Review

Behaviour of thermally sprayed coating for hot corrosion applications

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Abstract

As modern air engines’ working temperatures are increasing, materials and coatings' hot corrosion resistance characteristics gain significant attention. Hot corrosion is a type of degradation at high temperatures that involves oxidizing or sulfidation of the substrate behind a layer of salt melt deposit, which either causes the development of a thick layer of sulphide scale or the penetration of sulphur via grain boundaries into the matrix to a deeper depth. It may notably change the microstructure, phase composition, and characteristics of the thermally sprayed coating. In recent years, thermally sprayed cermet coatings on steel have been more well-liked as a possible method for enhancing hot corrosion resistance. This review paper qualitatively summarizes the recent development of thermal sprayed coatings to improve hot corrosion performance.

Keywords

Sulphidation; tribology; wear resistance; cermet coatings

Introduction

Hot corrosion is a type of degradation at high temperatures that involves oxidizing or sulfidation of the substrate behind a layer of salt melt deposit, which either causes the development of a thick layer of sulphide scale or the penetration of sulphur via grain boundaries into the matrix to a deeper depth. The typical morphology of hot corrosion products consists of a low-chromium metal matrix, a dense, porous oxide layer, and chromium-rich sulphides inside the oxides. The consensus among specialists is that initiating a hot-corrosion attack requires liquid Na sulphate. Generally, hot corrosion attack occurs between 800 and 950 °C, though this varies depending on the alloy.

If the melting point for salt deposits is at a lower temperature but the dew point is at higher temperatures, the corrosion is referred to as type I hot corrosion [1]. On the other hand, type II hot...
corrosion happens at lower temperatures (generally from 670 to 750 °C). Type II hot corrosion behind a protective layer with minimal to no interior attack indicates a pitting attack [2].

Some metals, such as zirconium, titanium, chromium, and others, form shielding nitride scales when exposed to nitrogen-rich environments. Carburization and decarburization problems that weaken or embrittles the component occasionally occur in carbon dioxide and carbon monoxide environments.

When fireside boiler tubes in coal-fired steam-generating plants started to deteriorate, high-temperature corrosion was first identified as a severe issue in the 1940s. Since then, fluidized bed combustion, gas turbines, I. C. engines, boilers, and industrial waste incinerators have all experienced the issue. In the late 1960s, turbine makers and users learned about hot corrosion due to the severe corrosive assault that occurred in the engines of rescue planes and helicopters operating over and near seawater during the Vietnam War [3,4]. The primary factor contributing to hot corrosion is the breakdown of ash and fuel compounds, which include Na, S, V and Cl, which are present in burning coal or fuel oil. When marine atmospheres are contaminated with NaCl, these pollutants may occasionally be consumed from the service environment. It is well acknowledged that hot corrosion requires condensed alkali metal salts, especially Na₂SO₄ [5]. A typical high-temperature corrosion promoter in these applications, besides Na₂SO₄, is V₂O₅.

In most cases, using these low-grade fuels is acceptable due to the significant expense of eliminating these contaminants. According to research, the most frequent salt buildup in boiler superheaters is sodium vanadyl vanadate (Na₂O x V₂O₅ x 5V₂O₅), which fuses at a comparably lesser temperature of 550 °C [6]. Na₂SO₄, V₂O₅, and Na₂V₂O₆ are also anticipated to be the main species in salt deposits accumulating on gas turbine surfaces [7].

