

High Temperature Oxidation & Hot Corrosion Behaviour of Detonation Gun Sprayed $\text{Al}_2\text{O}_3 - 40\%\text{TiO}_2$ Coating in Air & Salt on in Conel-600 at 800°C Under Cyclic Condition

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Abstract— Metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures. This is known as hot corrosion where a porous non-protective oxide scale is formed at the surfaces and sulphides in the substrate. Hot corrosion has been identified as a serious problem in high temperature applications such as in boilers, gas turbines, waste incinerations, diesel engines, coal gasification plants, chemical plants and other energy generation systems. It is basically induced by the impurities such as Na, V, S, K, and Cl, which are present in the coal or in fuel oil used for combustion in the abovementioned applications. The use of Ni-, Fe-, and Co- based super alloys in high temperature applications such as gas turbines, boilers, etc. is well known, and many more applications are still to be explored. Although the superalloys have adequate mechanical strength for such high temperature applications, they are prone to degradation by hot corrosion/high temperature oxidation during long term exposures. . Therefore, the superalloys need to be protected, however the protection system must be practical, reliable, and economically viable.

Key words: Metal Alloys, Super Alloys, Corrosion

I. INTRODUCTION

High temperature corrosion was first recognized as a serious problem in 1940s in connection with the degradation of fireside boiler tubes in coal-fired steam generating plants. Since that time, the problem has been observed in boilers, internal combustion engines, gas turbines, fluidized bed combustion and industrial waste incinerators. Turbine manufacturers and users became aware of the hot corrosion in the late 1960's when serious corrosive attack occurred in the engines of helicopters and rescue planes in service over and near sea water during the Vietnam conflict, (Rapp, [2,3]). Hot corrosion is basically the result of attack by fuel and/or ash compounds of Na, V, S, and Cl that are present in the coal or in fuel oil used for combustion in the mentioned applications. In some situations, these impurities may be ingested from the service environment, for instance in the case of NaCl contamination of marine atmospheres. There is a general agreement that condensed alkali metal salts including (notably) Na_2SO_4 , are a prerequisite to hot corrosion, (Beltran and Shores, [4]).

Metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures. This is known as high temperature or 'hot' corrosion where a porous nonproductive oxide scale is formed at the surfaces and sulphides in the substrate and the mechanism of attack does not involve aqueous

electrolytes, (Rapp and Zhang, [1]). The operating temperatures in the case of gas turbines are usually relatively high and are expected to increase further with the advances in materials development and cooling schemes for the new generation gas turbine engines. The combination of such high temperatures with an aircraft environment that contains contaminants such as sodium, sulphur, vanadium, and various halides requires special attention to the phenomena of hot corrosion, (Eliaz et al., [8]). At present, austenitic stainless steels continue to be one of the most frequently use bio materials for internal fixation devices and surgical instruments [7]. Ferritic stainless steels have been considered as promising interconnect materials in planar type anode supported solid oxide fuel cell (SOFC) stacks, which operate at temperatures below 800°C , because of their low cost and ease of fabrication when compared with the other ceramic alternatives [8].

At present, there exists a variety of ceramic coating methods for protective application ceramic coatings. These methods differ in terms of coating quality attained, deposition efficiency and complexity of process and investment costs [5].

This paper seeks to summarize the recent technological developed advanced ceramic coatings on stainless steel which have had an impact on the usage for high temperature applications. New applications which have emerged during the last 15 years are described and the areas of research needed to respond to the current market are discussed. Finally, new opportunities arising from the shift towards the SOFC applications are also described.

II. HOT CORROSION

According to [1], metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures. This is known as hot corrosion where a porous non-protective oxide scale is formed at the surfaces and sulphides in the substrate. If concentration of the sulphate exceeds the saturation vapor pressure at the operating metal temperature for turbine blades, vanes and energy generation components ($700-1100^\circ\text{C}$), then Na_2SO_4 will deposit on the surface of these components. At higher temperatures these deposits of Na_2SO_4 are molten (m.p. 884°C) and can cause accelerated attack of Niand Co-base superalloys. Furthermore, the accelerated corrosion can also be caused by other salts, such as vanadates or sulphate-vanadate mixtures and in the presence of solid or gaseous salts such as chlorides.

