International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.11, pp 4579-4584, Oct-Nov 2014

Comparative High Temperature Corrosion Studies on Zirconium Dioxide Coated Inconel 625 in Air and Molten Salt Environment

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Abstract: Zirconium Dioxide (ZrO_2) Thermal Barrier Coatings (TBCs) were produced on nickel based superalloys (Inconel-625) by plasma spray coatings. Hot corrosion behaviour of the ZrO_2 TBCs was investigated in presence of K_2SO4–40%NaCl at 800 °C in air oxidation and molten salt environment under cyclic conditions for 50 cycles. The thermo-gravimetric technique was used to establish the kinetics of corrosion. The corrosion products have been analysed using the SEM and EDS analysis. Results show that the ZrO_2 coating exhibits superior stability in air oxidation to molten salt environment against hot corrosion.
Keywords: Thermal Barrier Coating; Plasma Spray coating; Nickel based Superalloy; ZrO_2; Hot corrosion.

1. Introduction

Superalloys are generally used in the manufacture of components in power generation equipment, in gas turbines for ships and aircraft and in other energy conversion and chemical process systems e.g. in boilers, internal combustion engines, fluidized bed combustion and industrial waste incinerators (1-2). High temperature corrosion is the degradation of materials caused by the presence of deposit of salt or ash in general sense.in a more restricted sense, hot corrosion is caused by the usage of low grade fuels with high- concentration of Sulphur, Potassium and Sodium used in oil and coal fired power generation making there by making the environment aggressive (3-4). The boilers exposed in off shore industrial rigs undergo hot corrosion when the sodium chloride from the ocean breezes mixes with K_2SO_4 from the fuel and deposits on the hot-section of the components. There by oxidation, sulfidation, cholridation and hot corrosion are observed(5). In general sense oxides formed on the surface acts as a protection but due to the presence of molten salts such as K_2SO_4, Na_2SO_4, KCl and NaCl lowers the melting points to a considerable extent. These results in the damage to the protective oxides formed. These unwanted results of hot corrosion can be minimised by TBC's. Materials can be protected considerably when they are exposed to thermal spray coatings. Inconel 625 has been developed for high-temperature strength along with hot corrosion resistance. There are numerous inhibitors commercially available that are intended to reduce the severity of oil ash corrosion (hot corrosion) such as Mg- and Mn- based additives, CaO, MnO2, Al_2O_3, ZnO, BaO, PbO, SiO_2, BaO, $Ba(OH)_2$, $Ca(OH)_2$, and $CaCO_3$, as well as oil soluble Ni, Al, Fe and other compounds(6). However, in this paper, the effect of a relatively less studied oxide additive namely ZrO_2 on the high temperature corrosion behaviour of Inconel-625 has been investigated in the simulated environment of boilers, compromising of K_2SO_4-60% NaCl under cyclic conditions.

2. Experimental procedure

2.1 Formulation of coatings

The Inconel 625 superalloy was used as substrate material in the present study and its chemical composition is listed in Table 1.The procured alloy sheet was cut into rectangular samples of size 20mm×

15 mm × 5mm. The specimens were polished down to 1200 grit using silicon carbide papers to remove the scars and scratches, wheel polished with alumina powder (1µm) and later polished down to 200 grit so as to provide sufficient roughness. Finally it is washed with distilled water and cleaned with acetone. The physical dimensions of the samples were recorded carefully with a digital vernier calliper to evaluate their surface areas. The weights were determined using an electronic balance to an accuracy of 0.01mg. Commercially available ZrO_2 powder was used for coatings. The coating work was carried out by a commercial firm namely Spraymet Technologies Pvt Ltd, Bengaluru, India. They used 'Robotic Plasma spray 40Kw and 80Kw' plasma spray apparatus to apply the coatings. 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 1. The chemical composition of Inconel 625.

	Ni	Cr	Mo	Fe	Nb+Ta	C	Mn	Si	P	S
Inconel 625	58.0	20.0	8.0	5.0	4.15	0.10	0.50	0.50	0.015	0.015

Table 2. Process parameters for plasma spray process.