Due to molten salts in the fuel, such as KCl, NaVO₃, Na₂SO₄, V₂O₅, and NaCl, hot corrosion is the primary cause of failure in gas turbines [8-11]. This corrosion causes surface spalling by accelerating the oxidation and sulphidation of thermo-resistant materials. When contaminants like sulphur and/or chlorine are present in an oxidizing atmosphere, the rate of attack frequently increases in the sequence as first oxidation only, after that internal sulphidation, then after internal chlorination, then (sulphate salts) hot corrosion then (sulphate and chloride salts) hot corrosion. To compare other, more aggressive kinds of corrosion, oxidation in air or O₂ is typically employed as a baseline. Molten salt deposits can bring on rapid oxidation and hot corrosion. Internal chlorides, oxides, and/or internal sulphides are examples of corrosion products [12-14]. Gas turbine parts that work in the heated gas stream, such as vanes, blades and combustor cans, are exposed to severe corrosive conditions [15]. These types of corrosion can significantly reduce the lifespan of gas turbine parts. Type I hot corrosion (sulphidation and internal damage) takes place between 800 and 900 °C, whereas Type II hot corrosion (pitting) takes place between 600 and 750 °C [16]. Hot corrosion damage can be divided into two phases. First, in the incubation phase, during which the developed protective scale may be heeled by materials in the underlying substrate, metal loss rate is low. Second, in the propagation phase, during which the protective scale has been irreparably damaged, sulphides and oxides advance quickly into the surface of the substrate, and the metal loss rate is high [17].

Residual oil (fuel) is used in energy-generating systems, which is widely recognized due to the exhaustion of high-quality fuels and for financial reasons. Salt contamination from entrained brine and contaminants such as sodium, vanadium, and sulphur are present in residual fuel oil. The combustion system reacts with sodium and sulphur to produce Na₂SO₄ (melting point 884 °C). Vanadium and oxygen combine to generate the oxide V₂O₅ (melting point 670 °C) during fuel combustion. At the working temperatures of a gas turbine, V₂O₅ is a liquid in energy-generating
systems. These substances (also referred to as ash) cause rapid oxidation (also known as hot corrosion) and accumulate on the surface of the materials.

Hot corrosion is anticipated to be a concern when contemplating coal-gasification procedures since the feedstock also contains a significant quantity of salts, and the gas environment often contains sulphur and chloride compounds and low oxygen activity [18].

Gas turbines typically operate at relatively high temperatures. This trend is anticipated to continue when cooling technologies and new materials are developed for gas turbine engines of the next generation. Hot corrosion requires particular consideration due to the coupling of such elevated temperatures with an aviation condition that contains pollutants, including sodium, vanadium, sulphur, and several halides [7].

Therefore, power plants are one of the key industries affected by severe corrosion issues that cause significant losses. For example, the boiler and turbine thermal efficiency is affected by the creep and corrosion resistance of boiler and turbine elements, which limits the steam/gas temperature. The rate of power production is then lowered as a result of the decreased thermal efficiency [19].

Iron base alloys containing significant amounts of chromium and nickel are most frequently used in coal-fired power plants and oil refineries. The use of these alloys often results in their corrosion due to the attack of gaseous elements such as O_2, H_2S, SO_2, CO, and CO_2, as well as the deposition of meltable ash or salts. Numerous researchers have examined the corrosion caused by the deposit at the fireside. Alkali sulphates, which accumulate on the surface of alloy components and promote hot corrosion degradation because of less melting eutectics between Fe_2(SO_4)_3 and Na_2SO_4 and or K_2SO_4 or both, happen at relatively low temperatures [20-23], are the most prevalent forms of sulphates. Studies on cobalt, nickel, and Fe base alloys have shown that hot corrosion may initiate as low as 550 °C. Thus, the creation of low melting eutectics such as Na_2SO_4 + CoSO_4 (565 °C) and Na_2SO_4 + NiSO_4 (667 °C) appears to be the main cause.

Most of the time, high-temperature alloys subjected to corrosion displayed oxidation and sulphidation degradation. Type II hot corrosion is uncommon in aero engines since the blades are often operated at higher temperatures [24]. On the other hand, industrial and marine gas turbines operating at low temperatures may experience type II high-temperature corrosion at moderate temperatures.

High-temperature corrosion occurs when molten salt is applied to alloys and metals. In boilers that burn coal, corrosion arises at high temperatures due to low-emission combustion and low-quality fuel. When low-quality fuels burn, they release ash due to the presence of sulphur, salt, vanadium, chlorine, and other contaminants. On boiler parts, fly ash may create a layer of molten salt. Severe high-temperature corrosion is caused by the complex salt deposit’s attack on the developed protective oxide scale of the material [25-28].