A. High Temperature (Type I) Hot Corrosion (HTHC)

High temperature (Type I) hot corrosion (HTHC) is nominally observed in the temperature range of about $825-$

950 °C when the condensed salt film is clearly liquid. The typical microstructure for HTHC shows the formation of sulphides and a corresponding depletion of the reactive component in the alloy substrate. The external corrosion products frequently comprise oxide precipitates dispersed in the salt film [1]. The dominant salt in HTHC is Na_2SO_4 due to its high thermodynamic stability. The macroscopic appearance of HTHC is characterized in many cases by severe peeling of the metal and by significant color changes (greenish tone, resulting from the formation of NiO) in the area of the accelerated attack (Eliaz et al.,[8]).

B. Low Temperature (Type II) Hot Corrosion (LTHC)

Low temperature (Type II) hot corrosion (LTHC) occurs well below the melting point of pure Na. The reaction product morphology for this type of corrosion can be characterized by a non-uniform attack in the form of pits, with only little sulphides formation close to the alloy/scale interface and little depletion of Cr or Al in the alloy substrate [1]. This form of corrosion is observed mainly within the temperature range 650-800 °C (Nicholls, [13]). The formation of low melting point eutectics causes typical LTHC pitting, for instance the formation of Na_2SO_4 - $NiSO_4$ eutectics for nickel-based superalloys. Wright [14] suggested that a high partial pressure of SO_3 in the gaseous phase is required in the LTHC reactions to occur, in contrary to HTHC.

III. HOT CORROSION OF SUPERALLOYS

Hot corrosion degradation process of the superalloys usually consists of two stages, namely an initiation stage and a propagation stage (Pettit and Meier[15] and Pettit and Giggins [16]). According to Pettit and Meier [15], it is a fact that all corrosion resistant) alloys degrade via these two stages and it is the result of using selective oxidation to develop oxidation or corrosion resistance. They further elaborated that the conditions causing hot corrosion therefore do nothing more than shortening the time for which the superalloys can form protective alumina or chromia scales via selective oxidation.

During the initiation stage of hot corrosion, superalloys are being degraded at rates similar to those that would have prevailed in the absence of the deposits. Elements in the alloy are oxidized and electrons are transferred from metallic atoms to the reducible substances in the deposit. Consequently, the reaction product barrier that forms beneath the deposit on the alloy surface usually exhibits primarily those features resulting from the gas-alloy reaction (Pettit and Giggins, [16]). In some cases of hot corrosion, an increasing amount of sulphides particles become evident in the alloy beneath the protective reaction product barrier. In other, small holes become evident in the protective reaction product barrier where the molten deposits begin to penetrate it. Eventually the protective barrier formed via selective oxidation is rendered ineffective, and the hot corrosion process enters into the propagation stage. Obviously, in attempting to develop resistance to hot corrosion one should strive to have the superalloys remain in the initiation stage as long as possible (Pettit and Meier,[15]).

The propagation stage of the hot corrosion sequence is the stage for which the superalloys must be removed from service since this stage always has much larger corrosion rates than for the same superalloys in the initiation stage (Pettit and Meier,[15] and Pettit and Giggins, [16]). The pertinent Mechanism behind this mode of hot corrosion has been summarized in Section 4. However, Pettit and Giggins [16] opined that the hot corrosion degradation sequence is not always clearly evident, and the time for which protective reaction products are stable beneath the salt layer is influenced by a number of factors. The alloys must be depleted of certain elements before non-protective products can be formed, or the composition of the deposits must change to prevent the formation of protective scales. There are cases when the initiation stage does not exist at all and the degradation process directly enters into the propagation stage.

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Stringer [18] presented an excellent review of the work done in the field of hot corrosion up to about 1976, which was aimed at understanding the hot corrosion processes. Much of the mechanisms proposed during that period were focused on thermochemistry. Bornstein and DeCrescente [19,20] And Bornstein et al. [21] proposed a hot corrosion mechanism based on the basic dissolution of the Protective oxide scale by a reaction involving Na_2O , the basic minority component of the fused salt.