Coating powder	Argon Flow rate lit/min	Hydrogen Flow rate lit/min	Current (I)	Voltage (V)	Carrier gas (N 4mp)	Powder feed (gm/min)	Spray distance (mm)
ZrO2	80-90	15-18	500	50	37-39	65-70	80-120

2.2 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 1h heating in the furnace followed by 20 min cooling in the ambient air. 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) is dissolved in distilled water was coated on the warm polished with the help of a camel hair brush. The amount of salt coating varied from 3-5 mg/cm^2 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 weighed before exposed to hot corrosion tests. The alumina boats used in this experiment were preheated at a constant temperature of 1200^{O}C for 24 hours and it was assumed that their weights remain constant during the course of high temperature cyclic oxidation study. Rather the assumption was confirmed with the help of a pilot experiment on a boat at the temperature experiment that is 800^{O}C for 50 cycles. Then the boat containing the sample was inserted into the hot zone of Silicon Carbide tube furnace set at 800^{O}C. The furnace was calibrated to an accuracy of (+5°C to -5^{O}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 ZrO_2 coatings were successfully deposited on Inconel 625 plasma spray process. The coating process and powder play an important role especially for the application of high temperature aggressive environment. Sidhu Singh et al. reported that lifetime increases with increase in coating thickness and further found maximum life with 300 µm 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 thicker coatings usually restricts the thickness of the coatings. In the present study it was possible to obtain a thickness in range of 100-110 µm for the ZrO_2 coating and the final coating thickness of approximately 140-160 µm. Fig 1 (a-g) shows the macrostructure of hot corroded samples after 50 cycles.

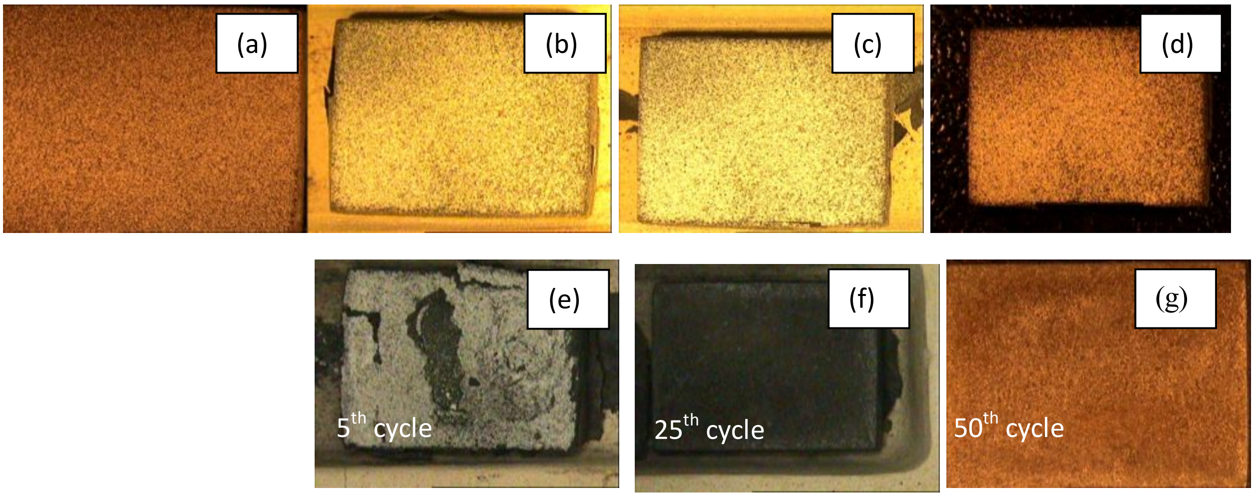


Fig 1. Macro images of ZrO_2 coated Inconel 625 before and after air oxidation (a) As coated condition; b, c and d after air oxidation; e, f and g after molten salt corrosion.

3.1 Visual examination

In the high temperature study of the uncoated Inconel 625, after completion of 35 cycles, the scale becomes 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 ZrO_2 coated Inconel 625 for both environments up to 50 cycles.

3.2 Kinetics of the high temperature corrosion

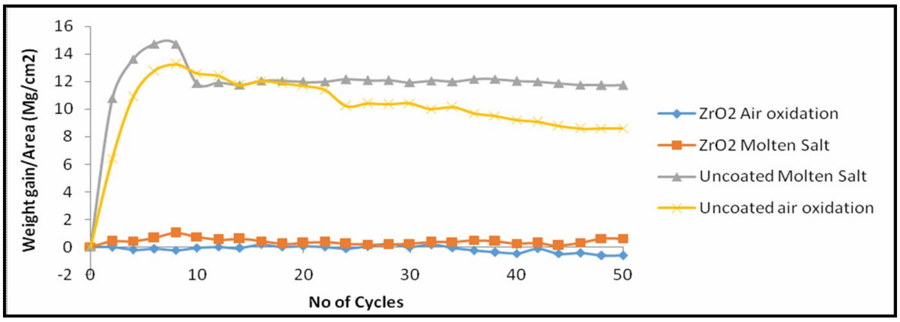


Fig 2. Thermo-gravimetric plot for uncoated and ZrO_2 plasma spray coated Inconel 625 exposed in air oxidation and K2SO4–60%NaCl environment at 800 °C under cyclic conditions.