**Research progress in hot corrosion**

Guo et al. [29] deposited an Al and Cr gradient NiCoCrAlYSiB coatings on to Ni based superalloy substrate and oxidised them at 900 °C for 20 hours in 0.5 mg cm⁻² of 20 % K_2SO_4  80 % Na_2SO_4 salt mixture to examine the effects of Al and Cr on the hot corrosion of coatings. XRD and EDS results show that there are only the alumina formed on the NiCoCrAlYSiB coatings, so the basic fluxing of Al_2O_3 occurred, which caused an accelerated hot corrosion after 10 h. The gradient coatings resulted from Al_2O_3 and Cr_2O_3 formed in the first stage of hot corrosion. Na_2SO_4's oxygen ion activity is lowered by Cr_2O_3, which reacts with Al_2O_3 more readily than Al_2O_3, protecting Al_2O_3. Similar to
oxidation kinetics, gradient coatings show hot corrosion kinetics due to the development of continuous and protective layer of \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \).

The hot corrosion and oxidation behaviour of the Ni and Fe-based superalloys Superni75 and Superfer 800H were investigated by Sidhu et al. [30]. The superalloy samples underwent cycle conditions, including exposure to air and a corrosive molten salt environment (75 % \( \text{Na}_2\text{SO}_4 \) + 25 % \( \text{NaCl} \)) at 800 °C. Superni75, a superalloy based on nickel, is more resistant to oxidation and heat corrosion than Superfer800H, a superalloy based on iron, in the given environment at 800 °C. Due to its tendency to produce protective spinel and chromium-nickel oxides, Superni 75 has performed better in both circumstances.

In a related investigation, Sidhu et al. [31] came to the conclusion that the oxides of the coatings’ active components, which developed on the scale’s surface and at the edges of Ni and W-rich splats, were responsible for the hot corrosion and resistance against oxidation of WC-NiCrFeSiB coatings. Developed oxides served as barriers to prevent the corrosive species from diffusing and penetrating through the coatings.

After being exposed to 950 °C for 20 hours, the DZ68 superalloy surface formed a protective scale, according to Liu et al. [32]. The procedure improved the alloy’s first incubation period at 900 °C in the slurry. According to their research, it may provide a special defence against corrosive salt and dramatically slow down the rate of deterioration.

Liu et al. [33] examined the effects of the hot corrosion behaviours of the M38G superalloy in a combination of \( \text{Na}_2\text{SO}_4\)-\( \text{NaCl} \) salt melts. Results indicated that the treatment could, in combination with melts at 850 and 800 °C, somewhat boost the M38G alloy’s resistance to hot corrosion. The protection provided by the oxide layer decreased with temperature, but the treatment at 875 °C had no effect on the hot corrosion of the M38G superalloy.

Kamal et al. [34] investigated the oxidation and hot corrosion behaviour of Ni-based superalloys exposed to ambient air and a corrosive fused salt environment (\( \text{Na}_2\text{SO}_4 - 60 \% \text{ V}_2\text{O}_5 \)) at 900 °C. Weight change observation and calculation on the superalloys during the entire cycle are used to develop hot corrosion and oxidation kinetics. The enhanced hot corrosion and oxidation resistance of Superni75 was attributed to the scale’s richness in \( \text{NiO} \), \( \text{Cr}_2\text{O}_3 \), and spinel \( \text{NiCr}_2\text{O}_4 \). On the other hand, non-protective iron oxides and nickel and iron sulphides cause Superfer800H to have a comparatively lower level of hot corrosion resistance. The parabolic rate constants computed for these materials indicate that the hot corrosion rate for superalloys is lowest in ambient air with respect to a fused salt condition.

According to Wang et al. [35], The Nb solid solution / \( \text{Nb}_5\text{Si}_3 \) alloys oxidised more quickly and left the porous surface when \( \text{NaCl} \) and \( \text{Na}_2\text{SO}_4 \) were present.

