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Characterization of oxide scales to evaluate hot corrosion behavior of ZrO₂ and Al₂O₃-TiO₂ plasma sprayed superalloy

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Abstract: Zirconium dioxide and Aluminium oxide–40% Titanium dioxide thermal barrier coatings (TBCs) were deposited on Nickel based Inconel 625 superalloy with plasma spray process. The aim of the present study is to compare hot corrosion behaviour of ZrO_2 and Al_2O_3 -TiO₂ plasma sprayed thermal barrier coatings on Nickel based Inconel 625 superalloy in air oxidation and in molten salt environment i.e K₂SO₄–60% NaCl environment at 800°C under cyclic conditions for 50 cycles. The thermo-gravimetric technique was used to establish the kinetics of corrosion. The corrosion products have been analyzed using the SEM and EDS analysis. Both coatings protect the underlying Inconel 625. The ZrO_2 coating performed relatively better than Al_2O_3 -TiO₂ coating against hot corrosion in air and in the given environment.

Keywords: Hot corrosion, Thermal barrier coatings, ZrO₂, Al₂O₃-TiO₂, Nickel based superalloy, Inconel 625.

1. Introduction

The mechanical components operating at high temperature environments such as power plants, gas turbines, industrial waste incinerators, energy conversion & chemical process systems, internal combustion engine, fluidized bed combustion etc. fail due to high temperature corrosion (1-4). High temperature corrosion is the degradation of materials caused by the deposit of salt or ash in general sense. Molten salts like K_2SO_4 , Na₂SO₄, KCl and NaCl lower the melting point of the metal and damage the protective oxide layer causing corrosion (5). In hot corrosion, metals and allows degrade at higher rates than in air oxidation with a porous, non-protective oxide scale formed at their surface and sulfides in the substrate. Superalloys are developed for high temperature application but they cannot meet the requirements of high temperature strength and high temperature erosion-corrosion resistance (6). Therefore we require a composite system with the superalloy on the surface so that it can provide high temperature erosion-corrosion protection. Thermal spray process can withstand these effects. Thermal spray coatings were studied by many researchers (7-13) and they stated that these coatings protect the substrate metal from hot corrosion and erosion. They also improve the life of the substrate. Plasma spray is the most versatile of the thermal spray processes. Plasma is capable of spraying all materials that are considered spravable. Plasma spraving is being utilized in a wide range of coatings. The range goes from low melting point polymers such as Nylon, to very high temperature melting materials such as refractory materials including Tungsten, Tantalum, Ceramic oxides.

Thermal barrier coatings provide thermal insulation to the hot section components in order to protect them from thermal degradation and also to enhance the operating temperature (14-16). The life of the TBCs depends on various factors. The resistance of the bond coat to high temperature corrosion such as oxidation and hot corrosion is a very important aspect. When TBCs are exposed to high temperature, oxides form at the top coat and bond coat interface. And it is called as thermally grown oxide. As the oxides grow, they cause compressive residual stresses leading to TBC failure near ceramic topcoat-Thermal Grown Oxide-bond coat interface and/or within the Thermal grown oxide (17–23). This causes spallation and a coefficient of thermal expansion mismatch between bond coat and ceramic topcoat can exasperate the coating failure during thermal cycles (24-27). There are numerous inhibitors commercially available that are intended to reduce the severity of hot corrosion such as manganese and magnesium based additives, CaO, MnO₂, Al₂O₃, ZnO, BaO, PbO, SiO₂, BaO, Ba(OH)₂, Ca(OH)₂, CaCO₃, oil soluble Ni, Al, Fe and other compounds (14). The Al₂O₃-TiO₂ coatings are commonly used to protect the underlying materials from hot corrosion degradation (28-29). Jafarzadeh et al (15) deposited the Al₂O₃-TiO₂ coating with plasma spray and they found that the as-sprayed carbon steel exhibits higher performance. Al₂O₃-TiO₂ coatings are most useful when one is seeking hot corrosion resistance for the components exposed in high temperature environment (16). Many investigations have been done up to now on the microstructure, mechanical properties of Al₂O₃-TiO₂ and their wear properties. However, despite the importance of Al₂O₃-TiO₂ coatings in power plant applications very limited studies have been reported.

