selected atom through the vacancies at elevated temperatures and interstitial diffusion. Figure 2 shows the schematic of these two major mechanisms in boronizing thermal diffusion on a steel substrate (Ref 18).

Corrosion Mechanisms

Various types of corrosive mechanisms may occur on the coatings that are developed by thermal spraying and thermal diffusion techniques including uniform, localized, and galvanic corrosion. The uniform corrosion, wherein the average rate of corrosion on the surface is almost uniform, has been responsible for less than 30% of industrial failures. Localized corrosion, on the other hand, contributes to about 70% of the failures in structures and components (Ref 19). Galvanic corrosion takes place when there is a considerable difference in the electronegativity of the materials of the coating and the substrate while they are in contact with an electrolyte.

The protection of carbon steel from corrosion is achievable by either anodic (e.g. nickel) or cathodic coatings (e.g. zinc or aluminum). In the case of anodic coatings, no discontinuity in the deposition could be tolerated due to formation of galvanic cell and accelerating the corrosion in the steel part (Ref 19, 20). Selective corrosion may occur when the alloys with noble and reactive components such as WC-Ni and WC-Co with varying quantitative compositions exposed to corrosive environment. Inappropriate heat treatment is another reason for depletion of specific element. For instance, chrome carbide precipitation at grain boundaries of stainless steel could result in Cr-depleted zone with less corrosion protection (Ref 20). Heterogeneous surface of the metals with step, kink, inclusion, cracks, and porosity may also accelerate the corrosion rate in metallic structures (Ref 21).

Elevated temperatures have usually resulted in more severe oxidation or sulfidation in materials. Hot corrosion has been considered as a two-stage process comprising incubation period exhibiting a low corrosion rate, and propagation of the actual corrosion (Ref 22). The incubation period has been referred to formation of a protective oxide scale and acceleration has occurred when the protective layer broke down. Various mechanisms have been proposed to explain the corrosion acceleration phenomenon. The most widely accepted corrosion mechanism at elevated temperature is salt fluxing, in which oxides

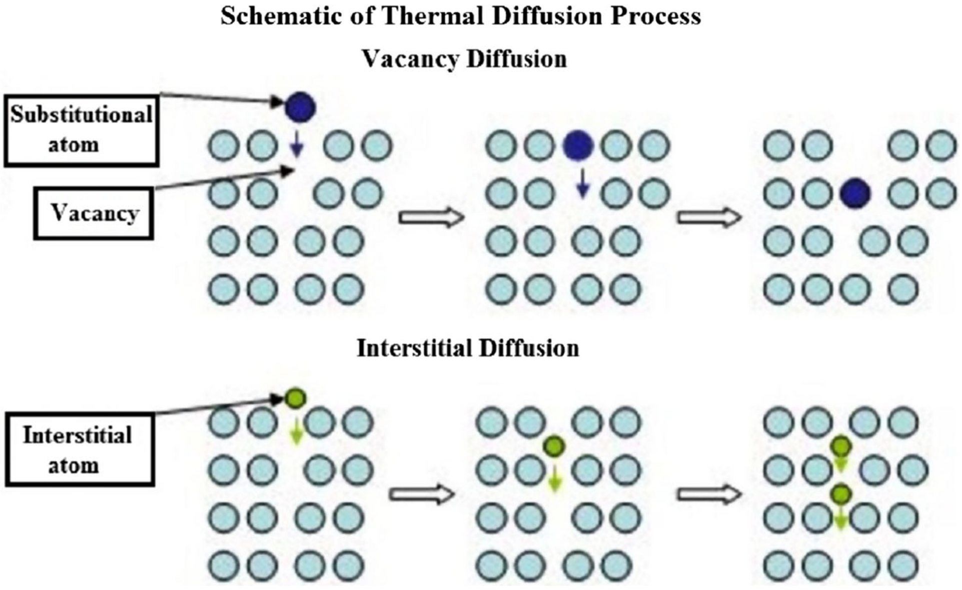

Fig. 2 Schematic of the primary mechanisms of formation of thermal diffusion coatings (Ref 18)

dissolve on the surface as anodic species (basic fluxing) or cationic species (acidic fluxing), depending on the salt composition (Ref 21, 22). Acidic salts are usually high in SO_3 and basic salts are low in SO_3 (Ref 20). Since, corrosion formation mechanism strongly depends on the type of materials, a complete study in this area is needed to examine the occurrence of corrosion in different coating materials. Therefore, the corrosion mechanisms in several common coating materials on steel structures have been explored in this study with special attention to aluminum, zinc, and their alloys, since they are among the most heavily utilized anti-corrosion coatings to protect carbon steel at ambient temperature (Ref 22-74). Nickel, chrome, tungsten carbide, and their alloys, on the other hand, were the focus of this study, in the case of high-temperature corrosion, due to their wide application to extend the service life of steel in elevated temperature service conditions (Ref 75-83).

Corrosion of Thermal-sprayed Coatings at Ambient Temperature

Table 1 has been provided to compare the corrosion mechanism of thermally sprayed coatings deposited on steel in ambient temperature. It has been tried to include coatings deposited by the most common thermal spray techniques such as D-gun, flame spraying (HVOF and HVAF), APS, VPS, atmospheric plasma spraying + quenching (APS + Q), cold spraying, and wire arc spraying. The corrosion behavior of the coating samples was evaluated using electrochemical impedance spectroscopy and polarization potential experiments in this table. The important parameters defined for indication and comparison of corrosion behavior of various materials are corrosion potential (E_{corr}) and corrosion current density (I_{corr}) which are listed in Table 1. Detail information regarding the corrosion mechanism of different coating materials shown in Table 1 will be discussed in next sections.

Aluminum-Based Coatings

Aluminum and its alloys have been known as one of the good candidates for protecting steel against corrosion due to their anodic nature compared to steel. In fact, aluminum coatings act as sacrificial protection to the steel substrate by formation of passive layer which protects both coating and substrate from further corrosion propagation. Plasma spraying, wire arc spraying, cold spraying, and flame spraying are the common techniques for deposition of aluminum-and its alloys to protect base materials against corrosive environments, mostly at lower temperatures (Ref 34-38, 52-56).

Long-term room temperature corrosion mechanism of arc sprayed aluminum wires with 99% purity deposited on steel samples has been evaluated by Esfahani et al. (Ref 34). The coating samples were tested after being immersed in 3.5 wt.% NaCl solution and at the neutral salt spray test condition for 1500 h. The coating contained about 7 vol.% porosity and its corrosion behavior was significantly influenced by the amount of exposure time. By increasing the time of immersion, the electrolyte penetrated through the pores and Warburg impedance observed indicating the corrosion was strongly under diffusion control. Further increase of exposure time could plug the defects by corrosion products (mainly comprised of Al_2O_3 and $Al(OH)_3$)

Table 1 Electrochemical behavior of thermal sprayed coatings deposited on steel at room temperature

Coating material	Coating method	Corrosive solution	E_{corr} (mV)	I_{corr} (μA/cm^2)	Observations
Ni-based					
NiTi	APS + Q	3.5%NaCl	− 600	3.3	High level of micro-crack and porosity. Corrosion occurred in internal coating (Ref 23). APS + Q: Air Plasma Spraying + quenching
	VPS	3.5%NaCl	− 177	0.052	More noble corrosion potentials and lower I_{corr} than that of APS + Q coating due to higher interlamellar cohesion and lower porosity and crack level (Ref 23)
	HVOF	3.5%NaCl	− 88 to − 470	0.085 to 0.3	
	APS	3.5%NaCl	− 320	2	More oxide phases, including TiO, and micro-cracks compared to HVOF coating (Ref 23)
NiCrBSi	HVOF	3.5%NaCl	− 75	14.6	Corrosion along the particles boundary, no change in their morphology (Ref 22)
	HVOF	3.5%NaCl	− 268	0.2838	High amount of corrosion products (Ref 24)
Cr-based					
Cr_2O_3	APS	3.5%NaCl	− 550	2000	No protection from the coating due to high porosity (Ref 25)
Cr_3C_2 + NiCr	D-gun	3.5%NaCl	− 600	500	Better protection than plasma sprayed Cr_2O_3 due to smaller porosity size (Ref 26)
Cr_3C_2-NiCr	HVOF	3.4%NaCl	− 210	...	High amount of corrosion product at coating/substrate interface and reduce in corrosion resistance after 12 h (Ref 26)
WC-based					
WC-12Co	HVOF	5%H_2SO_4	− 400	10−100	Dissolving the W and Co elements and formation of hydroxides and oxides and poor corrosion resistance (Ref 27, 28)
WC-17Co	HVOF	3.5%Na_2SO_4	− 330	0.7	Formation of CoO and WO_3 and increase in pit depth to 16 μm after 30 days of exposure (Ref 29)
WC-10Co-4Cr	HVOF	Sea water	...	3-9	Severe depletion of hard particles contains WC from the coating (Ref 30)
WC-10Co-4Cr	HVOF	5%NaCl	− 220	0.1	Less micro-galvanic/crevice corrosion than WC-Co (Ref 31)
WC-10Ni	HVOF	5% H_2SO_4	...	...	Selective corrosion of Ni binder and falling-off the WC particles after long time exposure (Ref 32)
WC-12Ni	HVOF	5%NaCl	− 260	60	Red rust spot formation occurred in the longer time compared to WC-20Cr_2C_3-7Ni and WC-10Co-4Cr coatings (Ref 33)
Al-based					
99%Al wire	WAS	3.5%NaCl	− 1030	5	Formation of passive layer made of Al_2O_3 and $Al(OH)_3$ by increasing the exposure time (Ref 34)
Al-Al_2O_3	WAS + PEO	3.5%NaCl	− 370	3.5-4.5	Dense coating and excellent corrosion behavior (Ref 35)
Al-Al_2O_3	CS	3.5%NaCl	...	...	High adhesion bonding strength (Ref 36)
Al-5 Mg	AS	3.5%NaCl	− 1070	1	Better corrosion resistance than Zn-Al alloys (Ref 37)
Al-Zn-Si	HVAF	3.5%NaCl	− 946	2.6	Self-sealing nature and good cathodic protection (Ref 38-42).
Al-Zn-Si-RE	HVAF	3.5%NaCl	− 965	36.54	Five steps during the corrosion: pitting-dissolution-redeposition, activation corrosion, cathodic protection, physical barriers formed by corrosion products, and the coating failure (Ref 40, 41).
Al-Zn-Si-RE	WAS	3.5%NaCl	− 965	36.54	Effective cathodic protection and self-sealing behavior (Ref 40, 41)
85Al-14.5Zn-0.5Zr	WAS	Sea water	− 1884 to − 984	1-10	Two reactions: concentration polarization by the reduction of dissolved oxygen, and active polarization by hydrogen gas generation (Ref 42).
Al_2O_3-13TiO_2	APS	6%Na_2SO_4	...	...	Corrosion occurred on the steel substrate due to high porosity level through which the electrolyte reached out to the surface and caused the corrosion (Ref 43)

Table 1 continued

Coating material	Coating method	Corrosive solution	E_{corr} (mV)	I_{corr} (μA/cm^2)	Observations
Alumina-13Ti with Sealant	APS	3.5%NaCl	− 220	1.9	APS deposited coating sealed with sealants such as phenol or epoxy has lower chance of existence of interconnection with the substrate due to lower porosity level compared to unsealed APS deposited alumina (Ref 44)
Zn-based					
99.5%Zn	CS	3.5%NaCl	…	28.24	As-coated zinc showed a high sacrificial nature (Ref 45).
99.5% Zn,	CS	3.5%NaCl	…	4.10	post-heat treated was beneficiary to the microstructure (Ref 45)
Zn-15Al	WAS	3.5%NaCl	− 1112	40.41	Lower porosity level compared to Zn-30Al and better corrosion resistance (Ref 46).
Zn-15Al	FS	Marine solution	− 1020	…	Improved cathodic protection, but lower long-term (after 30 days) durability compared to pure Al coating (Ref 47)
Zn-15Al	HVAF	SRB	− 1040	3.69	Corrosion of surface at first place, formation of ZnS and plugging the pores at the second stage (Ref 48)
Zn-Mg-Al	WAS	5%NaCl	− 992	2.08	Formation of dense corrosion products, clogging the pores and slowing down the corrosion (Ref 49)
Zn-Al-Mg-RE	HVAF	5%NaCl	− 1010 to − 1124	26.66-53.96	Better corrosion behavior than Zn-Al-Mg due to the microstructural refinement of coating by adding RE (Ref 50)
Zn-Al-Mg-RE-Si	WAS	3.5%NaCl	− 687.3	30.9	Self-sealing behavior due to formation of $Al_{3.21}Si_{0.47}$ and $Mg_3Al_2(SiO_4)_3$ (Ref 51)

and hindered higher penetration of the electrolyte into the coating. The microstructure of Aluminum coating before and after corrosion test (after 44 days) is shown in Fig. 3(a) and (b).

The effect of different thermal spray techniques comprising flame spraying and electric arc spraying on corrosion resistance of aluminum coating deposited on grade C steel substrate has been studied by Regina et al. (Ref 52). Both flame and arc sprayed coatings were exposed to saline mist inside a chamber simulating a marine atmosphere for 4000 h. Although both coatings could reduce corrosion formation and its propagation on the steel to some extent, better protection was provided by arc sprayed coating since the aluminum oxide/hydroxide phases persisted in the microstructure for longer exposure time during the salt spray corrosion test. Different corrosion performances of the thermally sprayed coatings were observed due to formation of different corrosion products after exposing to the marine solution. These corrosion products were mainly bayerite, boehmite and gibbsite in the flame sprayed coatings while aluminum, boehmite, and bayerite phases were formed in the case of arc spraying deposited coatings. (According to the work published by Han et al. (Ref 54), an increase in the thickness of the arc sprayed Al coating deposited on STS 304 steel could result in even higher corrosion resistance while exposed in sea water for 1260 h of exposure time.

Corrosion resistance of Al 7075 coating deposited by cold spraying technique on steel substrates using both air and nitrogen as secondary gas has been studied by Irissou et al. (Ref 53). It was concluded that cold spray process was more robust than the arc spray due to less complexity of spraying process that facilitated easier optimization of the coating properties to improve the corrosion protection.