According to the research of Sidhu et al. [36], WC-Co and WC-CoCr coatings on steel alloys T22 and T91 proved to be corrosion resistant in the boiler’s superheater area after ten cycles (each lasting 100 hours) at 900 °C. The following order of coating corrosion resistance demonstrations was observed: T22 coating with 86WC-10Co4Cr > T22 coating with WC-17Co > T91 coating with WC-10Co4Cr > T91 coating with WC-17Co

The \( \text{Cr}_3\text{C}_2\)-NiCrMoNbAl coating made by HVOF on P91 steel and its hot corrosion behaviour was described by Zhou et al. [37]. Compared to P91 steel, the \( \text{Cr}_3\text{C}_2\)-25(NiCr) coating showed better corrosion resistance at 650 °C.

According to Qiao et al. [38], Nb-Si-Ti alloy and its silicide covering were subjected to a heated corrosion process that was exacerbated by \( \text{NaCl} \).
Wei et al. [39] deposited the Mo-62Si-5B alloy using the SPS method. When an alloy is coated with molten salts, more significant mass changes occur compared to when exposed to dry air. The alloy’s mass changes in the Na$_2$SO$_4$+NaCl combination and Na$_2$SO$_4$ following 100 hours of hot corrosion at 900 °C are 0.50 and 0.24 mg cm$^{-2}$. There is a loss of mass when SiO$_2$ is created because more MoO$_3$ evaporates than is gained in weight. Most loose oxide scales on the alloy are made up of SiO$_2$ and amorphous borosilicate. The oxide scales become porous due to the mixture of Na$_2$SO$_4$ and NaCl, accelerating the oxidation process.

The corrosion behaviour of WC-CoCr coatings by HVOF spraying in 0.1 M HCl solution at 25 °C was investigated by Picas et al. [40] using the electrochemical polarisation method. In contrast to the steel base and thin electrolytic hard chromium coating, HVOF sprayed WC-CoCr coatings can provide better corrosion protection in the extremely corrosive 0.1 M HCl solution.

A significant improvement in corrosion resistance to both 1 mol/L HCl and 3.5 wt.% NaCl solutions was seen by Zhang et al. [41] when they investigated the corrosion characteristics of HVOF-sprayed nano-structured WC-10Co4Cr coating in two corrosive salt environments.

The hot corrosion performance of the austenitic steel weld metal was examined by Xu et al. [42]. It was established that the surface of the weld metal developed an outer face rich in iron and a protective layer of Cr$_2$O$_3$ after being exposed to temperatures of 700 and 800 °C for 100 hours in a fused salt environment. Yet, because the molten salt dissolves the oxide film in a 650 °C KCl-NaCl-Na$_2$SO$_4$ salt environment, significant oxidation still happens in the weld metal.

A general methodology adopted for hot corrosion includes the following steps, as shown in Figure 1. The sample is first cut to the suitable size. Before the development of the coating, the samples are prepared using sandblasting or emery paper, followed by cleaning with acetone to remove small debris. The coatings were developed by thermal spraying to the targeted substrate using prepared/available feedstock powder.

![Figure 1. A General process flow chart for hot corrosion study](http://dx.doi.org/10.5599/jese.2324)
of a still-air cooling period after a high-temperature heating period around a certain temperature in a furnace. Following each hot corrosion cycle, the crucible and samples were mixed and weighed using an electronic weighing device. The spalled scales were also considered for calculating the overall corrosion rate during the weight change measurement. Surface area/weight growth was utilized to create corrosion kinetics.

**X-ray diffraction analysis of the hot corroded scales**

Before heat corrosion, the XRD pattern of the WC-CoCr coated surface (Figure 2) exhibits clear, sharp peaks for both WC and W2C. The WC phase has been dissolved and decarburized, as shown by the rise in the height of the WC and W2C peaks. The high surface area to volume ratio of feedstock powder, which made it easy for the WC atoms to interact with spraying temperature, is the primary source of decarburization in coatings [43].