 ZrO_2 is an oxide additive that is less studied. Hence we chose the compound for our study. It is found from the literature that little work has been done on plasma spray coating for high temperature applications and hence this technique is used to develop high temperature resistant coatings on Ni-based superalloy. The aim of the present study is to evaluate and compare the hot corrosion behavior of Zirconium dioxide and Aluminium oxide–40% Titanium dioxide plasma spray coated on Ni-based superalloy in K₂SO₄–60% NaCl based molten salt environment at 800°C under cyclic study.

2. Experimental procedure

2.1 Substrate material and coating powder

The Inconel 625 superalloy was used as substrate material in the present study. It was obtained in plate form. The composition of the superalloy is provided in <u>**Table 1**</u>. Commercially available Al_2O_3 - TiO_2 (40%) and ZrO_2 powders were used as feedstock materials for coatings.

Table 1. The chemical composition of Inconel 625.

	Ni	Cr	Мо	Fe	Nb+Ta	С	Mn	Si	Р	S
Inconel 625	58.0	20.0	8.0	5.0	4.15	0.10	0.50	0.50	0.015	0.015

2.2 Formulation of coatings

The bare superalloy specimens were cut from the sheet into rectangular samples with dimensions $20 \times 15 \times 5$ mm. The specimens were polished using Silicon carbide paper emery papers with 100, 220, 400, 600, 800, 1000 and 1200 grit. And the samples were finally wheel polished with alumina powder (1µm) to eliminate rust, cracks and uneven surface. They were then washed with distilled water and cleaned with Acetone. Their surface area was measured using vernier calipers and weights were determined using an electronic balance to an accuracy of 0.01mg. The coating work was carried out by a commercial firm namely Spraymet Surface Technologies Pvt Ltd, Bengaluru, India. They used 'Robotic Plasma spray 40Kw and 80Kw' plasma spray apparatus to apply the coatings. Then specimens were grit blasted with alumina powders (grit 45) and ultrasonicated before developing the coatings by plasma spray process. Argon mixed with Hydrogen was used as powder carrying and shielding gas. All the process parameters were kept constant throughout the coating process while spraying distance was maintained in a narrow range of 80-120 mm. Ni-Cr powder was deposited as a bond coat around 40-50 µm thick before applying the final coatings. The process parameters for the plasma spray process employed for applying the coatings are listed in **Table 2.** Thickness of the coatings was controlled during the process of plasma spraying.

Table 2.	Process p	arameters	for p	olasma s	spray	process.
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Coating	Argon Flow	Hydrogen	Current	Voltage	Carrier	Powder feed	Spray
powder	rate lit/min	Flow rate	(I)	(V)	gas	(gm/min)	distance
		lit/min			(N 4mp)		(mm)
Al_2O_3 TiO_2	80-90	20-25	490	60-70	37-39	80-90	80-120
ZrO ₂	80-90	15-18	500	50	37-39	65-70	80-120

2.3 Hot corrosion

Oxidation and hot corrosion studies were conducted at 800°C in a laboratory Silicon carbide tube furnace. The air oxidation and molten salt (K_2SO_4 -60%NaCl) studies at 800°C were performed on plasma spray coated Inconel 625 in laboratory furnace up to 50 cycles. Each cycle consisted of 1 hour heating in the furnace followed by 20 minute cooling in the ambient air (room temperature). The plasma spray coated as well as uncoated specimens were prepared. The samples were heated in an oven to a temperature of 250°C. Mixture of K_2SO_4 -60%NaCl dissolved in distilled water was coated on warm polished sample with the help of a camel hair brush. The amount of salt coating varied from 3 mg/cm² to 5 mg/cm² surface area of the samples. The salt coating was provided only once at the start of the oxidation studies and no salt was applied during the oxidation studies. These salt coated samples were then dried for 2 hours at 200°C along with alumina boats and were weighed before exposed to hot corrosion tests. The alumina boats used in this experiment were preheated at a constant temperature of 1200°C for 24 hours and it was assumed that their weights remained constant during the course of high temperature cyclic oxidation study. The assumption was confirmed with the help of a pilot experiment on a boat at the temperature of the experiment i.e. 800°C for 50 cycles. Then the boat containing the sample was inserted into the hot zone of Silicon carbide tube furnace set at 800°C. The furnace was calibrated to an accuracy of $(+5^{\circ}C)$ to $-5^{\circ}C$). At the end of each cycle, the weight of the sample along with the boat (in their original condition) was measured to evaluate the total rate of corrosion. The corrosion products found in the boat, if any were included in the weight change measurements. However, when sputtering of the scale occurred, the corrosion products went out of the boat also. Visual observations were made after each cycle for their color, lustre, adherence, spalling tendency, presence/absence of the unreacted salt, etc. Surface morphology of the plasma sprayed coatings after corrosion cycles was also studied with the help of Scanning Electron Microscope (SEM). Whereas surface SEM/EDS analysis was performed to identify the elements or phases (oxides) present at a point along with their compositions.