Al/Al_2O_3 Coating The passive nature of alumina (Al_2O_3) has made it one of the most effective and commonly used coatings to protect steel from pitting corrosion because it can provide more uniform protective layer, which is less deteriorated during service (Ref 35-44, 55-61). Effect of Al_2O_3 fraction on corrosion resistance of Al-Al_2O_3 coating deposited by cold spray on steel substrate being exposed to salt spray (3.5 wt.% NaCl) for 1000 h has been studied by Irissou et al. (Ref 36). It was found that addition of Al_2O_3 to the pure Al powder could improve the coating deposition rate. The optimal deposition efficiency achieved with addition of ~ 30 wt.%Al_2O_3 to the feedstock powder. The bonding strength between Al and Al_2O_3 phases was also improved by increasing the fraction of Al_2O_3/Al.

Weichao et al. (Ref 36) suggested that a combination of arc spraying and plasma electrolytic oxidation for Al_2O_3/Al coating deposition on steel could significantly enhance the corrosion resistance. In this work, Aluminum alloy,

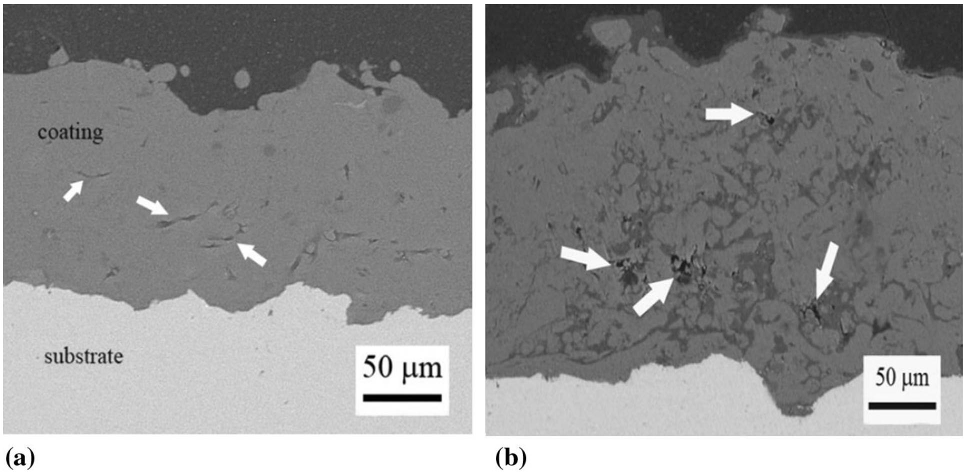

Fig. 3 Aluminum coating (a) before, and (b) after corrosion test (Ref 34)

A7, was deposited on Q235 steel by arc spraying technique, thereafter, it subjected to plasma electrolysis oxidation (PEO) in an aqueous electrolyte containing 5 wt.%NaOH and other additives (pH ~ 11.8). They observed that the duplex coating mainly composed of α-Al_2O_3, γ-Al_2O_3, θ-Al_2O_3 performed as a promising barrier for protection of steel substrate, while immersed in a 3.5 wt.%NaCl solution for 1 day.

In very few articles, the cold spraying technique has been used for deposition of aluminum alloys as corrosion protective layers. Irissou et al. (Ref 36) investigated the corrosion resistance of cold sprayed Al-Al_2O_3 powder in various mixture compositions (7, 10, 20, 30, 50, and 75% mass fraction Al/Al_2O_3) on steel substrates. They have reported that the addition of Al_2O_3 to the pure Al powder helped with improvement of the coating deposition efficiency and adhesion of the coating on the substrate. Optimal deposition efficiency was obtained at 30% of Al_2O_3 in the starting powder. Cold spray resulted in a very high bonding strength, ~ 60 MPa, and led in an effective corrosion protection against salt spray (3.5% NaCl) environment.

The microstructure of high-temperature thermal-sprayed deposited coatings tends to be such that the presence of three-dimensional defects such as porosity undermines the corrosion performance of aluminum coatings (Ref 34). The use of cold-spraying, however, results in denser coatings in which the reduction or absence of pores reduces or eliminates the propensity for penetration of corrosive media into the coating and pathways to the substrate. Further, given the relative low temperature operating conditions of the cold spray process, thermally-induced microstructural phase changes are limited or do not occur, which limited the occurrence of other auxiliary corrosion reactions. This was shown by Irissou et al. (Ref 53) in their work with Al 7075 coating. The development and use of Al/Al_2O_3 metal matrix composite coatings has not only resulted in improved deposition efficiency during the fabrication process (Ref 36), but the presence of the reinforcing hard Al_2O_3 phase served to consolidate the Al metal matrix and reduce the coating porosity. Thus, in addition to improved cohesive and adhesive strength of the metal matrix composite coatings, the reduction of coating porosity and fluid penetration pathways through the coating resulted in improved corrosion resistance of the coatings. The application of other thermal spraying methods, which include melting of feedstock aluminum, could introduce oxide phases to the coating microstructure. This is mainly due to the in-flight oxidation on the outer surface and possible penetration of oxides into the core of molten particles (Ref 34). Upon impact, flattening, and solidification, those oxide layers could end up inside splats or at their boundary regions, which results in decrease of the adhesion between coating and substrate and between the splats. This results in deterioration of corrosion resistivity in aluminum-based coatings.

Al-Mg Coating Magnesium is usually added to Al-based alloys to enhance the durability in corrosive environments for long time exposure as well as improve the mechanical properties such as hardness (Ref 37, 55, 56). Effect of variation of Mg content (Al, Al-3 wt.% Mg, Al-5 wt.% Mg) on cavitation damage behavior of arc sprayed Al-Mg coating on a mild steel in sea water, at room temperature after 90 min, has been studied by Park et al. (Ref 55). The resultant coatings had porosity level ranged from 6-9 vol.%. It is reported that the weight loss of the Al-Mg coatings was significantly lower than thermally sprayed pure Al coatings. Al-3 wt.% Mg coating exhibited the smallest surface damage as an indication to better corrosion behavior of the surface. Al-5 wt.%Mg has also been introduced as a high corrosion protection barrier on steel after 14,000 h exposure to salt water by Takeyoshi et al. (Ref 56).

A comparison between the corrosion performance of arc sprayed Al-5 wt.% Mg coating on steel with some other coatings such as: pure aluminum, Zn-35Sn, and Zn-27Al (by mass percent) in a solution containing 3.5 wt.% NaCl, at 25°C (by Choe et al. Ref 37) has shown that Al-5 Mg coating possessed superior corrosion performance among all tested coatings.

Al-Zn Coating As it is mentioned before, pure aluminum coatings function as a relatively good protective layer against corrosion for steel substrate but are yet prone to pitting and mechanical damages. Zinc coatings, on the other hand, are highly sacrificial metal providing cathodic protection, especially to steel substrate. However, Zinc coatings have shown poor durability in weak acid or marine environments (Ref 38, 39). According to a report published by the American Welding Society (Ref 39), Al-Zn alloys, even without sealing, exposed in marine and industrial environments, provided very high galvanic corrosion protection for steel substrate. In the case of Al-Zn, usually other alloying elements such as Si, RE (rare elements), Zr, and Mg are added to enhance the mechanical and corrosion behavior better than Al-Zn coatings.

Several published works introduced Al-Zn-Si-based alloys as self-sealing material in corrosive environments due to their capability to produce components to clog the pores and prohibit further penetration of corrosive solution into the coating (Ref 38-42). For instance, the anticorrosion behavior of HVAF sprayed Al-Zn-Si coating on a mild steel substrate in the simulated high concentration ocean environment contained 50 ± 5 gL^{-1} NaCl solution, for 240 h at room temperature, has been investigated by Yang et al. (Ref 38). According to these results, corrosion products mainly contained zinc, aluminum, carbonate, hydroxide, and hydrate clogged the pores and triggered self-sealing behavior and hindered the further corrosion propagation.

Addition of rare element to Al-Zn-Si coating enhanced self-sealing properties (Ref 40). Jiang et al. (Ref 40) have assessed the electrochemical behavior of Al-Zn-Si-RE alloy deposited on a mild steel, using HVAF. The corrosion medium used in this study was 3.5 wt.% NaCl solution at room temperature. The corrosion mechanism of Al-Zn-Si-RE explained to be very similar to that of Zn-15 wt.%Al, in which five distinct stages were observed: pitting-dissolution-redeposition, activation corrosion, cathodic protection, physical barriers formation by corrosion products, and finally the failure of the coating. The corrosion test results of Al-Zn-Si-RE coating deposited on mild steel by arc spray technique and immersed in 3.5 wt.%NaCl solution reported by Jiang et al. (Ref 41) were also supported by their next published results in this area (Ref 38). Both studies have described that the presence of the RE in the coating did not affect the phase compositions of the corrosion products, but improved the formation of fine, continuous, and uniform phases in the coating layers, which increased the stability of self-sealing barrier. A Schematic of self-sealing mechanism for a hypothetical metallic based thermal sprayed coating exposed to NaCl solution has been developed in this work as shown in Fig. 4. This model was developed according to the introduced concept by Jiang et al. (Ref 41). In the beginning, the pitting occurs on the surface of the coating in the initial stage and metal ion (M^{+}) is deposited on the coating surface in the form of dissolution and redeposition. This phenomenon has been known as "pitting-dissolution-redeposition period" (Ref 41). At the next stage, corrosive solution gradually diffuses through the pores and voids in the coating, and accumulation of the corrosion products at the surface of the coating hinders further penetration of the corrosive solution which is known as self-sealing behavior. In fact, evolution of the corrosion product film containing M^{+} particles resulted in formation of a very good physical barrier which hindered the electrochemical corrosion processes.

It has been shown that deposition of 85Al-14.5Zn-0.5Zr (in weight %) coating on steel substrate using arc spraying process could successfully help to prevent corrosion of steel in the ocean environment at room temperature (Kim et al. Ref 42). In this work, several sealants comprising: water-soluble fluorine (hereinafter W-F), nano-fluorine (hereinafter nano), hybrid ceramic (hereinafter ceramic), salt-tolerant epoxy (hereinafter epoxy), and fluoro-silicon (hereinafter F-Si) have also been used to enhance the corrosion resistance. Electrochemical evaluation of the coating showed two distinct reactions: concentration polarization by the reduction of dissolved oxygen ($O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$) and active polarization by hydrogen gas generation ($2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$). It was suggested that using sealant material could significantly increase the resistance against cavitation.

Other Al-Based Coatings There are several other published studies on the corrosion resistance of aluminum coatings after addition of other alloying compositions such as TiO_2, SiC, and ZrO_2. It has been reported that plasma spraying techniques could have significant effect on the porosity level of Al_2O_3-TiO_2 coating and the corrosion behavior as a resultant (Ref 43, 44, 57, 58). For instance, corrosion performance of plasma sprayed Al_2O_3-13 wt.% TiO_2 coating on a carbon steel used in aggressive environments composed of 6 wt.% Na_2SO_4 solution, has been investigated by Wang et al. (Ref 43). The results indicated that electrochemical corrosion mainly occurred on the steel substrate during immersion because corrosion products such as Fe and O could reach out to the surface due to high porosity level and induced the corrosion. Habib et al. (Ref

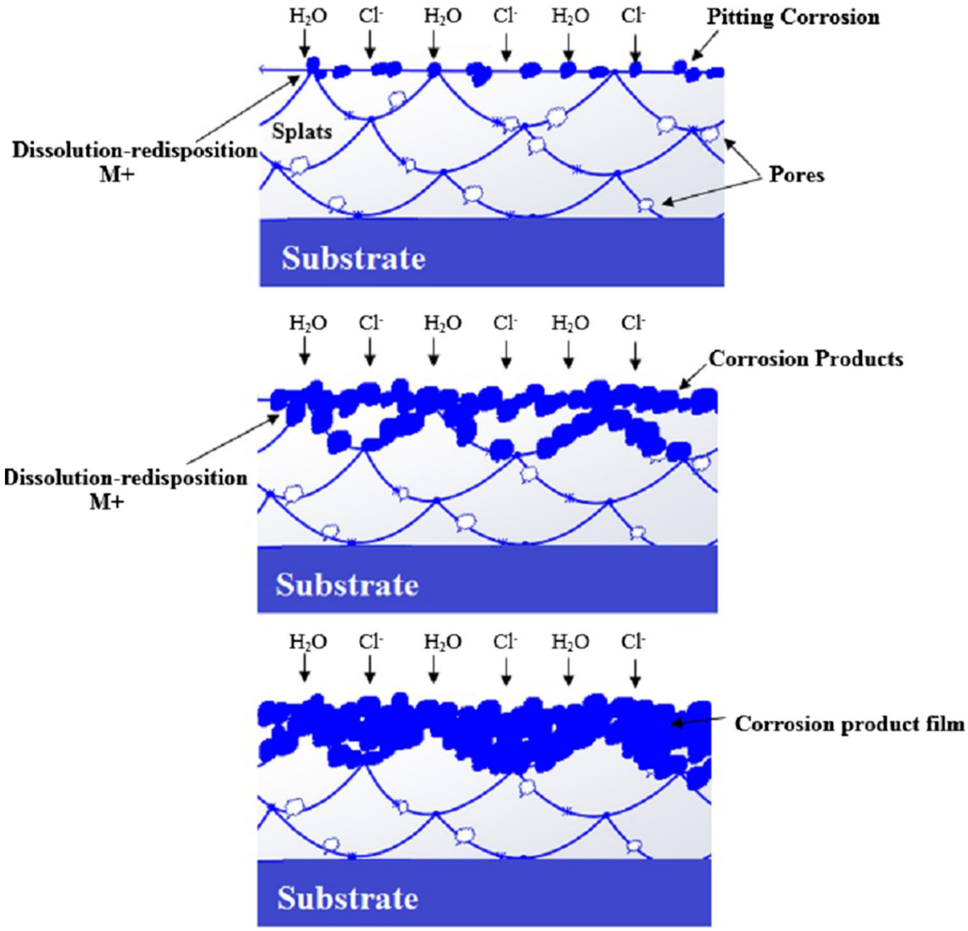

Fig. 4 Schematic of a self-sealing mechanism of a coating in a NaCl solution

57), however, have reported very low porosity in alumina-titania (Al_2O_3/TiO_2) coating formed by flame spray technique on a steel sample. Liscano et al. (Ref 44) have suggested that sealing the atmospheric plasma sprayed alumina-13 wt.% titanium coating, exposed to 3.5 wt.% NaCl, using different sealants such as phosphoric acid, phenol, and epoxy-based material could help decrease the interconnected porosities to the substrate and improve the corrosion resistance.