IV. PROPOSED SYSTEM DESCRIPTION

Superalloys exposed to high temperature tend to suffer degradation due to hot corrosion during service. Inutility gas turbine, contaminants in the fuel and air can cause serious hot corrosion problem [4–6]. One of the solutions to this problem is applying a thin layer of antiwar and anti-oxidation coating [6–8]. Thermal spraying is an effective and low cost method to apply thick coatings to change surface properties of the component. Coatings are used in wide range of applications including automotive systems, boiler components, power generation equipment, chemical process equipment, aircraft engines, pulp and paper processing equipment, bridges, rollers and concrete reinforcement, orthopedics and dental, land based and marine turbine, and ships [9]. Among the commercially available thermal spray coating techniques, Detonation Gun Spray and High Velocity Oxy Fuel(HVOF)

spray are the best choices to get hard, dense and wear resistant coating as desired [10]. Detonation Gun (D-Gun) Spraying is one of the thermal spray processes, which gives an extremely good adhesive strength, low porosity, and coating surface with compressive residual stress [11]. Detonation Gun (D-Gun) offers highest velocity (800–1200 ms) for the sprayed powders that are unattainable by the plasma and HVOF condition. The higher particle velocity during deposition of coating results in desirable characteristics such as lower porosity and higher hardness of the coating [12]. In thermal spray industry Al₂O₃ alloy with TiO₂ ceramics are known for easy spray and environmental compatibility [13, 14]. Al₂O₃ alloy with TiO₂ ceramics are popular in thermal spray industry due to easy spray and environment compatibility [15]. The presence of TiO₂ in the Al₂ powders contributes to lower porosity in the coating [13, 16]. The micro hardness of Al₂O₃-TiO₂ composite coating depends essentially on its composition. The objective of the present work is to investigate the role of Detonation Gun Sprayed coating in enhancing the properties of surface of substrate to counter the problem of hot corrosion. Al₂O₃-40TiO₂ coating is deposited on Superni 718 and AE 435 superalloys using the Detonation Gun Spray process. Hot corrosion test of specimens is carried out in the molten salt environment Na₂SO₄-82%Fe₂(SO₄)₃ at 900C for 50 cycles of one hour duration. Thermo gravimetric technique was used to approximate the hot corrosion kinetics of Al₂O₃-40TiO₂ coating and bare superalloy substrates. SEM is used to characterize the hot corrosion product of the coated and bare sample.

Parameters	Al ₂ O ₃ -40TiO ₂ coating
Oxygen flow rate (O ₂)	4,800 SLPH
Pressure	0.2 MPa
Acetylene flow rate (C ₂ H ₂)	1920 SLPH
Pressure	0.14 MPa
Nitrogen flow rate (N ₂)	800 SLPH
Pressure	0.4 MPa
Spray angle	90°
Spray distance	200 mm
Power	450 VA
Wire rate	1–10 Hz
Coating thickness (average)	250 μm

Table 1: Parameter Used In Detonation Gun Spray.

V. EXPERIMENTAL PROCEDURE

A. Materials & Coating Formulation

Two nickel based superalloys, namely, Superni 718 and AE 435, are selected as substrate materials procured from M/S Mishra Dhatu Nigam Limited, Hyderabad, India, in the rolled sheet form. The chemical compositions of Superni 718 and AE 435 are given in Table 1. Each specimen measuring approximately 20 mm × 15 mm × 5mm was cut from the rolled sheet and polished by using 180, 220, 320, 400, and 600 grades SiC emery papers. The specimens were blasted using alumina stones (grit 20) prior to coating. Commercially available Al₂O₃-40TiO₂ powder (H.C. Starck, Amperit 745.001) with its particle size 22–45 μm was used to coat the superalloys by Detonation Gun Spray process. The Characteristics of Al₂O₃-40TiO₂ coating powders is given in Table 2. D-Gun was used to apply Al₂O₃-40TiO₂ coating on the superalloys.