3. Results and Discussion

The ZrO₂ and Al₂O₃- TiO₂ (40%) coatings were successfully deposited on Inconel 625 by plasma spray process. The coating process and powder play an important role especially for the application of high temperature aggressive environment. Sidhu et al. [8, 9] reported that lifetime increases with increase in coating thickness and further found maximum life with 300 μ m coating thickness. It was aimed to produce thicker coatings because thicker coatings are generally required for the components of energy generation systems. But self-disintegration of thickness in range of 100-110 μ m for the ZrO₂ and Al₂O₃- TiO₂ (40%) coatings and the final coating thickness of approximately 140-160 μ m. Fig 1 (a-g) show the macrostructure of Al₂O₃- TiO₂ (40%) coated hot corroded samples after 50 cycles. Fig 2 (a-g) show the macrostructure of ZrO₂ coated hot corroded samples after 50 cycles.

3.1 Visual examination

In the high temperature study of the uncoated Inconel 625, after completion of 35 cycles, the scale became thicker and most of the scale spalled out in the molten salt environment. However, the scale was found to be continuous in the case of Al_2O_3 - TiO_2 and ZrO_2 coated Inconel 625 for both environments up to 50 cycles.

3.2 Kinetics of the high temperature corrosion

The weight gain data for the hot corroded bare and coated superalloys over 50 cycles has been shown in (Fig 4). Al_2O_3 - TiO₂ and ZrO₂ coated Inconel 625 showed much lower weight gain as compared to bare Inconel 625 in the given molten salt environment and air oxidation. It indicated that both the coatings have provided necessary protection against hot corrosion. The ZrO₂ coating provided relatively better protection to the Inconel 625 than the Al_2O_3 - TiO₂ coating. The coated superalloy has shown the parabolic behavior up to 50 cycles as can be inferred from square of weight change (mg²/cm⁴) vs. number of cycles plots (Fig. 4). Bare superalloy showed significant deviation from the parabolic path. Thermo-gravimetric curve for both environments shows the tendency of oscillation type reaction which could be due to changes in reaction rate as suggested by Arivazhagan et al. (26). Further, the graph indicates that the weight gain of the uncoated alloy was found to be more during initial cycles of study. This could be attributed to the rapid oxidation during initial stages to form oxide scale of the surface elements. Arivazhagan et al. (26-27) and Devendranath Ramkumar et al. (5) had also reported the high weight gain during initial cycles of hot corrosion. In addition, the weight gain trend indicates

deviation from the parabolic rate law due to spalling and sputtering of the oxide scale. The higher weight gain in the case of uncoated Inconel 625 may be attributed to the formation of Iron (Fe) rich oxide scale which is less protective in nature. Oxides of Chromium (Cr) and Titanium (Ti) resulted in more spalling and sputtering (fig 5-10).



Fig 1. Macro images of Al₂O₃-TiO₂ coated Inconel 625 before and after air oxidation (a) As coated condition; (b), (c) and (d) after air oxidation; (e), (f) and (g) after molten salt corrosion.



Fig 2. Macro images of ZrO₂ coated Inconel 625 before and after air oxidation (a) As coated condition; (b), (c) and (d) after air oxidation; (e), (f) and (g) after molten salt corrosion.



Fig 3. Macro images of uncoated Inconel 625 before and after air oxidation (a) As uncoated condition; (b), (c) and (d) after air oxidation; (e), (f) and (g) after molten salt corrosion.



Fig 4. Thermo-gravimetric plot for uncoated, Al_2O_3 -TiO₂ plasma spray coated Inconel 625 and ZrO₂ plasma spray coated Inconel 625 exposed in air oxidation and K_2SO_4 -60%NaCl environment at 800 °C under cyclic conditions.



Fig 5. SEM/EDS results of uncoated Inconel-625 after exposure to air oxidation at 800 °C.



Fig 6. SEM/EDS results of uncoated Inconel-625 after exposure to K₂SO₄ – 60% NaCl at 800 C.



Fig 7. SEM/EDS results of Al₂O₃-40 TiO₂ coated Inconel-625 after exposure to air oxidation at 800 °C.