The weight change data (Thermo-Gravimetric readings) for the ZrO_2 coated Inconel 625 and uncoated Inconel 625 when exposed to (K_2SO_4-60%NaCl) at 800°C under cyclic conditions is plotted in the Fig.2. In the case of ZrO_2 coated Inconel 625 showed less weight gain in both air oxidation and molten salt environment when compared to the uncoated alloy indicating the protective behavior of the coatings. 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. (7). Further the graph indicates that the weight gain of the uncoated alloy was found to be more during initial cycles of study. 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. (7-8), Devendranath Ramkumar et al.(4) 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 samples exposed in air oxidation and molten salt coated Inconel 625 may be attributed to the formation of Iron (Fe) rich oxide scale which is less protective in nature. Oxides of Chromium (Cr) resulted in more spalling and sputtering (Fig 3-5)

3.3 SEM/EDAX analysis

The SEM/EDS results indicates that the uncoated samples show a rough regular surface as well as spalling behavior of the scale after exposure to molten salt environment (Fig 5). The basic fluxing is caused by (K_2SO_4-60%NaCl) at 800^{O}C under thermal cyclic condition.

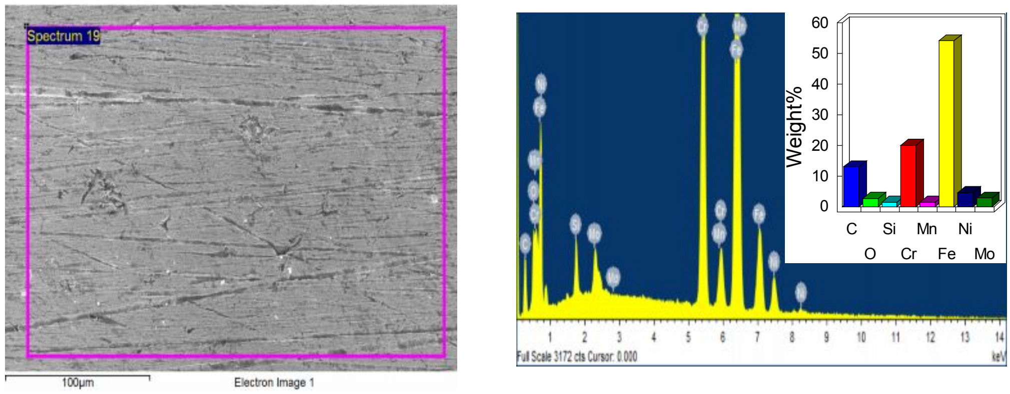


Fig 3. SEM/EDS results of uncoated Inconel-625, before corrosion treatment.

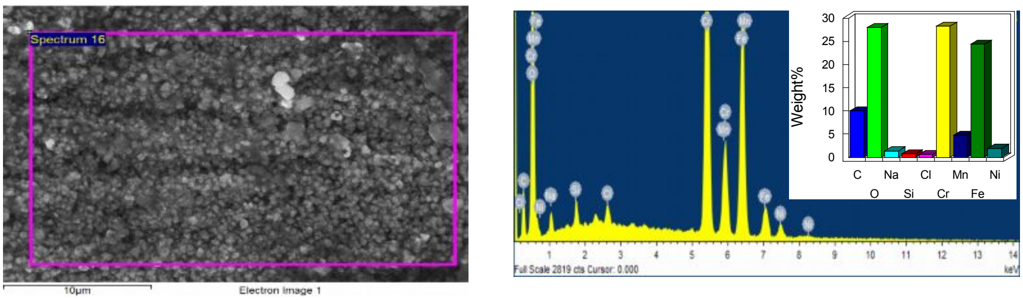


Fig 4. SEM/EDS results of uncoated Inconel-625 after air oxidation at 800 ^{o}C.