B. Hot Corrosion Text

Hot corrosion studies were performed in a molten salt Na₂SO₄-82%Fe₂(SO₄)₃ for 50 cycles under cyclic conditions. Each cycle consisted of 1 hour heating at 900°C in a Kanthol wire tube furnace followed by 20 minutes cooling at room temperature. The samples were washed in acetone for removing dirt, grease, and oil. The specimens were heated in an oven to about 250C before applying the salt layer. A salt of Na₂SO₄-82% Fe₂(SO₄)₃ thoroughly mixed with distilled water was applied uniformly on the warm polished specimens with the help of a camel hair brush. The amount of salt coating was kept in the range of 4.0-5.0 mg/cm². The salt coated specimens inside the alumina boats were then kept in the oven for 3-4 hours at 100C. They were again weighed before exposure to hot corrosion tests in the Kanthol wire tube furnace. During hot corrosion runs, the weight of boats and specimens was measured together at the end of each cycle with the help of electronic weighing balance with an accuracy of 1mg. The spelled scale was also included at the time of measurements of weight change to determine total rate of corrosion. The corrosion rate was calculated using the weight change measurements of the bare and coated samples. The surface of all the samples after corrosion tests was analyzed using SEM.

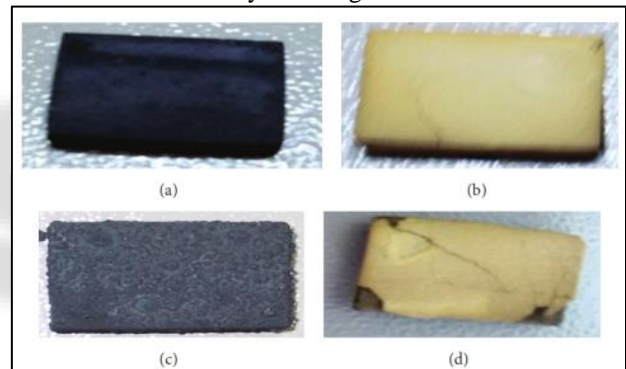


Fig. 1: Surface Macrographs for (a) Superni 718, (b) coated Superni 718, (c) AE 435, and (d) coated AE 435 after 50 cycles exposure to molten salt Na₂SO₄-82%Fe₂(SO₄)₃ environment at 900C.

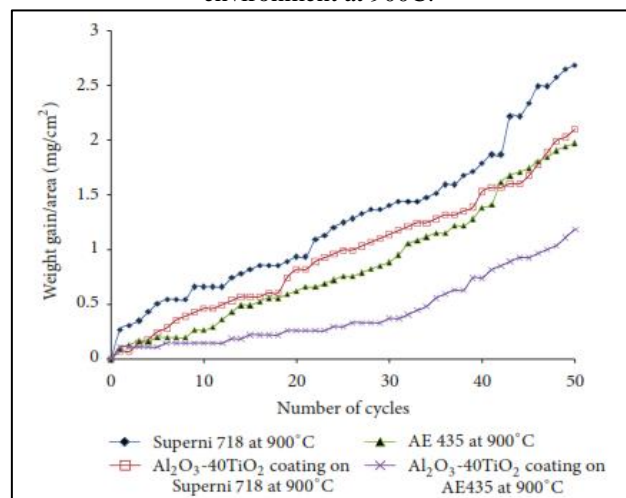


Fig. 2: Weight gain/area versus number of cycles plot for Al₂O₃-40TiO₂ coated and bare superalloys subjected to Na₂(SO₄)₃ at 900C for 50 cycles.