Yttria-stabilized zirconia is another alloy which has recently been added to the alumina-based coatings due to its good adhesion and strong oxidation protection ability (Ref 59-63). There are few literatures on corrosion resistance of alumina-zirconia coating deposited by thermal spraying techniques, which might be due to difficulty of deposition of such a combination because of huge difference in the melting points of the constituents. According to the results reported by Amaya et al. and Campo et al. (Ref 59-61), high level of porosity and crack have been found in the microstructure of the Al_2O_3-YSZ coating deposited by plasma spraying technique that followed by penetration of electrolyte contained sulfate into the steel substrate and formation of Fe_2O_3, FeS, and, $FeSO_3$ phases. They concluded that thermally sprayed Al_2O_3 coating have much higher long-term corrosion resistance than Al_2O_3-YSZ in molten Na_2SO_4 due to alkaline dissolution of Al_2O_3 in such an environment (Ref 59).

In summary, for thermal-sprayed Al-based coatings, wire arc spraying is a commonly used technique in industry. It has been noticed that addition of low amounts of Mg to Al could improve the mechanical properties of Al-based coatings in addition to their corrosion resistance performance. Recently, cold spray deposited aluminum-based coatings have shown excellent corrosion behavior. However, regardless of deposition technique, the resulting microstructure of the coatings has significant influence on the corrosion resistant properties of the coating. The density of the coatings, amount of porosity and voids, and formation of unwanted phases (i.e., oxides) during the spraying or solidification processes can directly and negatively alter the corrosion behavior of Al-based coatings. Recently, a new type of corrosion protection mechanism known as self-sealing aluminum coatings, such as Al-Zn-Si-RE, was discovered. This type of coating has the capability to produce components that can clog the pores and prohibit further penetration of corrosive solution into the coating.

Corrosion of Zinc-Based Coatings

Thermally sprayed zinc-based alloys have been vastly used to protect steel constructions due to its high stability in the sea water and lower electronegativity respect to steel which makes it act as a sacrificial anode (Ref 46-51, 62-74). However, if the coating is exposed to high humidity or mediums containing aggressive species such as chloride or sulphate ions, the Zn will dissolve in the solution and result in less dense protective layer following by localized corrosion (Ref 62). This issue is not critical when Al-based alloys have been used for corrosion protection. Thermal spray techniques have been employed for over fifty years to spray zinc and its alloys for a variety of applications (Ref 62). Wire arc is one of most recommended methods among the thermal spraying techniques in the case of deposition of zinc-based materials.

Corrosion resistance of wire arc deposited Zn coating on a steel sample has been compared with those of Al and Zn-15 wt.% Al coatings exposed to salt spray contained 5 wt.% NaCl, at room temperature by Gulec et al. (Ref 62). They reported that Zn-15 wt.%Al showed the best corrosion resistance because of two protection mechanisms: (1) creating a stable oxide, similar to Al coatings and (2) acting as sacrificial anode, alike Zn coatings (Ref 62). According to a report published by thermal spray committee of Japan Association of Corrosion Control (JACC) (Ref 63, 64), flame- and arc-sprayed Zn coatings developed on carbon steel pipes started to experience degradation after seven years of service in the marine environment. They reported that Al and Al-Zn coatings deposited with the same techniques performed with no significant corrosion observed on their surface after exposure to the same environment for eighteen years.

Results published by Katayama et al. (Ref 48) indicated that Zn coating deposited by gas wire flame spray technique on carbon steel and immersed in 0.1 M NaCl solution effectively retarded the corrosion rate by formation of corrosion products on the surface during long-term exposure. However, when it is compared to aluminum-based coatings, better performance of aluminum-based coatings in the most cases were reported for long-term exposure owing to the formation of thin film of aluminum oxide on the surface.

Chavan et al. (Ref 45) have used cold spraying technique to deposit a commercially available water atomized zinc powder on a mild steel and studied its electrochemical behavior in 3.5 wt.% NaCl solution (pH $\sim$ 7). The cold sprayed zinc coating was thick, dense and provided efficient barrier protection to mild steel substrate. Cold spraying could prove itself as a competitive technique capable of increasing the lifetime of sacrificial zinc coatings by virtue of high achievable thicknesses. Suitable post-spraying heat treatment has also proven to bring a beneficial change in the microstructure such as better bonding between the splats resulting in less intersplat cracks. This could improve the sacrificial nature of zinc coatings and its service life.

Zn-Al-Based Coatings Generally, corrosion in alloys containing zinc and aluminum is hindered due to two different protection mechanisms: (1) passivation due to formation of aluminum oxide which protects the surface against defusing corrosive elements, and (2) acting as sacrificial anode owing to electropositive nature of the zinc which prolongs the substrate's service life. These characteristics make Zn-Al alloys superior than single Al or Zn coating for corrosion protection. A comparison of the corrosion experiment results of arc sprayed Zn-15 wt.% Al and Zn-30 wt.% Al coatings, when subjected to a salt spray environment for 1000 h, has been addressed by Varacalle et al. (Ref 67). The porosity of the Zn-30Al coatings was higher than that of Zn-15Al, thus, higher corrosion resistance observed by applying Zn-15Al coating. Moreover, corrosion resistance of both coatings was affected primarily by diameter of spraying nozzles, and secondarily by current and spraying distance. Thirty-years exposure of flame sprayed Zn-30 wt.%Al coating on steel, has shown very high corrosion resistance due to the generation of thick layer of corrosion products formed by selective dissolution of zinc (Ref 48). Corrosion resistance of high speed electric arc sprayed Zn/Al (300/100 μm thickness) composite and Zn/Al (100/300 μm thickness) composite on steel exposed to salt spray contained 5 wt.% NaCl at room temperature after 30 days have also been investigated by Mio et al. (Ref 68). It was observed that the porosity of Zn/Al (300/100 μm) was lower than that of Zn/Al (100/300 μm) indicating better corrosion resistance of Zn/Al (300/100 μm). The flame sprayed Zn-15 wt.% Al exposed to marine atmosphere for one year has shown improved cathodic protection capabilities compared to pure Al coating tested at the same condition (Ref 69). However, the long-term corrosion durability of pure Al coating was yet higher than those of both pure Zn and Zn-15Al coated steels (Ref 46, 62, 64, 69). In other cases, dual system of Zn/Al formed by primer coat of flame sprayed zinc and second coat of Al as top coat generated with the same technique showed an excellent corrosion resistance due to cathodic protection ability of Zn and relatively good erosion resistance of Al (Ref 47). It has been suggested that, using sealant such as wash primer could improve the corrosion behavior and further extend its service life. Corrosion performance of Zn-15 wt.%Al coating deposited by high velocity arc spray technique in presence of sulfate-reducing bacteria (SRB) in seawater after eight days has been evaluated by Hong et al. (Ref 70). The coating was corroded at the early stage of immersion process mainly by metabolites, thereafter the ZnS formed as corrosion product and plugged the porosity and reduced the corrosion rate. They suggested sealing the coating system with silicon would help improving the corrosion performance (Ref 70).

Zn-Al-Mg-Based Coatings As it is previously mentioned, Mg is a potential candidate to be used as the sacrificial anode for protection of industrial components. Addition of Mg to Zn-Al-based alloy could significantly enhance the corrosion resistance due to self-sealing nature of Zn-Al alloys (Ref 49-51, 70, 73). This was attributed to formation of intermetallic phases such as $MgZn_2$ and $MgZn_{11}$ and, in some cases, $Zn_5(OH)_8C_{12}\cdot H_2O$ (Ref 70), of which plugs the pores and protects the substrate against electrolyte. As a result, Zn-Al-Mg coatings possessed even higher corrosion resistance than that of pure Zn and Zn-Al coatings (Ref 70, 73). It has been reported that the time for red rust to appear in the neutral salt spray test of Zn-Al-Mg coating is 4-20 times longer than that of Zn coatings (Ref 49, 70). In fact, Mg reacts with CO_2 to form $MgCO_3$ that hinders the formation of hydrozincite $Zn_5(CO_3)_2(OH)_6$, which is shown to be less protective than simonkolleite $Zn_5(OH)_8Cl_2\cdot H_2O$ (Ref 70). Another reason for the superior corrosion behavior of the Zn-Al-Mg coating is due to the buffering effect of the dissolved Mg which inhibits formation of ZnO and the pH at the cathodic sites (Ref 70, 73). Formation of layered double hydroxides (LDH) by co-precipitation of the corresponding ions is assumed to be the main contribution to enhance the corrosion resistance of these alloys (Ref 70, 71).

Corrosion performance of Zn-Al-Mg coating deposited by wire arc spraying technique using a $ZnAl_2$ sheath and $ZnMg_{6.3}$ has been investigated by Bobzin et al. (Ref 72). It is reported that the Zn-Al-Mg coating after 2448 h exposing to neutral salt spray contained 5 wt.%NaCl was remained uncorroded state. This has been explained due to formation of simonkolleite and LDH which could provide dense barrier against the electrolyte. It has also been found that the reaction of Mg ions with CO_2 and generation of $MgCO_3$ hindered further corrosion reaction and formation of hydrozincite. Usually, higher mount of hydrozincite on Zn and Zn-15Al coatings after exposure to the same medium detected in comparison with Zn-Al-Mg coatings. Zhu et al. (Ref 70) have shown that wire arc sprayed coating with a composition of Zn-15Al-6 Mg possessed better electrochemical behavior compared to that of Zn-Al coatings which was attributed to the formation of corrosion products that blocked the pores and prevented further corrosion at room temperature.

Similar to Al-Zn-Mg-based coating, addition of RE to Zn-Al-Mg alloys could improve the self-sealing behavior due to the reduction in the size of in-flight droplets and formation of more stable phases that directly affected the corrosion resistance (Ref 50, 70, 74). Corrosion behavior of cored wires and high velocity arc sprayed Zn-Al-Mg-RE coatings immersed in 5 wt.% NaCl solution has been evaluated by Liu et al. (Ref 74). It has been concluded that addition of small amount of RE markedly enhanced the anticorrosion properties of the coating in accordance to the formation of denser, more compact, and uniform corrosion products as a result of coating refinement. According to the work done by Yan et al. (Ref 50, 70), addition of RE element could increase the liquidity of Al and improve the microstructural properties of the coating by decreasing the porosity level. The measured corrosion resistance of the high velocity arc sprayed Zn-Al-Mg-RE coating exposed in 5 wt.%NaCl compromised with those reported by (Ref 70) advocating the self-sealing nature of the coating due to formation of corrosion products such as Zn, $Zn_5(CO_3)_2\cdot(OH)_6$, $ZnO\cdot ZnCI_2\cdot 2H_2O$, $ZnCl_2\cdot 4Zn(OH)_2\cdot H_2O$, $Mg_2(OH)_3$-$C1\cdot 4H_2O$ and $Mg_6A1_2(OH)_{18}\cdot 4.5H_2O$ (Ref 70). Effect of addition of silicon (1-6%) on corrosion behavior of high velocity arc sprayed Zn-Al-Mg-RE coating exposed to 3.5 wt.%NaCl solution was investigated by Kuiren et al. (Ref 51). The results indicated that Zn-Al-Mg-RE-Si coating had higher corrosion resistance than Zn-Al-Mg-RE due to presence of glass-like state phase attributed to $Al_{3.21}Si_{0.47}$ and $Mg_3Al_2(SiO_4)_3$ formed on the external surface of Zn-Al-Mg-RE-Si coating which acted as self-sealing barrier, depressed the porosity of coating and hindered reaching the electrolyte to the substrate. They also reported that addition of 3 wt.% silicon to the initial feedstock resulted in the best corrosion resistance.

In summary, the corrosion protection of thermal-sprayed Zn-based coatings is basically due to its lower electronegativity compared to that of steel. In fact, the formation of a zinc rich sacrificial anode could protect steel against corrosion during typical service conditions. Although, microstructural properties may have some effect on corrosion attack and propagation through zinc-based coatings, electronegativity differences between coating and substrate promotes corrosion through the coating. The addition of magnesium to Zn-Al-based coatings resulted in the formation of some intermetallic phases that could improve the corrosion behavior of the coatings. Moreover, the addition of Si to zinc-based alloys containing Al, Mg, and RE could create an external barrier layer, which could improve the anticorrosion behavior of the deposited coating.

Corrosion of Thermal-sprayed Coatings at High Temperature

Table 2 presents a summary of the high-temperature corrosion behavior of different thermal-sprayed coatings. Table 2 shows that nickel, chrome, tungsten carbide, and their alloys have been the most commonly-used corrosion protection coatings that are deposited by thermal spraying techniques such as D-gun, APS, and HVOF for elevated temperature applications. Ni-Cr alloy has also been deposited successfully using the cold spraying technique. The range of the temperature used to evaluate the hot corrosion behavior of the coatings was within 500-900 °C.

The most common parameters considered for hot corrosion evaluation were weight-loss and weight-gain which usually works based on loss of materials due to corrosion or formation of unwanted phases. Electron probe microanalysis (EPMA) is also a promising technique for evaluating hot corrosion by accurate measurement of oxygen concentration after service and exposure to hot and humid environment. Porosity is also considered as one of the major contributors which significantly interfered in the corrosion formation at higher temperatures.

Corrosion of Nickel-Based Coatings

Nickel-based coatings are often deposited by thermal spraying processes to improve corrosion resistance, wear resistance, and mechanical properties such as toughness and hardness of the surface to function in advanced engineering applications, especially at elevated temperature (Ref 4). Nickel commonly was combined with other elements such as titanium, chrome, silicon, and boron to increase the passivity behavior and mechanical properties of the coatings. Plasma spraying, HVOF, and flame spraying have commonly been used to deposit Ni-based alloys for corrosion protection application. Among Ni-based alloys, Ni-Cr-based, NiCrBSi, and Ni-Ti-based, have attracted more attention due to their excelled corrosion resistance and will be discussed in this study.

Ni-Cr Coatings Nickel-chromium alloys have mostly been used as welded and thermally sprayed coatings in fossil fuel-fired boilers, waste incineration boilers, and electrical furnace due to their superior mechanical and corrosion resistance behaviors at elevated temperatures (Ref 22, 75-77, 84-87). Thus, most of the published works in the area of Ni-Cr coatings have evaluated corrosion behavior of these coatings in high temperature conditions ranged within 700-900 °C. The high corrosion resistance of Ni-Cr-based alloys attributed to the formation of Cr_2O_3 passive layer which protects the material from corrosion up to ~ 1200 °C (Ref 75).