![XRD Pattern before and after Hot Corrosion](image)

*Figure 2. XRD plot for WC-CoCr coatings and coated hot corroded scales. Reproduced from [44] with permission from Springer Nature*

Following fifty hot corrosion cycles, the XRD analysis of the WC-CoCr coated 316L steel substrate (Figure 3) revealed the formation of WO3, CoW3C, and CoWO4 as the main phases. The intermediate phase, Cr2O3 and its spinel CoCr2O4, was caused by the chromium content and also contributed to the coating’s ability to resist corrosion in a Na2SO4 25 % NaCl salt environment. Notable oxides were Fe2O3, CoSO4, and FeCr2O4. There were also some Na traces found. A sizable number of oxide phases occurred after fifty cycles in a fused corrosive salt environment, indicating fast oxidation.

Figure 3 depicts the identified phases subjected to a salty environment 12Na2SO4-88Fe2(SO4)3 at 800 °C. XRD reveals that after hot corrosion, the specimen mainly consists of the following phases FeSCr2S3, Na2FeO2, NiCr2O4, and FeS phase.

A fused state of NaFe(SO4)2 is thought to develop (Equation (1)) when Na2SO4 and Fe2(SO4)3 are mixed:

\[
\text{Na}_2\text{SO}_4 + 2\text{Fe}_2\text{(SO}_4\text{)}_3 \rightarrow 2\text{NaFe(SO}_4\text{)}_2
\]  

(1)
The Cr₂O₃ coating on the 316L steel is degraded (Equation (2)) when the alloy and this fused phase interact:

\[
3\text{Cr}_2\text{O}_3 + 4\text{NaFe(SO}_4)_2 \rightarrow 2\text{Na}_2\text{CrO}_4 + 2\text{FeS} + 2\text{Cr}_2\text{S}_3 + 2\text{Fe}_2\text{O}_3 + 15\text{O}_2
\] (2)

As a result, the oxide scale will be destroyed and sulphides and fluxing products will appear, as shown by Equations (3) and (4). The liquid phase further deteriorates the alloy:

\[
3\text{Fe} + 2\text{NaFe(SO}_4)_2 \rightarrow 4\text{FeS} + \text{Na}_2\text{FeO}_2 + 7\text{O}_2
\] (3)

\[
3\text{Ni} + 2\text{NaFe(SO}_4)_2 \rightarrow 2\text{FeS} + 2\text{NiS} + \text{Na}_2\text{NiO}_2 + 7\text{O}_2
\] (4)

The entire corrosion attack is controlled by the liquidus NaFe(SO₄)₂, and corrosion will likely be less severe because there isn't any Na₂SO₄ emission. The oxide scales on an alloy that corrodes at 800 °C are thicker than those that form at lesser temperatures. The fluxing products Na₂CrO₄, Na₂FeO₂, and Na₂NiO₂ and the development of gases cause the scales to crack or become disrupted. This causes the fused salt to contact metal and initiate a potent oxidation attack. The steel oxidizes and fluxes more quickly due to its easy oxygen availability.

![XRD pattern of WC-CoCr coatings by HVOF spraying on 316L steel substrate in corrosive salt Environment. Reproduced from [45] with permission from Springer Nature](image)

**Figure 3.** XRD pattern of WC-CoCr coatings by HVOF spraying on 316L steel substrate in corrosive salt Environment. Reproduced from [45] with permission from Springer Nature

**Scanning electron microscopy analysis of the hot corroded scales**

When exposed to a Na₂SO₄ + 25% NaCl salt environment, the unprotective oxide (Fe₂O₃) is generated as the surface scale of the uncoated steel substrate, allowing corrosive elements to penetrate the surface. Hot corrosion of an uncoated steel substrate results in unprotective Fe₂O₃ scales. Fe and Cl are shown as active elements in Figure 4’s SEM image of the bare hot corroded sample. Fe creates an unprotective Fe₂O₃ oxide layer that is loosely retained after oxidation. Melted salt diffuses slits and cracks when it interacts with a steel substrate over 628 °C. This causes oxide scale development and oxidation to occur first.