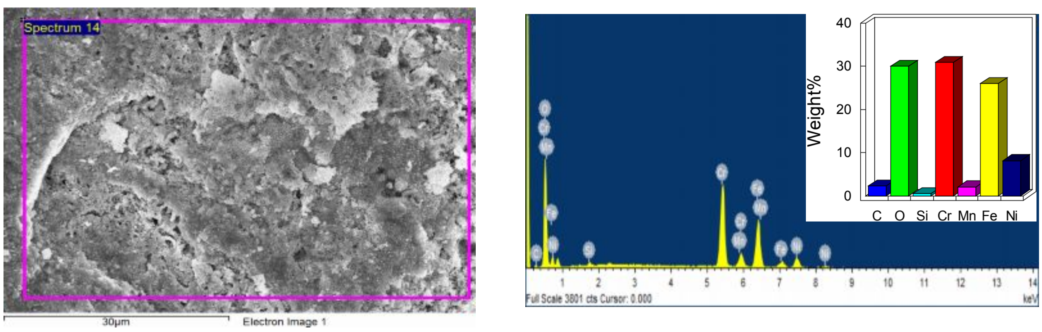
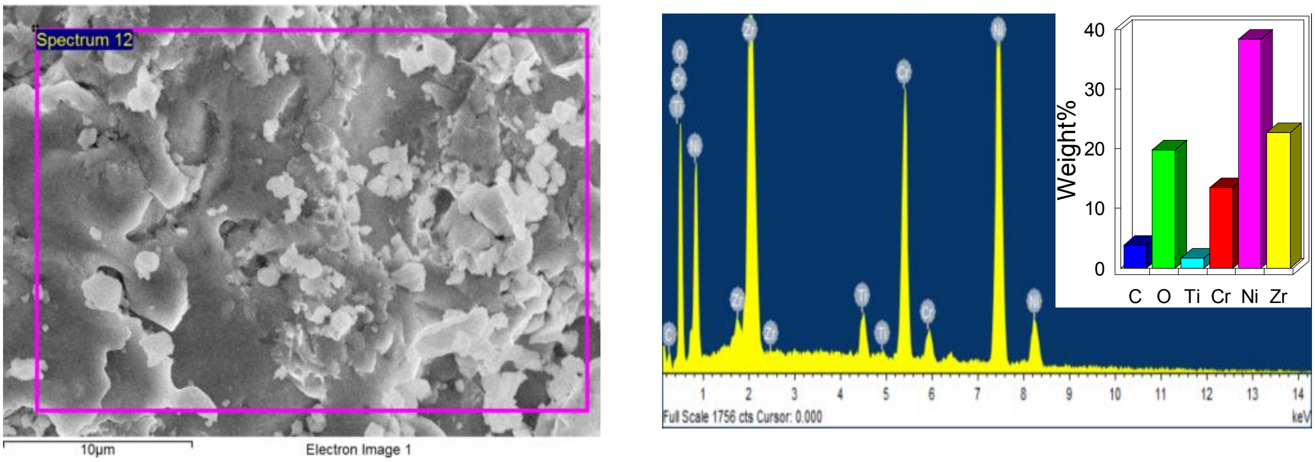


Fig 5. SEM/EDS results of uncoated Inconel-625 exposed to molten salt medium (K_2SO_4 –60%NaCl) at 800 ^{o}C.

It is observed strong oxides of Zr, Ni and Cr on ZrO_2 coated samples before corrosion treatment (Fig 6). The SEM/EDS maps of the samples after exposure to air oxidation has indicated (Fig 7) the formation of upper layer rich nickel and inner layer is mainly chromium and the presence of oxygen content suggests the formation of oxides. Along with these minor amounts of Nickle (Ni), Titanium (Ti), and Manganese (Mn).The SEM/EDAX results of the ZrO_2 coated samples after exposure in (K_2SO_4-60%NaCl) has indicated (Fig 8) the formation of scales rich in Nickel and Iron while the inner layer is mainly Chromium.



Figs 6. SEM/EDS results of ZrO_2 coated Inconel-625 before corrosion treatment.