The hot corrosion resistance of cold sprayed Ni-50 wt.%Cr coating deposited on boiler steel SA-213-T22 and SA516 (Grade 70) samples has been investigated by Niraj et al. (Ref 75). The coated samples were exposed to an aggressive environment of $NaSO_4$-60 wt.%V_2O_2 under a cyclic condition in which after 50 cycles each sample was hold at 900 °C in a tube furnace for 1 h followed by 20 min cooling in ambient air. The authors have not observed any indication of spalling in the both coatings after exposed to corrosive environment. Ni- and Cr-oxides were detected in the EDS results of the both coatings after corrosion test which illustrated formation of the passive layer. In the work done by Yamada et al. (Ref 76), Ni-50 wt.%Cr alloy coating was produced on carbon steel boiler tubes by denotation spraying method and exposed to corrosive bath in the furnace at temperatures of 500 °C and 600 °C. Sample was exposed to refuse incineration ash contained 4.66 Na, 5.11 K, 15.4 Ca, 1.8 Mg, 5.4 Fe, 0.11 Pb, 0.66 Zn, 7.04 S, and 11.3 Cl (wt.%). The corrosion gas containing $8\%CO_2 + 8\%O_2 + 18\%H_2O + 0.1\%(HCl + N_2)$ was blown into the electric furnace. The EPMA results on the coating confirmed the presence of Cr, which has been identified as one of the major reasons for hot corrosion. The high porosity in the sprayed coating, allowed Cr and oxygen diffuse into the substrate leading to internal chlorination and oxidation that weakened the bonding between the coating and the substrate (Ref 76, 77).

Elevated temperature corrosion performances of Ni-20 wt.%Cr coating deposited by low pressure plasma spraying (LPPS) method on UNS S30400 stainless steel has been evaluated by Longa-Nava et al. (Ref 77). The coating was exposed in thin fused films of sodium sulfate and sodium metavanadate (Na_2SO_4-0.3 mol.%$NaVO_3$) at 900 °C in a 1% sulfur dioxide-oxygen (SO_2-O_2) atmosphere for 16 h. The authors have reported the formation of Cr-rich oxide layer of ~ 30 μm on LPPS coating which effectively prevented its sulfidation. The cyclic hot corrosion behavior of the same nickel-based alloy (Ni-20 wt.%Cr) deposited by another thermal spraying technique (HVOF) on the T91 boiler, has been investigated by Chatha et al. (Ref 78). The coating was subjected to an aggressive environment of Na_2SO_4-60%V_2O_5 molten salt at 750 °C for 50 cycles, for the corrosion assessment. In contrast with the results reported by Longa-Nava et al. (Ref 77), significant cracks propagation was observed on the edges and corners of the sample by the completion of 6th cycle following by the swelling and spallation of the scale by the 8th cycle. The possible corrosion mechanism could be the formation of cracks on the surface of the specimen and, subsequently, removal of the scale in the form of tiny flakes which were non-protective and rich in Fe_2O_3.

In the study presented by Abualigaledari et al. (Ref 80), the electrochemical behavior of Inconel 718 coating

Table 2 Hot corrosion behavior of thermal sprayed coatings deposited on steel

Coating material	Coating technique	Corrosive environment	Temperature (°C)	Observations
Ni-based				
Ni-50Cr	CS	$NaSO_4$-$60V_2O_2$	900	Formation of passive layer contained Cr_2O_3 and nickel oxide, but yet high porosity in the coating (Ref 75)
Ni-50Cr	D-gun	$8CO_2 + 18H_2O + 0.1HCl + N_2$	500 and 600	Chlorination and oxidation of the substrate due to high porosity of the coating (Ref 76)
Ni-20Cr	APS	$0.7Na_2SO_4$-$0.3NaVO_3$	900	Generation of Cr-rich oxide layer of ~ 30 μm as a passive layer (Ref 77)
Ni-20Cr	HVOF	Na_2SO_4-60%V_2O_5	750	Mechanism: formation of cracks and, subsequently, removal of the scale in the form non-protective flakes rich in Fe_2O_3 (Ref 78)
NiCrBSi	HVOF	Na_2SO_4-60 V_2O_5	900	Passive layers made of oxides of silicon/chromium/nickel, and spinels of nickel and chromium (Ref 22, 23, 76-81)
83Ni10Cr3.5B3.5Si	FS	Cyclic-oxidation	1000–1600	Non-homogeneous, high porosity, low bonding compared to HVOF deposited coating. Reaction of the corrosive elements with the substrate (Ref 79)
Inconel 718	HVOF	3.5%NaCl	250	Incomplete oxidation, unstable passive layer due to high solubility of chromium oxide in the solution (Ref 80)
Ni-20Cr-10Al-Y	APS	Cyclic-oxidation	900	Formation of protective layer composed of scale on the NiCrAlY coating contained NiO, Cr_2O_3, Al_2O_3, Fe_2O_3, $NiCr_2O_4$ and $NiAl_2O_4$ (Ref 22)
Cr-based				
Cr_3C_2-25NiCr	D-gun	$75Na_2SO_4 + 25K_2SO_4$	900	Diffusion of elements such as Fe, Cr, and Ni from the substrate to the coating and high gained weight due to high porosity level (Ref 81)
Cr_3C_2-25%NiCr	HVOF	Cyclic-oxidation	900	Formation of protective oxide layers composed of Cr_2O_3 and spinel of nickel and chromium (Ref 82)
Cr_3C_2-25%NiCr	HVOF + Heat treatment	(Na_2SO_4-60%V_2O_5	900	formation of oxides of Cr, Ni, and their spinels clogged the interconnected to the surface and led to better corrosion performance (Ref 81)
WC-based				
WC-NiCrFeSiB	HVOF	Na_2SO_4-25NaCl	800	Formation of Cr_2O_3, NiO, $NiCr_2O_4$, and Fe_2O_3 and sealing the pore hindering the aggressive species penetration (Ref 83)

deposited by HVOF spraying on carbon steel substrate has been examined using an innovative device: High Temperature Corrosion Measurement Device (HTCMD), in 3.5 wt.% NaCl solution at 250 °C. According to the results, the coating was not able to grow a stable passive oxide layer to protect the steel against corrosion effectively. This was explained due to the high solubility of the oxide layer (mainly chromium oxide) in the corrosive environment as well as insufficient oxygen content at high temperature condition which resulted in incomplete oxidation on the surface (Ref 80).

NiCrBSi Coatings NiCrBSi alloys can be deposited using different thermal spraying techniques such as HVOF, Plasma and flame spraying to protect steel against chemical interaction with its environment (Ref 84, 85). This alloy has shown excellent corrosion resistance in alkaline solution, due to the self-passivation of the coating even under very severe corrosive environments (Ref 24, 88-91). The corrosion resistance of NiCrBSi coating deposited via HVOF process was higher than the other commonly-used thermal spraying techniques due to its lower porosity content (Ref 88, 89). This alloy usually has shown no selective corrosion (Ref 89). Corrosion in this type of coating was mostly attributed to the presence of un-melted particles, pores, inclusion, and micro-cracks which can be minimized by optimization of process parameters (Ref 90). Corrosion performance of NiCrBSi coating deposited by HVOF on Fe-base substrates at 900 °C in molten salts containing Na_2SO_4-60 wt.%V_2O_5 for 50 cycles has been examined in multiple works published by Sidhu et al. (Ref 22, 24, 83-86, 91). They found that the coatings were very effective in decreasing the corrosion rate of the steel samples at the elevated temperature. It was mostly attributed to the formation of passive layers made of oxides of silicon/chromium/nickel and also spinel's of nickel and chromium (Ref 22, 24, 83-86, 91, 92).

In other work by Chaliampalias et al. (Ref 79), 83Ni10Cr3.5B3.5Si (in wt.%) was deposited on St-37 steel substrate by flame spraying process. The coating/substrate system was subjected to high temperature oxidation tests through thermogravimetric measurements (TG) at 1600 °C (non-isothermal) and 1000 °C (isothermal). Comparison between the results obtained in this work with those reported by Sidhu et al. (Ref 91) emphasizes on the role of different thermal spraying techniques on corrosion resistivity of the protective layer. Unlike HVOF deposited NiCrBSi coating, flame sprayed one was not homogeneous and exhibited high porosity with low adherent to the substrate and for this reason the corrosive elements have penetrated into the coating and reacted with the substrate.

Other Ni-based Coatings Titanium has been one of the most well-known elements added to nickel-based alloys to protect the surface of engineering alloys including steel (Ref 93-97). Ni-Ti intermetallic compounds are famous due to their shape memory effect (SME). This compound has also shown excellent corrosion resistance in various environments (Ref 98). The high corrosion resistance of titanium alloys is attributed to the formation of TiO_2 that acts as passive film on the surface (Ref 99). However, manufacturing process of NiTi alloy is very complicated and expensive. Thus, coating techniques such as thermal spraying methods have been used to deposit this alloy on the surface of engineering components (Ref 23, 100, 101). NiTi has been developed by several thermal spraying techniques such as HVOF, VPS, and atmospheric plasma spray quenching (APS + Q) (Ref 23, 102-105). This alloy is known to be very susceptible to react with oxygen, hydrogen, and nitrogen during exposure to high temperature conditions. Thus, in the case of deposition of this alloy in low pressure mode, the spray chamber is filled with inert gas and maintained at low pressure ($\sim$ 100 mbar) to avoid oxidation. Ni_3Ti and Ti_2Ni are two undesirable intermetallic phases formed during deposition of NiTi coating due to their poor corrosion and mechanical properties (Ref 23, 100, 101). NiTi coatings possess lower electronegativity compared to steel substrate. Thus, in the case of formation of galvanic corrosion between the coating and the steel substrate, NiTi coatings will act as cathode and accelerate the corrosion in steel (Ref 23).

Chiu et al. (Ref 96) has shown that pitting potential of NiTi deposited on AISI 316 steel were comparable to that of the substrate, but the protection and corrosion potential were somehow lower. The authors have reported that laser surface modification of NiTi alloy in order to produce a crack- and porosity-free layer resulted in a significant corrosion improvement due to reduction in the corrosion current density (I_{corr}) (Ref 96).

NiAl alloy has been considered as another protective coating for boiler tube steels and their characteristics were studied by Sidhu et al. (Ref 106). Plasma spraying processes were used as deposition technique and a premier Ni-20Cr-10Al-Y bond coat were used prior to spraying NiAl on steel substrate. The scale on the NiCrAlY coating contained NiO, Cr_2O_3, Al_2O_3, Fe_2O_3, $NiCr_2O_4$ and $NiAl_2O_4$. Hot corrosion behavior of the coatings after exposure to air and molten salt at 900 °C was studied under cyclic conditions (50 cycles).

In summary, the primary mechanism for high-temperature corrosion resistance of thermal-sprayed Ni-based coatings containing Cr/Ti has been attributed to the formation of Cr_2O_3/TiO_2 passive layers. Formation of the protective layer on the surface of the coating is due to the fact that the oxidation mainly occurs after deposition and during the solidification process on the surface of coating layers (Ref 107). The oxidation mechanism is different from the oxidation in-flight, which can penetrate to the core of the splats as described for aluminum and zinc. Microstructural characteristics of the Ni-based coatings also play a major role in corrosion resistance of Ni-based coatings. To this end, HVOF is the highly recommended thermal spraying technique for deposition of Ni-based materials due to the deposition of coatings with relatively low oxide and porosity content. Most of the previous studies on thermally-sprayed Ni-based coatings speculated on the appearance of the coating and the amount of formation of the new products (weight-gain) or reduction in the weight of the coating (weight-loss) as indicative of corrosion behavior. Thus, the electrochemical behavior of Ni-based coatings at high temperatures still remains to be elucidated.

Corrosion of Chrome-Based Coatings

Chromium has been used for many years as an effective protection for corrosion, repair applications, and to reduce the surface friction. Due to low deposition rate of the electro-plating, thermal spraying technologies such as plasma spraying and denotation gun were introduced as the alternative deposition processes (Ref 92). However, it has been reported that plasma-deposited chromium has not shown good wear resistant properties compared to electroplated chromium at ambient temperature. This could be due to high residual stress induced in the coating during the thermal spraying process (Ref 92). To improve the mechanical properties of the chrome-based coatings deposited by thermal spraying techniques, alloys comprised chromium carbide dispersed in a chromium matrix have been utilized. The majority of the published works for thermally sprayed Cr-based coatings, suggested Cr_2O_3 (Ref 25, 92, 108) and Cr_3C_2-NiCr (Ref 26, 34, 52, 81, 109-114) as two high corrosion resistant coatings while their mechanical properties pertained in a good condition as well.

Cr_2O_3 Coatings Chromium oxide (Cr_2O_3) coatings are considered as one of the best corrosion resistant materials among the other Cr-based alloys to hinder the possible chemical attack on metallic components especially in the case of exposure to alkaline and acidic environments. Corrosion behavior of Cr_2O_3 coating has found to be very high specifically at elevated temperature and severe environments (Ref 26, 107, 108). However, their relatively higher cost compared to the other corrosion resistant alloys such as aluminum, zinc, and tungsten carbide has limited Cr-based alloys' applications. Using thermal spraying technologies such as plasma spraying (Ref 107) to deposit chrome oxide mostly demands surface modification due to high porosity evolution. Due to relatively high level of porosity ($\sim$ 3 vol.%), Ashby et al. (Ref 107) suggested using either a crevice-corrosion-resistant substrate or applying an epoxy sealant (not applicable for high temperature conditions) to close the pores on plasma-sprayed Cr_2O_3 coatings. Atmospheric plasma-sprayed Cr_2O_3 coating that was sealed by using aluminum phosphate has been introduced by Leivo et al. (Ref 25). The aluminum phosphate sealant was impregnated into the chromium oxide coating under ambient temperature and pressure conditions. Here, the presence of the open porosities could improve the corrosion resistant behavior of the substrate.

Cr_3C_2-NiCr Coatings There was a growing interest between 1990- 2010 in the deposition of coatings fabricated from nickel-chrome matrix which contained chrome carbide particles uniformly dispersed in the matrix (Ref 26, 81, 109-114). The most common thermal spraying techniques used to deposit Cr_3C_2-NiCr coating on steel substrates have been HVOF (Ref 26, 81, 109-114) and denotation gun (Ref 81, 114). However, HVOF was found to be the most desirable method to substitute chrome plating due to the low porosity, good oxidation resistance, high bonding strength, and high deposition rate of the deposited coatings (Ref 26, 81, 109-114).