Fig 8. SEM/EDS results of Al₂O₃-40 TiO₂ coated Inconel-625 after exposure to K₂SO₄ –60% NaCl at 800 °C.



Fig 9. SEM/EDS results of ZrO₂ coated Inconel-625 after air oxidation at 800 °C.



Fig 10. SEM/EDS results of ZrO₂ coated Inconel-625 exposed to molten salt medium (K₂SO₄ –60% NaCl) at 800 °C.

3.3 SEM/EDAX analysis

SEM/EDAX of Al_2O_3 - TiO₂ coating has revealed that the top layer contains higher amount of Ti and Al as can be seen in Fig 7 and Fig 8. To provide long-term stability at elevated temperatures, it is necessary to develop diffusion-barrier coatings to minimize the inter-diffusion between the coating and the substrate. However, he further added that some inter-diffusion is necessary to give good adhesion; hence, the diffusion barriers must be tailored to limit the movements of particular problematic elements. Inter-diffusion observed in the present study is very minor and might be helpful for providing better adhesion between the substrate, bond coat and the top coat.

The SEM image indicates that the uncoated samples show a rough irregular surface as well as spalling behavior of the scale after exposure to molten salt environment (Fig 6). The basic fluxing is caused by K_2SO_4 – 60%NaCl at 800 °C under thermal cyclic condition. The EDAX analysis on the sub-scale reveals that scale mainly consists of the oxides of Chromium (Cr) as the major phase along with significant amounts of Iron (Fe) and Nickel (Ni). The scale formed on Al_2O_3 -TiO₂ coated Inconel 625 is almost consistent and continuous when exposed in air oxidation (Fig 7). Furthermore, the EDS analysis reveals Titanium (Ti) as a principal phase along with small percentage of Aluminum (Al) and Nickel (Ni) phases. Sufficient amount of Oxygen (O) is also present to form oxides. Therefore, the surface might contain TiO₂ as the major phase along with NiO and Al_2O_3 . Where as in the case of ZrO₂ coated Inconel 625 it was observed that strong oxides of Zr, Ni and Cr are found on samples after corrosion treatment (Fig 9-10). The SEM/EDS map of the samples after exposure to air oxidation indicate the formation of upper layer rich in Nickel & Iron and inner layer of mainly Chromium (Fig 9,10). The presence of oxygen content suggests the formation of oxides. Along with these minor amounts of Nickle (Ni), Titanium (Ti), and Manganese (Mn) were found.

This study shows that the environment has been found to have pronounced effect on weight gain. Based on the magnitude of weight gain, molten salt environment found to undergo accelerated oxidation under cyclic conditions in this particular environment of K_2SO_4 - 60%NaCl as compared to air oxidation. This result is also well supported by Devendranath Ramkumar et al. (4).

4. Conclusion

- a) A 40-50 µm thick coating of Ni-Cr powder bond coat was deposited on all the samples. 100-110 µm thick top coating (Al₂O₃-TiO₂ powder/ ZrO₂ powder) were successfully deposited on Inconel 625 using plasma spray coating process.
- b) The coating showed effective hot corrosion resistance in air oxidation. However, the hot corrosion resistance in molten salt environment is relatively inferior.
- c) The corrosion rates for the investigated with and without coated Inconel 625 based on the overall weight gains after 50 cycles in all the environments could be arranged in the following order: Uncoated

Inconel 625 in the molten salt environment > Uncoated Inconel 625 in air Oxidation > Al_2O_3 -TiO₂ coated Inconel 625 in the molten salt environment > Al_2O_3 -TiO₂ coated Inconel 625 in air oxidation > ZrO_2 coated Inconel 625 in the molten salt environment > ZrO_2 coated Inconel 625 in air oxidation.

- d) ZrO_2 coating provided better corrosion resistance than Al_2O_3 -TiO₂ coating.
- e) The plasma sprayed Al₂O₃-TiO₂ coating protects the substrate with the formation of Cr₂O₃ scale at the top and Al₂O₃ scale beneath in K₂SO₄-60%NaCl molten salt environment at 800 °C for 50 cycles. Better hot corrosion resistance of plasma sprayed Al₂O₃-TiO₂ is due to the formation of some Ni-Cr spinels oxides.
- f) The plasma sprayed ZrO₂ coated Inconel 625 protects the substrate with the strong oxides of Zr, Ni and Cr in the lower layers.
- g) Plasma spray has showed good hot corrosion resistance results.

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