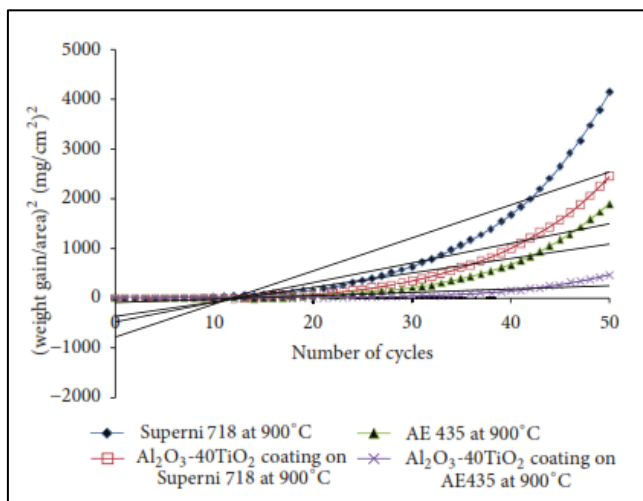


Fig. 3: (Cumulative weight gain/area) vs. number of cycles for bare and Al_2O_3 -40 TiO_2 coated superalloys subjected to Na_2SO_4 -82% $\text{Fe}_2(\text{SO}_4)_3$ at 900C for 50cycles

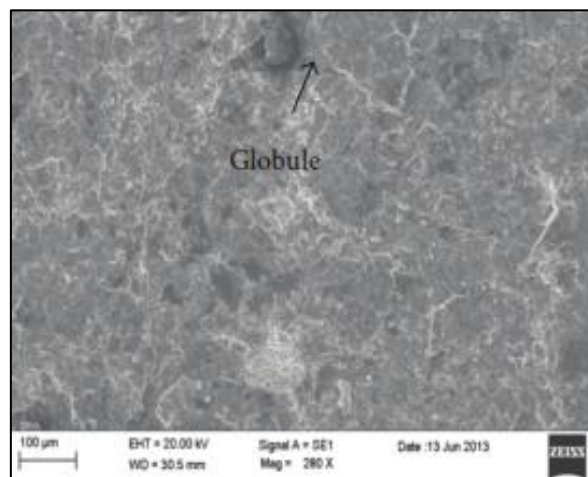
VI. RESULTS & DISCUSSIONS

In case of Superni 718 superalloy (Figure 1(a)), spalling was observed after the completion of the 8th cycle. The colour of Superni718wasblackishuptothe6thcycle.The colour of AE 435 superalloy was light blackish upto the 4th cycle and for subsequent cycles the colour was dark blackish.The colour of coated Superni 718 and AE 435 was light blackish colour upto the 5th cycle and for further cycles they showed yellowish colour. Figure 2 shows the weight gain/unit area for the bare as well as coated superalloys in the presence of molten salt where W/A is the weight gain per unit surface area (mg/cm) and t indicates the number of cycles, representing the time of exposure [14]. The parabolic rate constant K for both super alloys is given in Table 4.

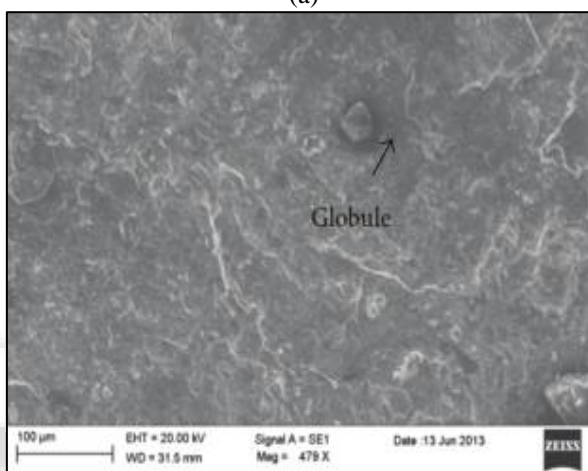
TABLE 4: Parabolic rate constant (K_p) for the Al_2O_3 -40 TiO_2 coated and uncoated Superni 718 and AE 435 superalloys.