The corrosion resistance of hard chromium coating has been compared to that of HVOF deposited Cr_3C_2-NiCr in 3.4 wt.% NaCl solutions at room temperature, for long immersion times (Ref 109). The corrosion performance of deposited Cr_3C_2-NiCr coating on a UNS-G41350 steel substrate using HVOF technique has also been investigated by Espallargas et al. (Ref 111). According to the results of electrochemical measurements, Cr_3C_2-NiCr coating has exhibited better corrosion resistance compared to WC-Ni under corrosive conditions. Guilemany et al. (Ref 113) have studied the effect of coating thickness (151, 285, 430, 542, and 715 µm) on the electrochemical behavior of the HVOF sprayed Cr_3C_2-NiCr coating on UNS G11200 steel immersed in 3.4 wt.% NaCl solution. The author reported low porosities (1-2%) for the all coatings with various thicknesses. However, the results showed that although higher thickness diminished the probability of pore interconnection with the substrate, it resulted in higher number of cracks, interlayer separation, and residual stress distribution that may have adverse effects on the corrosion behavior. They suggested an optimized thickness value to improve the anticorrosion behavior.

Hot corrosion resistance of Cr_3C_2-NiCr coating deposited by denotation gun spraying technique has also been investigated (Ref 81, 114). Kamal et al. (Ref 110) have evaluated cyclic hot corrosion resistance of denotation gun sprayed Cr_3C_2-25 wt.% NiCr coating on superfer 800H in the presence of Na_2SO_4 + 25 wt.% K_2SO_4 film at 900°C for 100 cycles. The detection of the phases such as NiO, Cr_2O_3, $NiFe_2O_4$, $NiCr_2O_4$, Fe_2O_3, Ni_3S_4, and Ni_2FeVO_6 in the XRD profile of the corroded coatings indicated that all the major elements from the substrate (e.g. Fe, Cr, and Ni) diffused into the coating (Ref 81). The author described that concentration gradient helped this inter-diffusion of the substrate elements into the coating. Thus, the weight gained after corrosion was relatively high.

Shukla et al. (Ref 82) used austenitic stainless steel (310S) as substrate and coated with Cr_3C_2-25% NiCr alloy using HVOF technique. Cyclic oxidation of the resultant coating has been studied in air for 50 cycles with one-hour heating at 900 °C in a SiC tube furnace followed by 20 min cooling at room temperature. The deposited coatings possessed high density followed by imparting resistance against degradation during the oxidation experiment. It is speculated that formation of protective oxide layers composed of Cr_2O_3 and spinel of nickel and chromium was responsible for high oxidation resistance.

In other work by Chatha et al. (Ref 115), influence of post-treatment methods (sealing and heat treatment) on hot corrosion behavior was investigated on HVOF sprayed Cr_3C_2-25%NiCr coating deposited on ASME-SA213-T91 boiler steel in a molten salt (Na_2SO_4-60%V_2O_5) environment at 900 °C under cyclic conditions. Each cycle consisted of 1 h heating in the silicon carbide tube furnace followed by 20 min cooling in air. They proposed that hot corrosion could occur in two stages of the initiation and the propagation. In the propagation stage, the protective scale rendered ineffective and substrate became vulnerable to hot corrosion. Post-heat treatment resulted in rapid formation of oxides of chromium, nickel, and their spinel's in splat boundaries and within open pores, which could clog the interconnected ones to the surface that led to better corrosion performance.

In summary, for thermal-sprayed Cr-based coatings, formation of a passive layer, comprised primarily of Cr_2O_3, is responsible for the excellent corrosion resistance of the Cr-based coatings. Similar to what recommended for Ni-based coatings, HVOF spraying has been proven to be the most desirable thermal spray technique to generate Cr-based coating as a substitution to chrome plating due to low porosity, low oxidation, high bonding strength, and high deposition rate. Since most of the Cr-based coatings deposited with thermal spraying techniques possessed relatively higher level of porosity compared to the other materials mentioned before, effect of post-heat treatment on their corrosion behavior could be an interesting topic for future research. Some studies suggested using a variety of sealant materials (i.e. epoxy, aluminum phosphate, etc.) for hindering of corrosion when base material is protected by Cr_2O_3 coating. An accurate optimization of spraying process parameters such as: gas composition, flow rate, energy input, torch offset distance, and substrate cooling could significantly improve coating quality by reduction of the porosity content. The electrochemical behavior of the Cr-based coatings at high temperature has also remained unknown and requires further attention.

Corrosion of Tungsten Carbide-Based Coatings

Due to the excellent abrasion, high temperature durability, and good insulation properties, tungsten carbide (WC) based alloys are considered for corrosion protection (Ref 116) and sometimes an alternative replacement to the more traditional hard chrome plating to reduce the pollution issue (Ref 32, 33, 116, 117). Pure WC coating has not shown good corrosion resistance (Ref 118) and mechanical stability. Therefore, some other elements such as Co, Co-Cr, Cr_3C_2-Ni, and Ni were usually added as mechanical binders to improve the corrosion resistance and mechanical stability of WC alloys. The most common thermal sprayed WC-based alloys used to protect steel components are WC-Co, WC-Co-Cr, and WC-Ni. However, majority of the studies on thermal sprayed WC-based coatings on steel substrate have emphasized on their corrosion performance at room temperature. Thus, there is a potential interest to address their hot corrosion performance.

WC-Co Coatings It has been reported that HVOF sprayed WC-Co coating on steel substrate has superior long-term atmospheric corrosion resistance compared to electrochemical hard chrome coatings (Ref 33). The results of corrosion test reported by Takeda et al. (Ref 117) taken from WC-12 wt.%Co deposited by HVOF on a steel sample in 0.05 kmol.m^{-3} Na_2SO_4 indicated that oxides and hydroxides of W and Co formed on the coating surface due to dissolution after long-term immersion and it resulted in weak corrosion resistance of the coating system. HVOF deposited WC-12 wt.%Co on steel exposed to 5 wt.% H_2SO_4 solution after 120 h also confirmed poor corrosion resistance behavior due to considerable micro-galvanic corrosion occurred between WC particles and binder metal and poor corrosion resistance of binder materials (Ref 32). The schematic of galvanic corrosion has been shown in Fig. 5, where the particles with lower electronegativity (anode) were dissolved in the electrolyte and caused separation of the cathodic particles from the surface of the materials. WC-17 wt.% Co coatings in both 0.5 M H_2SO_4 and 3.5 wt.% NaCl, have shown active corrosion process due to inhomogeneous binder comprising a Co(W, C) matric with varying compositions (Ref 33). The active dissolution of WC-17 wt.% Co coating in 0.5 M H_2SO_4 solution has been attributed to anodic polarization of the binder phase (Co), which followed by pseudo-passivity

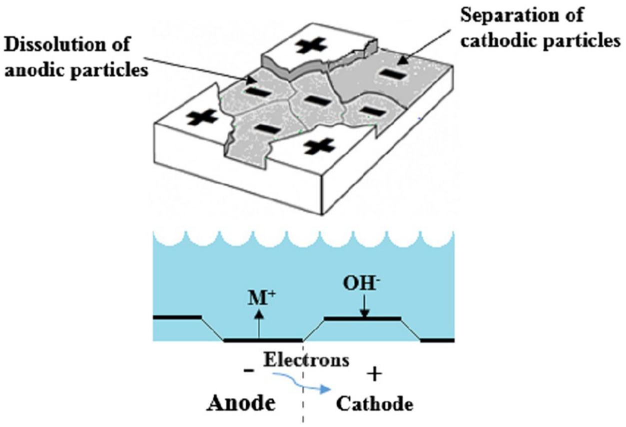

Fig. 5 Schematic of micro-galvanic corrosion occurring in thermal-sprayed coatings

associated with oxidation of W, Co, and C (Ref 33, 119, 120). The corrosion resistance measured by potentiodynamic scanning study indicated weaker performance of HVOF sprayed WC-12 wt.% Co compared to the stainless steel substrate (Ref 33). In general, thermal-sprayed WC-Co coatings have not shown very good corrosion resistance (Ref 29, 30, 119-125).

WC-Co-Cr Coatings It is well-documented that addition of Cr to WC-based alloys has resulted in formation of Cr_2O_3 and could significantly improve the corrosion resistance of steel (Ref 27-31, 119-126). However, there have been some controversial reports on the corrosion behavior of WC-Co-Cr compared to WC-Co. For instance, corrosion assessment of HVOF sprayed WC-Co-Cr and WC-Co coatings on stainless steel exposed to artificial seawater, by Bjordal et al. (Ref 119, 120), showed that addition of Cr as binder to a cobalt matrix increased the corrosion resistance of HVOF deposited WC-based cermet. However, they reported higher localized corrosion occurred at 18 °C on WC-10Co-4Cr compared to WC-Co. As the temperature increased to 50 °C the more Co content dissolved in the solution and the corrosion resistance considerably decreased, which is explained due to higher selective corrosion of Co content by increasing the temperature.

Wang et al. (Ref 127) has been reported that HVOF sprayed WC-10Co-4Cr coatings on steel substrate in neutral saline of 5 wt.% NaCl solution performed better than WC-Co deposited coating with the same technique. It has been observed that potential gap between WC particles and binder matrix in WC-Co has been higher than the one in WC-10Co-4Cr, resulting in more significant micro-galvanic corrosion in WC-Co coating. Voorwald et al. (Ref 30) have also confirmed that HVOF sprayed WC-10Co-4Cr coating possessed much better corrosion resistance, compared to HVOF deposited WC-17 wt.% Co deposited when both were examined in salt spray test condition containing 5 wt.% NaCl.

The presence of Cr_2O_3 in HVOF-sprayed WC-10Co-4Cr coating, detected by Takeda et al. (Ref 117), has suppressed dissolving of coating components in the corrosive solution. The effect of metallic matrix composition and spray size distribution on corrosion behavior of different HVOF deposited WC-10Co-4Cr coatings has been studied by Berget et al. (Ref 128). According to their observations, smaller powder size distribution range resulted in better quality of the coating. Moreover, corrosion resistance of the coating in sea water increased when the Cr content in the metallic binder increased from 5 to 8.5 wt.%.

A closer look at corrosion mechanism of HVOF sprayed WC-Co-Cr coating in static and liquid-solid impingement saline environment has been taken by Perry et al. (Ref 129). They reported that corrosion mostly occurred at the carbide/matrix interface resulted in extensive removal of the hard phase. By increasing the temperature, more severe corrosion took place on the overall surface and promoted severe attack in random localized regions not associated with specific microstructural features. Temperature also played an important role in the electrochemical corrosion rate of the coating.

WC-Ni Coatings It has been reported that the addition of Ni as the binder to WC-based coatings has resulted in lower porosity and better corrosion resistance when deposited on mild steel substrates (Ref 125, 130). It has been speculated that subjecting the WC-12 wt.% Ni coating, deposited by HVOF in salt spray test after 397 h resulted in the red rust spot formation (Ref 33). However, these features appeared in shorter immersion duration for the WC-10Co-4Cr and also WC-20Cr_2C_3-7Ni coatings tested at the same condition.

According to the work published by Cho et al. (Ref 33), micro-galvanic cell generated between the WC particles and Ni binder phases in the HVOF sprayed WC-10 wt.% Ni coating exposed in the 5 wt.%H_2SO_4 resulted in corrosion of anodic binder materials. In such a case, the galvanic corrosion has even been more sever if large cathode and small anode was presence, considering the area ratio effect. They observed the selective dissolution of Ni binder at the first stage of corrosion followed by separation of the WC particles.

Corrosion resistance of composition matrix made of 50WC-12Co balanced with Ni9Cr2Si3.5Fe2B.5C coating deposited by HVOF has been much higher than WC coating with pure Co binder due to higher corrosion rate of cobalt in the electrolyte solution as reported by Bjordal et al. (Ref 119, 120). Oxidation and hot corrosion resistance of HVOF deposited WC-NiCrFeSiB coating on a Fe-based superalloys at 800 °C when exposed to the air and molten salt containing Na_2SO_4-25 wt.% NaCl, under cyclic condition, has been evaluated by Sidhu et al. (Ref 83). The

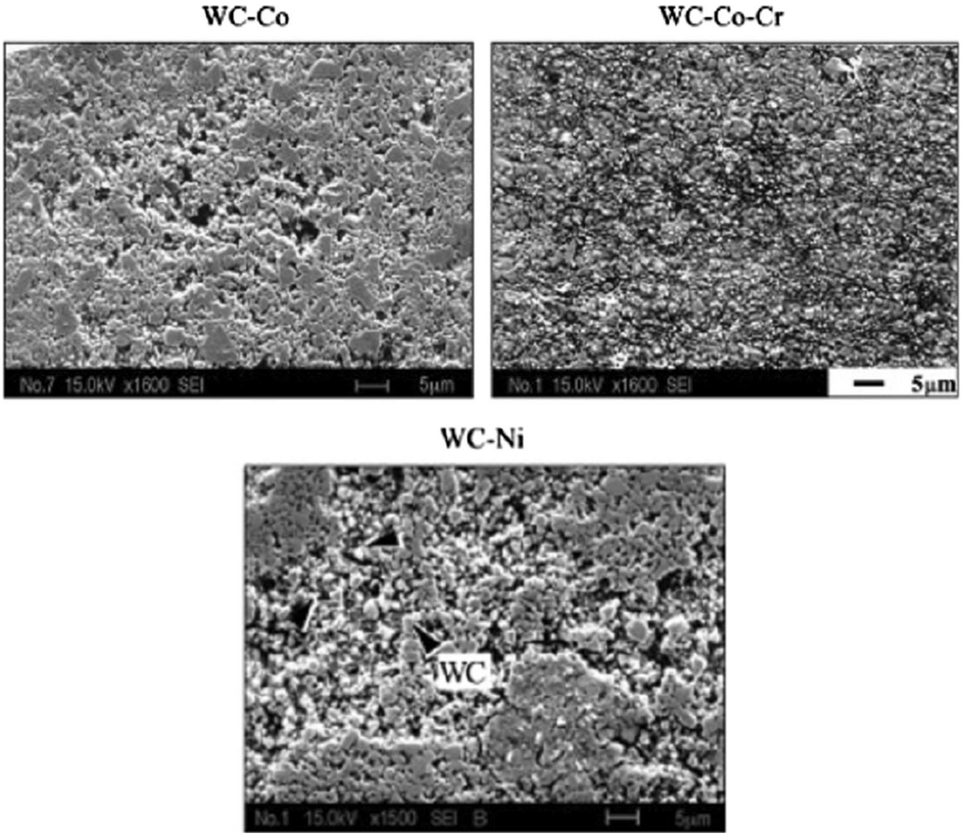

Fig. 6 Representative SEM micrographs of HVOF-sprayed WC-based coatings deposited after 120 h of immersion in aerated 5 wt.% H_2SO_4 solution (Ref 28)

coating was made of protective oxides of mainly chrome and less protective oxides of nickel and cobalt and their spinels formed in the surface scale and the boundaries of Ni and W rich splats. These oxides plugged the pores and hindered the possible diffusion paths in the coatings for penetration of aggressive species. The WC-NiCrFeSiB coating showed better resistance to oxidation as compared to hot corrosion.