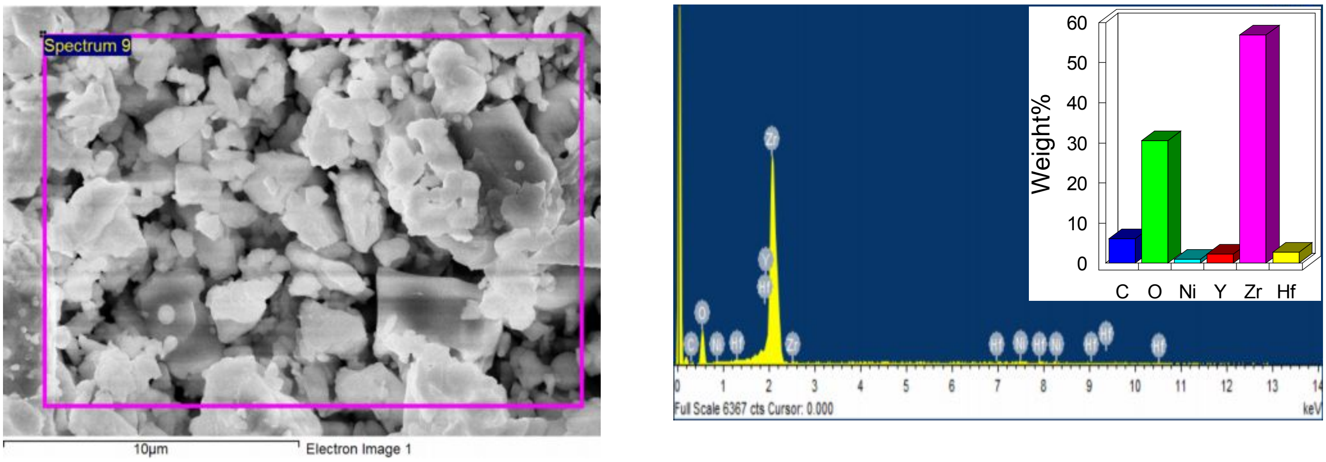


Fig 7. SEM/EDS results of ZrO_2 coated Inconel-625 after air oxidation at 800 ^{o}C.

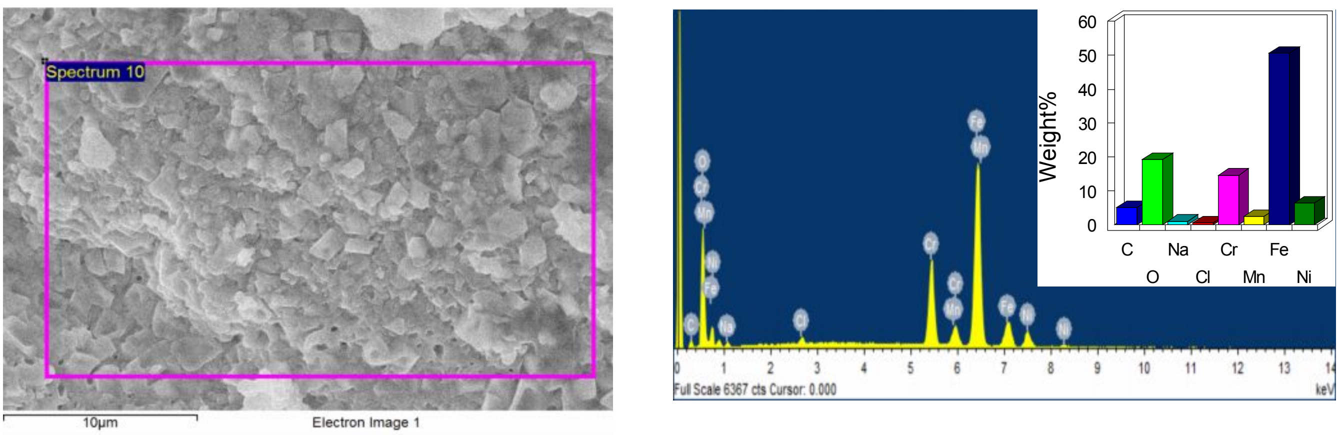


Fig 8. SEM/EDS results of ZrO_2 coated Inconel-625 exposed to molten salt medium (K_2SO_4 –60% NaCl) at 800 °C.

To provide long term stability at elevated temperature, it is necessary to develop diffusion barrier coatings to minimize the inter diffusion between the coating and the substrate. However, 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.

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 and 100-110 μm thick coating of ZrO2 powder were successfully deposited on Inconel 625 using plasma spray coating process.
b. The coating showed the effective hot corrosion resistance in air oxidation. However, the hot corrosion resistance in molten salt environment is relatively inferior.
c. The highest corrosion rate was noticed in the uncoated Inconel 625 in the molten salt environment followed by air oxidation.
d. The weight gain of ZrO2 coated inconel 625 is found to be considerably less in both environments due to dense coating structure obtained by the plasma spray coating.

5. References

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