Substrate	K_p Values ($\times 10^{-10} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$)
Superni 718	66.376
Coated Superni 718	39.443
AE 435	28.995
Coated AE 435	6.7245

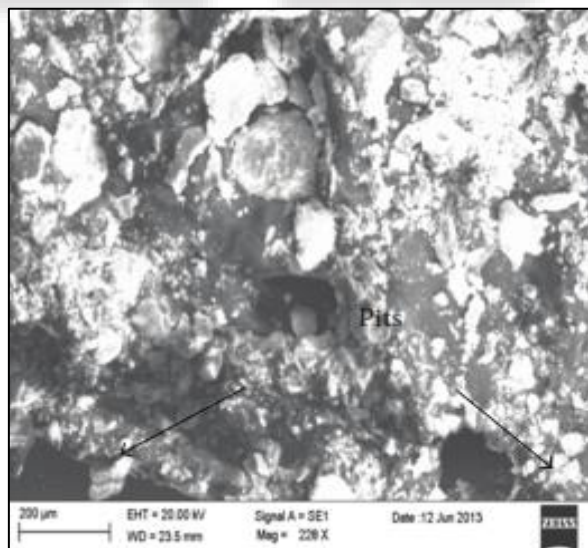
The SEM micrographs of Al_2O_3 -40 TiO_2 coating and uncoated superalloys after exposure to hot corrosion environment are shown in Figure 4. The surface morphology of both the coated substrates is almost similar with some globular like structure on the surface as seen from Figures 4(a) and 4(b). The surface of Superni718 is rough as seen from Figure4(c). Some pits are also visible in Figures4(c) and 4(d). This may be due to spalling behavior of the scale. Similar results have been reported by Sidhu et al. [17]. According to them, the presence of different phases in the superalloys might impose severe strain on the surface thin layer during cooling period which may result in cracking and exfoliation of the scale.



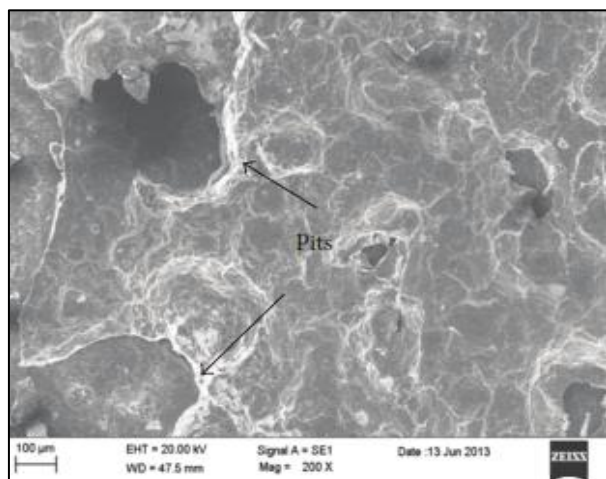
(a)



(b)



(c)



(d)

Fig. 4: SEM micrographs of (a) Al₂O₃-40TiO₂ coated Superni 718 (b) Al₂O₃-40TiO₂ coated AE 435 (c) Superni 718 (d) AE 435 superalloys subjected to Na₂SO₄-82%Fe₂(SO₄)₃ at 900° C for 50 cycles.

VII. CONCLUSIONS

In the present work, hot corrosion behavior of detonation gun sprayed Al₂O₃-40TiO₂ coated on Superni 718 and AE 435 superalloys in aggressive environment of Na₂+82%Fe(SO₄)₃ at 900° C has been investigated and the following conclusions are made.

- 1) The bare superalloys have shown some pitting and peeling of scale and mass gain was relatively more.
- 2) The parabolic rate constants of Al₂O₃-40TiO₂ superalloys are lower than the bare superalloys subjected to cyclic hot corrosion in molten salt environment. The values of parabolic rate constant K_p for coated Superni 718 were obtained to be 39.443 mg/cm and for coated AE435 were obtained to be 6.7245 mg⁴/cm⁴.
- 3) The hot corrosion resistance of Al₂O₃-40TiO₂ coating on AE 435 was better when compared to that Superni 718 superalloy in the given molten salt environment.
- 4) Al₂O₃-40TiO₂ coating is successfully deposited using Detonation Gun Sprayed on Superni 718 and AE 435 superalloys. The Detonation Gun Sprayed Al₂O₃ - 40TiO₂ coating improved the hot corrosion behaviour in aggressive environment of Na₂ 82%Fe(SO₄)₃ at 900° C by 14.8% and 36.8% for Superni 718 and AE 435, respectively.

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