The SEM micrographs of three WC-based HVOF sprayed coatings with different binding materials are shown in Fig. 6. It illustrates the effect of using various binders on the severity of micro-galvanic corrosion formation in tungsten carbide based coatings. The black regions on the micrographs has represented voids resulted from separation of WC particles from the surface. It can be concluded that WC-Co-Cr coating possessed the lowest level of micro-galvanic corrosion compared to the other coatings. a selective dissolution of the Co/Ni binder has first occurred in the HVOF deposited coating and led to separation of the WC particle for both WC-Co and WC-Ni coatings (Ref 32). Presence of Cr in HVOF deposited WC-Co-Cr coating has resulted in the formation of a stable chromium oxide passive layer, detected by XRD (Ref 32), which reduced the amount of Co dissolution and led to less separation of WC particle.

In summary, for the thermal-sprayed WC-based coatings, binders such as Co, Co-Cr, and Ni have usually been added to WC-based coatings deposited by thermal spraying techniques in order to increase their stability. Micro-galvanic corrosion is the most common corrosion mechanism which usually occurred due to potential gap between the constituents. Selective dissolution of the binder materials at the different stages of corrosion was followed by falling off the WC particles. Addition of Cr to WC-based alloys has resulted in formation of Cr_2O_3 and significantly improved the corrosion performance. In general, the chemical composition of metallic binder materials and occurrence of micro-cracks and micro-galvanic cell were the most crucial factors affecting the corrosion behavior of the HVOF sprayed WC coating. Thus, the possibility of introducing new binders with smaller potential gap respect to the WC matrix may improve the corrosion resistance.

Corrosion Resistant Coatings for Molten Salt Attack: From Thermal Spraying to Thermal Diffusion

Thermal-Sprayed Coatings for Molten Salt Attack

High-temperature corrosion caused by residual molten salt attack is a major challenge that occurs as a result of combustion of black liquors, waste, biomass, and high-chlorine coals, commonly in components of waste-to-energy plants around the super-heaters and recovery boilers (Ref 131-136). For instance, in Kraft pulping process, recovery boilers are extensively utilized to generate electrical power and high-pressure process steam by burning black liquor fuel (an aqueous solution of lignin-hemicellulose-and inorganic chemicals) (Ref 131-134). The process of combustion of black liquor results in production of various low-melting temperature ash or smelt, depending on the used starting materials and process features. The produced smelt predominantly comprises various salts, e.g. calcium-, sodium- and potassium-chlorides, -sulphates, and -carbonates containing heavy-metals such as lead or zinc (Ref 137). The presence of these heavy-metals would decrease the melting point of the produced deposit and as a result, the aforementioned salts in certain combination likely become molten at high temperatures (mostly greater than 500 °C), which can be highly corrosive when exposed to oxygen (Ref 132, 133, 137). Moreover, combustion of the black liquor fuel forms hot corrosive gases such as SO_2, CO_2, Cl_2, among others (Ref 138). Lee et al. (Ref 138) pointed out two primary mechanisms that lead to high-temperature black liquor corrosion, namely, (1) active oxidation at elevated temperatures and (2) interaction of the produced sulphidic and chlorine gases and residual deposits of molten salts with the components of the recovery boilers.

Active oxidation at elevated temperatures is one of the mechanisms that cause high-temperature black liquor corrosion in recovery boilers. At elevated temperatures (above 450 °C), the anions of the molten salt, such as chlorides (Cl^-), sulphates (SO_4^{2-}), and sulphides (S^{2-}), form at the steel surface by continuous oxidation of hydrogen halides in the gas with water vapor. The produced anions continuously diffuse into the oxide-metal interface and react with the metal components of the surface and actively sustain the oxidation (Ref 139).

High-temperature black liquor corrosion can also be caused by the interaction of the produced sulphidic and chlorine gasses and residual deposits of molten salts with the steel surface of the super-heaters used in recovery boilers (Ref 139). The presence of the anions of the molten salt at elevated temperatures forms low melting point eutectics. Subsequently, these eutectics progressively dissolve the protective oxide layer from the metal surface and accelerate the oxidation of the metal surface (Ref 139). As a result of the high-temperature interaction of the molten salts and newly formed metal oxides and salts (e.g., iron and chromium salts and oxides), some corrosive gases such as Cl_2, CO_2, HCl and others are produced, which in turn can facilitate the corrosion of the steel surfaces. This so-called "self-catalytic active oxidation" corrosion can be dependent on the process parameters, gas temperature and the steel surface temperature, the type of the formed molten salt, and compositions of the gaseous phase. Further information on the corrosion process and the progressive chemical reactions occurring during the interaction of the steel surface, formed molten salts and corrosive gases at high temperatures can be found elsewhere (Ref 140-145). Moreover, stress corrosion cracking and thermal fatigue cracking may also occur at specific locations within the components of waste-to-energy plants (Ref 146-148).

In practical applications, the molten salt corrosion can affect the longevity of the components of the evaporators, fireside, fans and exhausting systems in the pulp and paper industry. Since carbon steel, low-alloy steel, and expensive stainless steels are the commonly used materials in the metallic components of the aforementioned industries and parts, they are the primary target of detrimental degradation caused by high-temperature molten salt corrosive attack (Ref 132, 133, 145). As a result, reduced equipment efficiency, expensive maintenance, and in some severe cases unexpected shutdown of the waste-to-energy plants are inevitable consequences of molten salt corrosion problems of steel components. Therefore, reliable and long-lasting protection of steel components, including long length tubing, is crucial.

Thermal spraying techniques can be utilized to fabricate protective coating in order to increase the corrosion resistance of the steel surfaces of boilers and super-heater tubes. In this regard, application of Inconel alloy 625 (21Cr-9Mo-3.5Nb-Ni base) surface welding (cladding), thermal-sprayed coatings, and weld overlays received tremendous attention in early 2000. Cladding of layers of Inconel 625 was successfully utilized in the water-wall tubes and parts in many waste-to-energy plants and facilities, since the water-wall areas that were not protected by the refractory lining were the most corrosion vulnerable parts. Rademarkers et al. (Ref 148) showed an excellent corrosion resistance of the steel surfaces of the water-wall tubes when Inconel 625 cladding applied to protect them from the corrosive attack of HCl/Cl_2 at 400 °C. The enhanced resistance of Inconel 625 corresponded to its higher thermal conductivity (~ 15 W/m- °C at 400 °C) compared to that of the refractory material, which likely entailed reduction in gas temperature in the first gas pass. However, the performance of Inconel 625 cladding on steel surfaces with relatively high temperatures such as super-heater tubes might be challenging. It was reported that the application of Inconel 625 cladding on super-heater tubes with temperature exceeding 400-420 °C did not resist corrosive attack successfully (Ref 138). In a complementary study, Wilson et al. (Ref 149) confirmed that the wastage rate of Inconel 625 cladding on super-heater tubes at temperatures of 540 °C was relatively high (0.2 µm/hr). The corrosion rate of Inconel alloy 625, however, was

10-20 times lower than pure carbon steel. The other issue with Inconel 625 cladding is its unpredictable longevity, to the extent that the lifetime of Inconel 625 claddings may vary from three months to two years. Therefore, application of Inconel 625 cladding for super-heater tubes with operating temperature over 420 °C was not recommended (Ref 138).

An alternative to cladding of Inconel 625 was using thermal spray technologies such as high-velocity oxy-fuel (HVOF) and plasma spraying to deposit Inconel 625 (Ref 150, 151). Al-Fadhli et al. (Ref 150) evaluated the erosion-corrosion behavior of HVOF thermal-sprayed Inconel 625 on three different steel substrates that were exposed to natural seawater (pH ~ 8.3) at elevated pressures (14 and 17 bar) and a temperature of 50 °C. They proposed that the coated substrate successfully resisted against the attack of the simulated corrosive environment. In spite of the fact that seawater may consist of different salts based on ions, such as chloride (Cl^-), sodium (Na^+), sulfate ($SO_2{}^{4-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+), the exposure of the steel substrate to a seawater slurry at 50 °C cannot be considered similar to or equivalent to molten salt corrosion. Moreover, the working temperature in this study was much lower than that for typical super-heaters, black liquor recovery boilers, and waste incubators (~ 400-560 °C) (Ref 133, 152, 153). In an experimental study with immediate focus on the molten salt attack corrosion, Uusitalo et al. (Ref 151) applied different thermal spray deposition techniques such as HVOF, arc spraying, and plasma spraying to study the corrosion resistance of materials similar to Inconel 625 (Ni-21.5Cr-9Mo-Fe-Nb, or Ni-21.5Cr-9Mo-Fe-Nb) against molten potassium chloride (KCl) attack at elevated temperatures (~ 850 °C). The results of the experimental tests indicated that the corrosion resistance of the plasma-sprayed and HVOF Inconel 625 was the best combination among the other thermal spray techniques. Fukuda et al. (Ref 154) also observed that for practical waste-to-energy application, Inconel 625 plasma-sprayed coatings and NiCrSiB HVOF coatings were suitable for water-wall tubes. On the other hand, in order to have a long-term protection (~ 3 years) of the steel substrate of the super-heater tubes, TiO_2-Al_2O_3-Inconel 625 cement HVOF coatings were recommended (Ref 154).

More recently, it has been observed that thermal-sprayed yttria-stabilized zirconia (YSZ)-based coatings could provide successful resistance to steel surfaces of the super-heater tubes and recovery boilers against the molten salt corrosive attack at elevated temperatures (Ref 155-168). In an early study, Jones (Ref 155) reported on a detailed review of the utilization of YSZ-based coatings for protection of the thermal barrier coatings against hot corrosive attack. It was concluded that YSZ showed successful resistance against corrosive attack when the corrosive salt compounds were only sodium and sulfur. In this regard, Marple et al. (Ref 156) studied the corrosive resistance of both atmospheric plasma-sprayed lanthanum zirconate ($La_2Zr_2O_7$) and YSZ for use as thermal barrier coatings in industrial gas turbines applications. In this study, the coatings were exposed to molten vanadium- (V_2O_5) and sulfur-containing salts ($Na_2SO_4 + MgSO_4$) at 1000 °C and it was found that the YSZ coating rapidly degraded by the vanadium compounds, while showed successful resistant to molten sulfur-compounds corrosive attack, which was in good agreement with the results of the study by Jones (Ref 155). Moreover, it was found that the lanthanum zirconate coating, on the contrary, was less degraded by the molten vanadium-compounds, while it seriously damaged by the sulfur-containing molten salt (Ref 156).

In addition to the applications of YSZ in gas turbines and engines (Ref 156, 157), significant attention has been directed to the application of YSZ in environmental thermal barrier coatings which have been exposed to harsh corrosive environments. Shankar et al. (Ref 158) showed that plasma-sprayed YSZ coatings performed successfully against molten corrosive salt attack ($LiCl + KCl$) at 600 °C. In a similar study to evaluate the corrosion resistance of the plasma-sprayed YSZ coating against lithium-based molten salt ($LiCl + Li_2O$) at elevated temperatures (650 °C), Lee and Baik (Ref 159) showed that the YSZ coating can protect the surface (or the bond coat in thermal barrier coatings) well. It was found that the formation of a dense reaction layer of nano-crystalline phase which can act as a protective oxide layer on the surface and at the inter-splat pores of the coating attributed to the successful corrosion resistance of the YSZ coatings.

In light of the detrimental impact of the corrosive molten salts, combined with flue gases that were produced in the components of the waste-to-energy plants such as recovery boilers and super-heater tubes, Rao et al. (Ref 160) evaluated the corrosion resistance of the air plasma-sprayed YSZ environmental barrier coatings that were exposed to molten salt which was a synthetic mixture of reagent grade chemicals (10.2 wt.% KCl + 11.5 wt.% Na_2CO_3 + 73.9 wt.% Na_2SO_4 + and 4.4 wt.% K_2SO_4) at elevated temperatures (600 °C). The salt compounds were used to simulate upper boiler tubes deposits. In this study, moreover, the performance of two different types of YSZ coatings, namely, conventional YSZ and nanostructured YSZ were studied. It was found that the corrosion resistance of the nanostructured YSZ coatings was superior, since the presence of semi-molten nano-agglomerates in the nanostructured YSZ coating microstructure caused the accumulation of the penetrating molten salt in this so-called "collecting points" of the coating. The aforementioned feature attributed to further protection of the nanostructured YSZ coatings against the molten salt corrosive attack (Ref 160). In a similar study, Jamali et al. (Ref 161) investigated the corrosion behavior of plasma-sprayed conventional and nanostructured YSZ thermal barrier coatings against molten salt mixture (V_2O_5 + Na_2SO_4) at 1000 °C. Similar to the results presented by Rao et al. (Ref 160), it was found that in spite of a higher level of reaction with the molten salt, the nanostructured YSZ coating performed better in molten salt corrosive attack in comparison with the conventional YSZ coatings.

Recently, significant studies have been done to modify the coating powder in order to fabricate more efficient corrosion resistant coatings (Ref 162-167). The corrosion resistance of plasma-sprayed nanostructured Ceria-Yttria co-stabilized zirconia (CYSZ) coating (ZrO_2-2.5 wt.% Y_2O_3-25 wt.% CeO_2) that was exposed to corrosive molten salt mixture (45 wt.% Na_2SO_4 + 55 wt.% V_2O_5) at 1000 °C was studied by Hajizadeh-Oghaz et al. (Ref 162). The results showed that the nanostructured CYSZ coating resisted molten salt attack remarkably well, which was likely due to the high diffusional resistance of the nanoporous media that restricted diffusion of molten salt into the coating. The significant corrosion resistance of the coating could have been a result of the addition of ceria (CeO_2) in the coating. It has been reported that superficially applied CeO_2 coating on the different superalloy substrates can noticeably increase the corrosion resistance of the substrate against molten salt corrosive attack. A study by Gitanjaly et al. (Ref 163) confirmed the successful corrosion resistance of superficially applied ceria coatings when exposed molten salt environment (40 wt.% Na_2SO_4 + 60 wt.% V_2O_5) at 900 °C. In this regard, Habibi and Guo (Ref 164) also compared the molten salt corrosion resistance of air plasma-sprayed Yttria-stabilized (YSZ), ceria-stabilized (CSZ), and titania-stabilized zirconia (TiSZ) coatings against the corrosive attack of molten salt mixture (50 wt.% Na_2SO_4 + 50 wt.% V_2O_5) at elevated temperatures (1050 °C). It was observed that among the three coatings, titania-stabilized zirconia coating was more thermally- and chemically-stable and also showed improved molten salt corrosion resistance. This was due to the fact that for TiSZ coatings, unlike YSZ and CSZ coatings, no phase transformation happened, i.e. tetragonal zirconia remained stable and no monoclinic zirconia was formed after the molten salt attack. It is worth mentioning that high-temperature phase transformation may increase the possibility of the formation of detrimental cracks within the coating, which in turn would facilitate the penetration of the molten salt into the coating (Ref 164).