Through the process of dissolution (Equations (5) to (10)), the fused salt paste's NaCl dissolves into Cl⁻ and Na⁺ ions. The Cl⁻ ions then enter the substrate and react to form metal chlorides like FeCl₂ and CrCl₂.

\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-
\] (5)
Fe + Cl₂ → FeCl₂  
4FeCl₂ + 3O₂ → 2Fe₂O₃ + 4Cl₂  
2Cr₂O₃ + 8Cl⁻ → 4CrCl₂ + 3O₂  
Na₂O + Cr₂O₃ + 1/2 O₂ → 2NaCrO₄  
4Fe + Na₂SO₄ → 3FeO + Fe₅ + Na₂O  

Figure 4. SEM images of uncoated hot corroded scales. Reproduced from [44] with permission from Springer Nature

On the top surface of the plasma sprayed WC-CoCr coated steel substrate, an adhering homogenous and continuous globular scale has formed after fifty hot corrosion cycles in a Na₂SO₄-NaCl fused salt environment (Figure 5a). Scales have largely maintained their lamellar structure throughout the investigation, as the SEM micrograph shows. Thermal stress is the cause of the microcracks that form in the scale. Open fissures expedited the entrance of corrosive materials during heating and cooling in hot corrosion cycling testing. This has made the coating’s inner surface degradation more severe.

In the SEM image (Figure 5b), the scale appears to have a loose, hairy structure at higher magnifications. The ensuing interactions between coating elements such as tungsten, cobalt, chromium, iron and the chlorine created by dissociation of NaCl result in highly volatile chlorides, which in turn cause a loose and uneven oxide scale [46]. These chlorides release chlorine when they diffuse from the scale and interact with the surrounding air oxygen.

Figure 6(a-d) shows the SEM evaluation of the cyclic corrosion of 316L steel, both bare and sprayed, in settings with 12% Na₂SO₄-88% Fe₂(SO₄)₃. The surface of the nude specimen is rather uneven. As demonstrated in Figure 6(a) and (b), the uncoated sample is considerably comparable at higher magnification, revealing some pit and fracture patterns. The SEM analysis suggests that intergranular cracking on the oxide scale may be indicated by certain surface cracks on the scale. Fe₂O₃ may form since oxygen and iron are found in significant concentrations throughout the scale’s composition. There are also trace amounts of Mn, Cr, and Co.

SEM image of the hot corroded HVOF WC-CoCr 316L steel at high magnification (Figure 6(c,d)) reveals some visible globules and some unmelted powder.
Figure 5. SEM images of WC-CoCr coated hot corroded scales. Reproduced from Ref. [44] with permission from Springer Nature

Figure 6. SEM images (a-b) bare 316L steel (c-d) HVOF sprayed 316L steel in the corrosive salt environment at 800 °C. Reproduced from [45] with permission from Springer Nature

The cross-sectional SEM images of the coated and bare samples following the hot corrosion test are displayed in Figure 7 (a) and (b). Figure 7(a) displays the surface for spalling and corrosion pits on bare samples when the magnification is increased [47]. Figure 7(b) shows the coated, hot-corroded sample's surface separation and microholes. This is the consequence of high-speed melt and semi-fused particles crossing over the substrate [48].

Some findings have been highlighted in Table 1
Thermally sprayed coating for hot corrosion

Figure 7. SEM image of cross-section (a) bare hot specimen (b) coated hot corroded specimen after hot corrosion. Reproduced from [45] with permission from Springer Nature

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Summary and outlook

This article examines the most recent research and breakthroughs in the field of hot corrosion performance of various coatings. The coatings on the substrate exhibited greater hot corrosion resistance due to the protective WO$_3$/Cr$_2$O$_3$, etc. phases. The developed phases serve as a mechanism of transportation across this scale. These are typically slow growth in nature. Thus, an oxide retards/prevents the inward diffusion of gaseous/vapour impurities and the outward diffusion of other alloy elements.

References


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