While plasma spraying was known to be the most commonly used technique of deposition of YSZ coatings for thermal and environmental barrier coatings, Ahuja et al. (Ref 168) utilized a D-gun technique to deposit zirconium incorporated Cr_3C_2-(NiCr) coating on different nickel-based superalloys substrates to evaluate the corrosion resistance of the fabricated coating. The high temperature corrosion, erosion, and wear resistance of Cr_3C_2-(NiCr) coatings is well-reported and they are often used in turbine engines due to their high thermal stability (Ref 169, 170). The coatings were exposed to molten salt mixture (40 wt.% Na_2SO_4 + 40 wt.% K_2SO_4 + 10 wt.% NaCl + 10 wt.% KCl) at 900 °C to simulate the incinerator environment condition and a promising corrosion resistance was observed. A brief summary of the performance of the thermal-sprayed YSZ-based coatings in molten salt corrosive environment is presented in Table 3.

Thermal Diffusion Surfaces for Molten Salt Attack

In the past decades, thermal spray technologies have been used extensively to overcome the detrimental effect of molten salt corrosive attack in steel material used for tubing and piping in waste-to-energy plants and oil and gas industries. However, due to difficulties and restrictions of application of thermal-sprayed coatings on complex shape parts and inner surface of long size pipes with small inner diameter, there are some serious limitations in utilizing thermal spray technologies in practical applications. Moreover, spallation and delamination of the protective coatings layer in long size pipes and tubes, as well as the unexpected and sudden demolition of the micron-size coatings under harsh high-temperature corrosive and abrasive conditions can challenge the application of the majority of these thermal spray processes. Therefore, reliable protection of steel components from the corrosive attack in super-heater tubes and recovery boilers is crucial. In this regard, some surface engineering methods related to chemical vapor deposition (CVD) principles can be utilized to alleviate the issues around cracking and delamination of the surface treatment (Ref 12, 13, 16).

Due to the nature of thermal diffusion techniques, as a result of the inward diffusion of the coating active atoms (e.g., B, Al, and Cr) and outward diffusion of the metallic components of the steel substrate (e.g., Fe, Cr, Ni, and others), a few layers comprises borides, aluminides, or chromides of certain compositions may be formed simultaneously within the thermal diffusion coating. According to the initial (starting) mix compositions, substrate constituent materials, as well as the process parameters such as temperature, exposure time, and gas pressure, the structure of the formed layers, thicknesses, and compositions may differ. Figure 7 shows the microscopic images of the cross-section of the boronizing, aluminizing, and chromizing thermal diffusion coatings on low carbon steel substrates (Ref 171). Further information on the thermal diffusion process and its coating formation can be found in detail elsewhere (Ref 172, 173).

Table 3 Molten salt corrosion behavior of thermal-sprayed Yttria-stabilized zirconia-based coatings on steel

Coating material	Coating technique	Molten Salt Corrosive environment	Temperature (°C)	Observations
Yttria-stabilized Zirconia-based				
YSZ	PS	V_2O_5 and $Na_2SO_4 + MgSO_4$	1000	YSZ coating rapidly degraded by the vanadium compounds; successful corrosion resistant to molten sulfur-compounds corrosive attack (Ref 156)
YSZ	PS	$LiCl + KCl$	600	Yttria-stabilized zirconia coatings successfully resisted against molten salt attack without showing significant degradation (Ref 158)
YSZ	PS	$LiCl + Li_2O$	650	Formation of protective oxide layer on the surface and at the inter-splat pores of the coating attributed to the successful corrosion resistance (Ref 159)
Nanostructured YSZ	PS	$KCl + Na_2CO_3 + Na_2SO_4 + K_2SO_4$	600	Nanostructured YSZ coatings protected the stainless steel substrate better than their conventional counterparts (Ref 160)
Nanostructured YSZ	PS	$V_2O_5 + Na_2SO_4$	1000	Similar to (Ref 160), the nanostructured YSZ coating performed better in molten salt corrosive attack (Ref 161)
Nanostructured CYSZ (ceria-yttria co-stabilized zirconia)	PS	$V_2O_5 + Na_2SO_4$	1000	Nanostructured CYSZ coating remarkably resisted against the molten salt attack (Ref 162)
YSZ CSZ TiSZ	PS	$V_2O_5 + Na_2SO_4$	900	Among the three coatings, titania-stabilized zirconia coating was more thermally- and chemically-stable and also showed a better molten salt corrosion resistance (Ref 164)

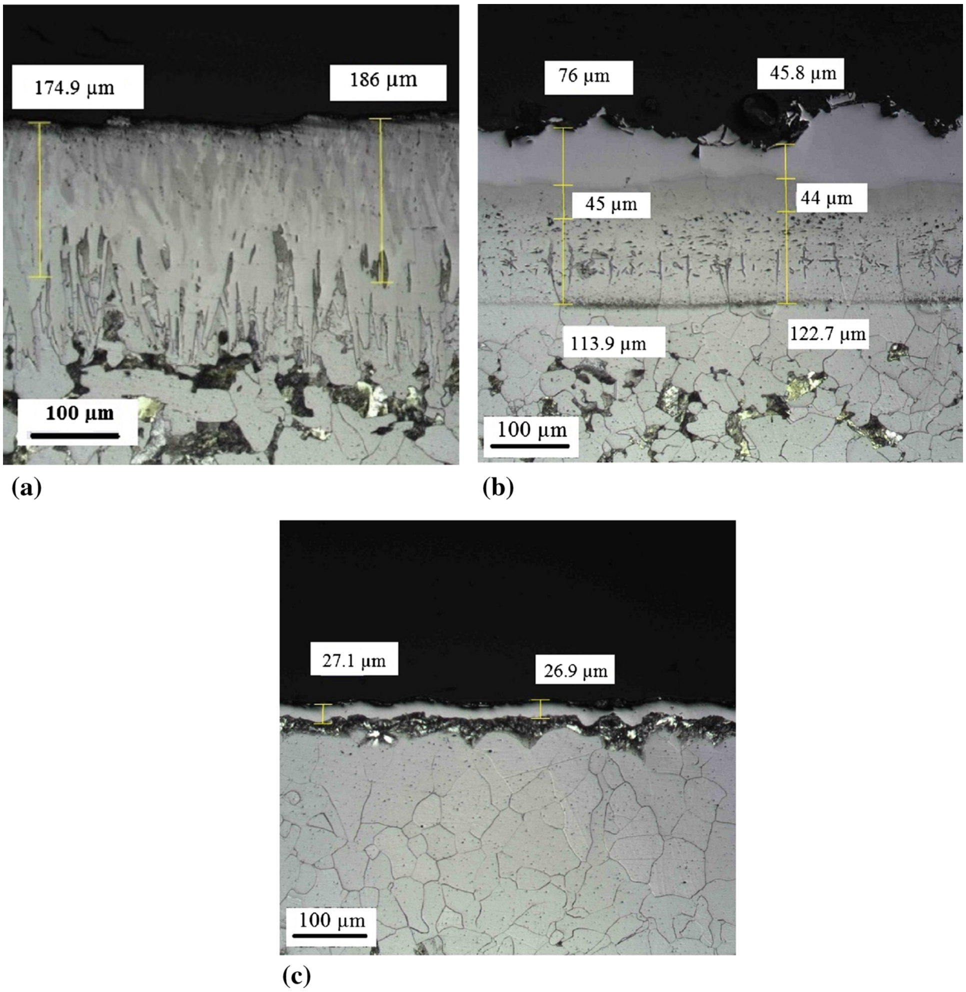

Fig. 7 Microscopic images of the cross-section of (a) boronizing, (b) aluminizing, and (c) chromizing thermal diffusion coatings on low carbon steel substrate (Ref 171)

The thermal diffusion process has been used extensively for boronizing steel substrates to protect them against corrosion in a variety of practical applications, particularly for waste-to-energy plants, oil and gas production, refinery, and power generation applications (Ref 174-179). Telle et al. (Ref 174) and Dearnley and Bell (Ref 175) summarized the chemical bonding and crystal chemistry of borides that were produced by chemical vapor deposition method and thermal diffusion technique. It was reported that metal boride materials showed relatively high hardness and chemical inertness which put these coatings in a superior position for applications where corrosion and wear resistance coatings were required. The corrosion resistance of the boronized steel substrate by CVD and thermal diffusion processes was studied by Sinha (Ref 176). It was suggested that iron borides and some other brides in the coating can successfully protect the steel substrate against corrosion at high temperatures. Petrova and Suwattananont (Ref 177) studied the corrosion behavior and oxidation resistance of the boronized coatings on three different steel substrate, namely, plain-carbon steel AISI 1018, high-strength alloy steel AISI 4340, and austenitic stainless steel AISI 304. The boronized coatings were exposed to hydrochloric acid (HCl) at room temperature for corrosion resistance and at elevated temperature (600 °C) for oxidation resistance of the coatings. It was observed that the boronizing coating on ferrous alloys significantly improved their corrosion and oxidation resistance. Similar studies confirmed the oxidation and corrosion resistance of the boronized coating on low-carbon steel AISI 1018 at elevated temperatures (up to 900 °C) (Ref 178, 179).

In a more detailed and practical study on the corrosion behavior of thermal diffusion boronized coatings, Medvedovski et al. (Ref 18) exposed the boronized steel substrates to the corrosive condition of water steam with the presence of various salt mixtures of hydrocarbons, carbonaceous gases ($CO + CO_2$), hydrogen sulfide (H_2S), and chloride salts such as NaCl and $CaCl_2$) at high temperatures of 200-300 °C and elevated pressure (12-28 MPa). The corrosive environment was chosen to simulate the actual oil well condition. The results indicated the boronized coatings provided a successful and promising corrosion and wear resistance under the simulated harsh environment. In a similar study by Medvedovski (Ref 172), it was shown that the boronizing thermal diffusion coatings can promote corrosion resistance of steel components, especially for applications where large-size and multiplex shapes and long tubular components. These boronized thermal diffusion coatings also provided a remarkable extension of the service life, i.e. ~ 3-10 times higher durability in comparison to uncoated steel substrates, in corrosive environments, especially in oil well production conditions and power generation. However, it was suggested that due to their detrimental oxidation at higher temperatures, boronized coatings can be applicable in environment with relatively low temperatures (up to 500 °C) (Ref 173).

Medvedovski (Ref 172) demonstrated that the successful protection of the steel substrate through thermal diffusion boronized or intermetallized coatings is a consequence of two main mechanisms that occur in this process, namely, formation of crystalline structure in the coating and substrate and robust diffusion bonding to the substrate. In other words, thermal diffusion coating compounds (borides or other intermetallides) show high values of thermodynamic properties such as crystalline lattice energy and enthalpies which corresponded to higher stability of crystalline structure, as well as strong and short covalent bonds of Fe-B (or Fe-Al or Cr-Al for other intermetallic coatings) which associated with chemical stability and integrity of the thermal diffusion coatings (Ref 180, 181). The direct consequence of the aforementioned phenomena was high corrosion resistance of the thermal diffusion coatings (Ref 182, 183). Moreover it was observed that the thermal diffusion boronized coatings, on the contrary to steel, did not accommodate free iron (Fe), or other constituent elements of steel, and the "introduced" elements (e.g. boron) in the coating. Therefore, the interaction of the anions of the corrosive environment (e.g., of the salts such as Cl^-, SO_4^{2-}, and CO_3^{2-}) with the positive ions of free metal elements is hindered (Ref 171-173). However, at high temperatures, covalent bonds of Fe-B might break and the interaction with the corrosive medium might entail corrosion and oxidation of the thermal diffusion coatings. Similar observation regarding the sign of corrosion at elevated temperatures (above 500 °C) was reported by Medvedovski et al. (Ref 173).

While significant attention has been directed toward the CVD and thermal diffusion boronized coatings, some studies have been conducted to investigate the corrosion behavior of aluminizing and chromizing steels and alloys that were exposed to corrosive liquid and gaseous environments at high temperatures (Ref 184, 185). In an early study be Bangaru and Krutenat (Ref 184), the microstructure and formation mechanisms, as well as the mechanical and thermal stabilities of aluminum diffusion coatings on various steel substrates were investigated. It was found that for all thermal diffusion aluminized coatings, two separate layers, an outer aluminide layer and an inner inter-diffusion layer, that are formed on top of the original stainless steel substrate were formed. Vokál et al. (Ref 185) studied the corrosion performance of two aluminized steel substrates, P91 ferritic-martensitic steel and 800 austenitic stainless steels, after exposure to molten salt (K_2SO_4-KCl) at 650 °C. It was found that aluminized austenitic stainless steel substrate was corroded noticeably through via intergranular and internal chloridation-sulphidation-oxidation; however, the aluminized P91 ferritic-martensitic steel remained unattacked. The corrosion resistance of the aluminized steel substrates was linked to the aluminum content and the distribution of chromium within the coating (i.e. coatings with grain boundary chromium enrichment experienced intergranular corrosion). Kiamehr et al. (Ref 186) investigated the corrosion resistance of aluminum diffusion coatings on ferritic-martensitic steel P91 substrate that was exposed to molten potassium chloride salt (KCl) at 600 °C. It was observed that two aluminide coatings, $Fe_{1-x}Al$ and Fe_2Al_5, were formed. It was found that a protective layer was formed on large parts of the $Fe_{1-x}Al$ coating, except some local failure which was associated to the dilatation of aluminum. However, on small parts of the Fe_2Al_5 coating on the steel substrate, corrosion in the form of selective aluminum removal occurred and voluminous corrosion products were created. In a comparative study, Wang (Ref 187) studied the corrosion behavior of both the aluminized and chromized thermal diffusion coatings on 2.25Cr-1Mo steel substrates at temperature of 740 °C when exposed to simulated medium-BTU product gas (composed of CO, CO_2, CH_4, H_2S, H_2, and H_2O). The results showed that chromized coating with more than 30 wt.% Cr and a thickness of 120 µm provided suitable corrosion resistance in sulfidation-oxidation conditions. However, it was fund that aluminized coatings were not suitable for use within the application of coal gasifier atmosphere due to internal sulfidation-oxidation and detrimental cracking within the coating. Moreover, Bai et al. (Ref 188) investigated the carrion resistance of chromized thermal diffusion coating on low-carbon AISI 1020 steel when exposed to H_2SO_4 solution at 700 °C. It was shown that the corrosion resistance of the chromized substrate improved compared to the original substrate.

With respect to the discrepancy among the results of the studies on the corrosion behavior of the boronized, aluminized, and chromized thermal diffusion coatings on steel substrates, a comparative research study was conducted by Mahdavi et al. (Ref 171) to explore the corrosion behavior of the aforementioned thermal diffusion coatings on both low-carbon steel and 316 stainless steel. The coated substrates were exposed to simulated molten salt-oxidation environment (10.2 wt.% KCl + 11.5 wt.% Na_2CO_3 + 73.9 wt.% Na_2SO_4 + and 4.4 wt.% K_2SO_4) at different temperatures of 220 °C (low-temperature) and 600 °C (high temperature) to simulate industrial corrosive conditions in recovery boilers in the pulp and paper processing. The results suggested that the aluminized samples had successful corrosion resistance in both low- and high-temperature molten salt-oxidation environments which was due to the formation of a thin layer of chemically inert Al_2O_3 that promoted the corrosive resistance of the aluminized coatings. The boronized and chromized thermal diffusion coating on both steel substrates were not affected by the low-temperature corrosive attack; however, some phase changes after the high-temperature corrosive attack was observed for the chromide coatings which was due to the significant formation of chromium oxide (Cr_2O_3) (Ref 189). Moreover, the corrosion resistance of thermal diffusion coatings with more complex architectures, where a few protective layers such as SnO_2, ZrO_2, BN were applied on the top of the aluminized and boronized coatings, were studied. The application of the additional top coatings promoted the corrosive resistance of the coatings by inhibiting the interaction of the coatings with the corrosive salts, especially at high temperature. The aluminizing thermal diffusion coatings were recommended for application in the pulp and paper processing (Ref 171). A brief summary of the corrosion behavior of thermal diffusion coatings is presented in Table 4.

Conclusions and Perspectives for Future Research and Development

A schematic summary of the possible corrosion mechanisms of thermal-sprayed coatings at both ambient and elevated temperatures is shown in Fig. 8. As it is seen in this graphical scheme, formation of passivation layers (e.g., oxides of chromium, Ni/Cr/Ti/Si, and Al) have played an important role in the corrosion behavior of the coatings either in high or ambient temperatures. Self-sealing is another dominant mechanism, especially, in thermal-sprayed Zn-based and Al-based coatings, through which the pores and cracks were clogged and the corrosion rate was significantly decreased. Galvanic corrosion between the coating constituents can be considered as the dominant corrosion mechanism in thermal-sprayed WC-based coatings. The galvanic corrosion rate can be hindered by addition of Cr, reducing the potential gap between the elements which may result in formation of a Cr_2O_3 layer, which is considered to provide good protection for metallic surfaces against corrosion at low and medium-high temperatures.

The main purpose of application of protective coatings fabricated by thermal spraying and thermal diffusion techniques is to increase the life-span of the steel components and structures when exposed to harsh and corrosive. Better understanding of the nature of deterioration processes could help to prolong their service life. In summary, this paper provides a road map for corrosion mechanism and corrosion resistance of thermal-sprayed and thermal diffused coatings applied on steel structures. In this regard, several studies related to corrosion performance of the variety of coating materials deposited by different surface engineering technologies have been reviewed and evaluated in this investigation. The highlight of corrosion mechanism for each major deposited element can be summarized as followings:

(1) Formation of passive layers, made of aluminum oxide and aluminum hydroxides, in Al-based coatings plugged the defects and hindered further penetration of the electrolyte into the coating. Arc spray is the most recommended technique for developing of Al-based coatings. Addition of Si and RE elements could result in better corrosion resistance due to self-sealing phenomena.

(2) Zinc-based alloys act as sacrificial anode when they have been added to steel. Alloys containing zinc and aluminum possess two corrosion protection mechanisms during the corrosion which are passivation due to aluminum oxide formation and acting as sacrificial anode owing to zinc nature.

(3) The corrosion protection mechanism of Ni-based coatings attributed to formation of passive layers of alloying elements such as TiO_2, Cr_2O_3, and oxides of silicon/chromium/nickel. HVOF is the most recommended coating techniques for Ni-based alloys. Post spraying laser surface treatment is advised to produce a crack- and porosity-free layer and improve the corrosion resistance.

(4) Passivation (Cr_2O_3 layer) is the major mechanism protecting the Cr-based coatings against corrosion. However, evolution of high level of porosity in Cr-based coating requires supplemental surface modification. HVOF has been favored, among thermal spraying techniques, for applying Cr-based coating. Effects of thermal spraying process parameters and post-heat treatment on anticorrosion behavior is still needed to be studied for these types of coatings.

(5) Micro-galvanic corrosion is the most common mechanism in WC-based coatings due to potential gap between the WC and the binding materials (e.g. Co, Cr, and Ni). Addition of Cr to WC-based alloys has resulted in formation of protective Cr_2O_3 layer and significantly improved the anticorrosion

Table 4 Corrosion behavior of thermal diffusion coatings on steel

Substrate material	Corrosive environment	Temperature (°C)	Observations
Boronizing			
Plain-carbon steel AISI 1018	HCl	600	Boronizing coating significantly improved their corrosion and oxidation resistance (Ref 177)
High-strength steel AISI 4340			
Austenitic stainless steel AISI 304			
Low-carbon steel AISI 1018	HCl	900	Successful corrosion resistance was observed (Ref 178, 179)
Carbon steel	CO + CO_2, H_2S, NaCl, $CaCl_2$	200-300	Boronized coatings provided a successful and promising corrosion and wear resistance under the simulated harsh environment (Ref 18) Sign of corrosion was observed at elevated temperatures (above 500 °C) (Ref 173)
Low-carbon steel	KCl, Na_2CO_3, Na_2SO_4, K_2SO_4	220	Boronized thermal diffusion coating on both steel substrates were slightly affected by the high-temperature corrosive attack (Ref 171)
316 Stainless steel		600	
Aluminized			
P91 ferritic-martensitic steel	K_2SO_4, KCl	650	Aluminized austenitic stainless steel substrate was corroded noticeably through via intergranular and internal chloridation-sulphidation-oxidation (Ref 185) Aluminized P91 ferritic-martensitic steel remained unattacked (Ref 185)
800 austenitic stainless steels			
P91 ferritic-martensitic steel	KCl	600	Two aluminide coatings, $Fe_{1-x}Al$ and Fe_2Al_5, were formed. Protective layer was formed on large parts of the Fe1-xAl coating, except some local failure which was associated to the dilatation of aluminum (Ref 186) corrosion in the form of selective aluminum removal occurred on the small part of Fe_2Al_5 coatings (Ref 186)
2.25Cr-1Mo steel	CO, CO_2, CH_4, H_2S, H_2, H_2O	740	Aluminized coatings were not suitable for use within the application of coal gasifier atmosphere due to internal sulfidation-oxidation and detrimental cracking within the coating (Ref 187)
Low-carbon steel	KCl, Na_2CO_3, Na_2SO_4, K_2SO_4	220	Aluminized samples had successful corrosion resistance in both low- and high-temperature molten salt—oxidation environments which was due to the formation of a thin layer of chemically inert Al_2O_3 (Ref 171)
316 Stainless steel		600	
Chromized			
2.25Cr-1Mo steel	CO, CO_2, CH_4, H_2S, H_2, H_2O	740	Chromized coating with more than 30 wt.% Cr and a thickness of 120 µm provided suitable corrosion resistance in sulfidation-oxidation conditions (Ref 187)
Low-carbon AISI 1020	H_2SO_4	700	Corrosion resistance of the chromized substrate improved compared to the original substrate (Ref 188)
Low-carbon steel	KCl, Na_2CO_3, Na_2SO_4, K_2SO_4	220	Chromized thermal diffusion coating on both steel substrates were not affected by the low-temperature corrosive attack; however, some phase changes after the high-temperature corrosive attack was observed for the chromide coatings (Ref 171)
316 Stainless steel		600	

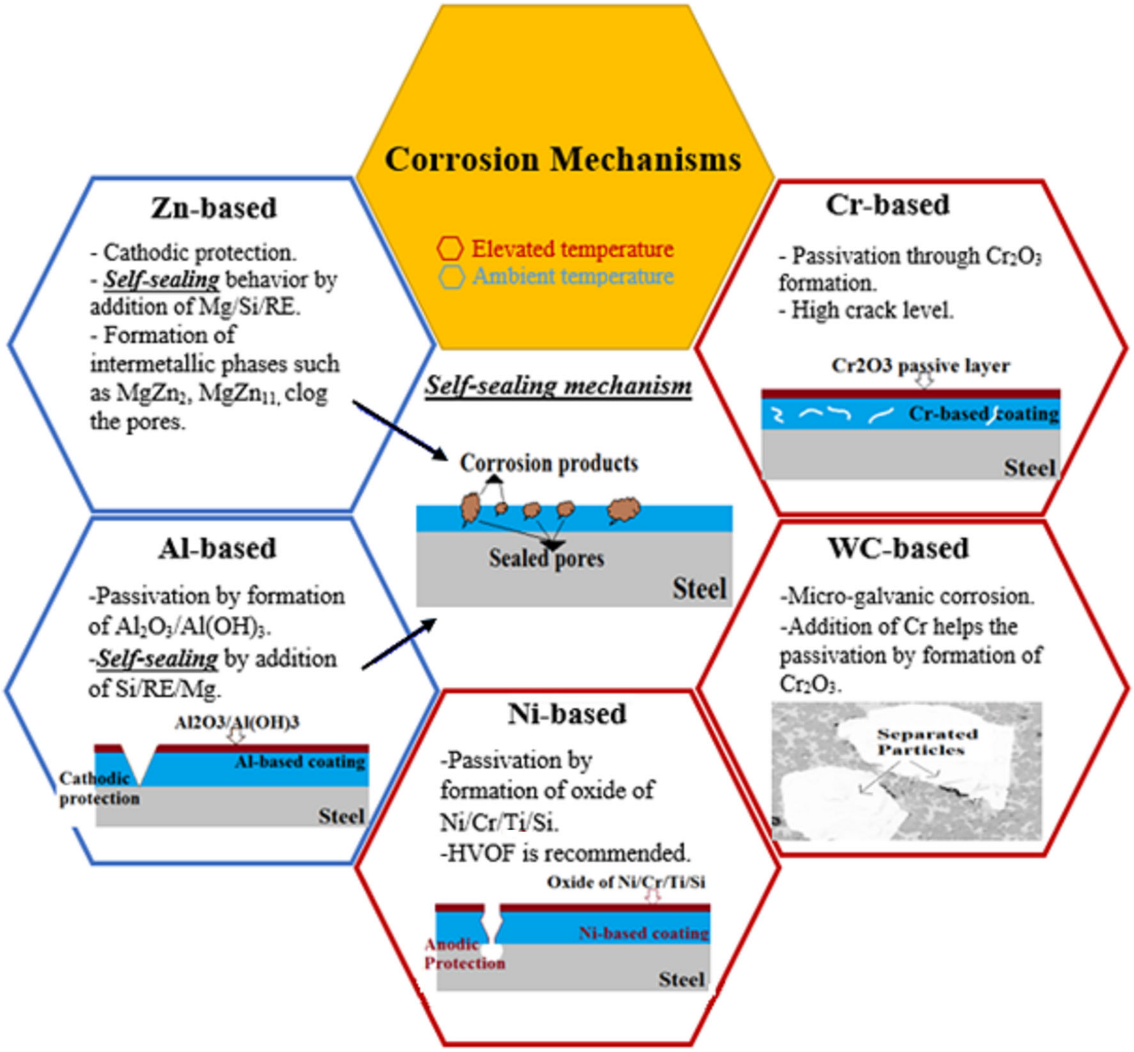

Fig. 8 Comparison between the corrosion mechanisms of various thermal-sprayed coatings at room and elevated temperatures

performance. Introducing a new binder with lower potential gap respect to WC matrix could significantly help the corrosion behavior of WC-based coatings.

(6) Molten salt corrosive attack can affect the performance and the life span of the components of the super-heater tubes, recovery boilers, evaporators, fireside, fans and exhausting systems in the waste-to-energy plant. In this regard, thermally-sprayed Inconel 625 and yttria-stabilized zirconia can demonstrate a successful corrosion resistant in the aforementioned application, depending on the working temperature of the components of the waste-to-energy plants. Moreover, thermally-sprayed nanostructured Yttria-stabilized zirconia coatings are highly recommended for long-lasting and reliable protection against molten salt corrosive attacks.

(7) Thermal diffusion coatings can also provide promising protection against corrosive environment due to the formation of crystalline structure in the coating and substrate as well as the robust diffusion bonding of the coated material to the substrate. Thermal diffusion boronizing, aluminizing, and chromizing coatings can be utilized in applications where the working temperature is relatively low (below 500 °C). However, in practical application where high-temperature (above 500 °C) molten salt attack plays a major role in degradation and oxidation of the steel substrate, thermal diffusion aluminizing coatings, with an additional top layer of SnO_2, ZrO_2, BN are recommended.

Future research work may be advanced in the development of duplex coatings, wherein wear resistant coatings are combined with corrosion resistant coatings. Preliminary studies has been conducted to fabricate thick coating interlayers, deposited by HVOF spraying, followed by deposition of physical vapor deposition (PVD) (TiN, TiAlN) or plasma-enhanced CVD (DLC) hard top layers. Alternatively, novel techniques such as plasma spray-physical vapor deposition (PS-PVD) have been utilized in order decrease wear rates, while producing successful resistance against corrosive attack (Ref 190, 191). Moreover, wear resistant WC-based or boron carbide (B_4C)-based coatings or overlays can be treated with the deposition of PVD or CVD layers of chemically resistant coatings to produce combined wear and corrosion resistant coatings.

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