Thermal Spray Coatings for Hot Corrosion Resistance

Subhash Kamal, K.V. Sharma, P. Srinivasa Rao and Othman Mamat

Abstract Hot corrosion arises when metals are excited in the temperature range 700–900 °C in the existence of sulphate deposits, formed as a result of the reaction among sodium chloride and sulphur mixtures in the gas phase adjoining the metals. No alloy is resistant to hot corrosion occurrence indefinitely even though there are certain alloys that require a prolonged origination time at which the hot corrosion progression from the beginning stage to the circulation stage. Superalloys have been established for high-temperature applications. However, these alloys are not constantly able to meet both the high-temperature strength and high-temperature corrosion resistance simultaneously, so the need is to protect from hot corrosion. The high-temperature guarding system must meet numerous benchmarks, provide satisfactory environment resistance, be chemically and mechanically compatible with the substrate, be practically applicable, reliable and economically viable. This chapter briefly reviews the hot corrosion of some Ni- and Fe-base superalloys to recognise the occurrence. Extensive reviews on the hot corrosion of coatings have looked regularly since early 1970; the purpose of this chapter is not to repeat the published resources but relatively to emphasis on research developments and to point out some research forecasts.

Keywords Hot corrosion · Oxidation · Nano coating · Thermal spray coating

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1 Introduction

Hot corrosion is one of the severe difficulties for high-temperature application, such as helicopter, marine, utility, industrial and land-based gas turbines; boilers; oil refinery furnace; and engines. The use of widespread collection of fuels from natural gas, kerosene, diesel oils, lingering oils and gaseous fuels together with enhanced operating temperatures cause hot corrosion (Nicholls et al. 2002). Eliaz et al. (2002) defined hot corrosion as an accelerated corrosion, resulting from the presence of salt contaminants such as Na_2SO_4, NaCl and V_2O_5 that combine to form liquefied deposits, which damage the shielding surface oxides.

Hot corrosion has been detected in boilers, aircraft, IC engines, gas turbines, fluidised bed combustion, and industrial waste incinerators since the 1940s. However, it turns out to be an issue of importance and current interest in the late 1960s when gas turbine engines of military aircrafts grieved with severe corrosion attacks when it is flying over and near sea water during the Vietnam conflict (Rapp and Mehl 2000; Rapp 2002).

Corrosion occurs when molten compounds (Na_2SO_4 melting point 884 °C) soften the shielding oxide layers, which obviously form on materials during boiler/gas turbine operation. Moreover, the vanadium compounds are excellent oxidation substances and permit oxygen and other gases in the combustion.

Atmospheric air penetrates through the metal surface and further pramotes oxidation. Once the metal is oxidised, the cyclic process starts over again resulting into greater corrosion degradation (Kamal et al. 2008; Sharma 1996).

In the present-day gas turbines, the stress is on saving energy and decreasing the amounts of contaminants emitted. This can be achieved only by creating alloys with higher melting points and the ability to retain mechanical strength at higher temperatures. The improvement of nickel-based superalloys has reached the limit, with blades exposed to critical temperatures close to melting points. Further increase in the operating temperature will result in termination of the strengthening phases and even melting.

An operation of gas turbines is usually restricted by hot corrosion, because of catastrophic failures. High temperatures have a disparate effect on the corrosion of the alloys (Maledi et al. 2006). In the beginning, gas turbines developed after the 1940s and were considered to operate at 700 °C. Developments in metallurgical methods, blade cooling performances and application of thermal spray coatings permitted for increased operating temperatures (Eliaz et al. 2002). Coatings have greater influence towards increased operating temperatures and safeguard against environmental pollutants (Stringer 1987; Gurrappa 2003).

In the power production processes, the mechanism of hot corrosion is reliant on the creation of a liquid phase that is largely Na_2SO_4 or K_2SO_4. The sulphur produced from the coal is SO_2 and SO_3 which responds to volatile alkalis to produce Na_2SO_4 vapour; further, it combines with fly ash on the boiler tubes of superheater and reheater. Such a molten phase melts the chromium oxide in the defending coating, which permits the base metal to come in contact with sulphate ions to form sulphide ions and non-shielding oxides (Kamal et al. 2008; Rapp and Goto 1981).

Among high-temperature alloys, the promising alloys are "superalloys", namely nickel-, cobalt-, and iron-based superalloys, which show high-temperature mechanical properties and moderate resistance to hot corrosion. Investigations in the area of doping, such as magnesium oxide, cerium oxide, and calcium oxide, is already done and the reduction in the amount of hot corrosion in violent atmosphere of Na_2SO_4–60 %V_2O_5 at 900 °C has been achieved. However, the major problem being faced is how to inject these inhibitors into the combustion chamber along with the fuel in actual industrial environment (Tiwari and Prakash 1998; Gitanjaly et al. 2002).

Thermal spray coatings are widely used in aqueous, wear, erosion and high-temperature applications such as diesel and gas turbine engines. Power generation with the help of coal gasification and waste incineration involves severe degradations, and therefore, coating has demonstrated to be effective (Hocking 1993). Superior understanding of the degradation behaviour and catastrophe failure devices of coatings need to be accomplished, particularly with respect to the effects of engine operating temperature and atmosphere on the coating recital (e.g. thermal cycling) (National Materials Advisory Board 1996).

Detonation-Gun is accomplished of producing the maximum pressure, velocity and density in the flow, which is higher than other spraying techniques. Therefore, the detonation-gun coatings are characterised by exceptionally high density, less oxide formation, superior bond strength, greater impact velocity and low porosity, which are suitable for applications requiring very high standards, such as aircraft engine components (Saravanan et al. 2000; Murthy and Venkataraman 2006).

2 Hot Corrosion

Simons et al. (1955) published first practical journal on hot corrosion; he described that hot corrosion is an electrochemical process in which the liquefied salt acts as an electrolyte. Seybolt (1968) ascribed Na_2SO_4 encouraged hot corrosion of Ni–Cr alloys to enhanced depletion of chromium by oxidation succeeding favoured inner fluxing of Chromium. Bornstein and DeCrescente (1969) described that during the oxidation of three different presulphidised superalloys enhanced mechanism of hot corrosion were not detected and projected a hot corrosion device proposed on the termination of protecting oxide film formed by a reaction connecting Na_2O. Goebel and Pettit (1970) prolonged this kinetics which comprises bitter dissolution, and oxide redrizzle leads disastrous oxidation due to Na_2SO_4 for alloys comprising solid acidic elements, such as vanadium or Molybdenum.

Enhanced corrosion attack is caused by other salts, viz. vanadate or sulphates–vanadate combinations and also in the presence of solid or gaseous salts such as chlorides (Bornstein et al. 1973). However, manufacturers of turbines and users of turbines conscious about hot corrosion in the 1960s, and Stringer (Stringer 1977) have conducted experimental as well as field tests to identify the nature of attack and explained its temperature dependence and the corresponding morphologies. Hot corrosion was first associated with Na_2SO_4 in the mid-1950s (Luthra and Shores 1980). Hot corrosion became a theme of significance and most popular attention in the late 1960s when gas turbine engines of military aircraft suffered excessive corrosion attack during the Vietnam War when it is operating over sea water (Rapp and Mehl 2000). When metals are exposed to temperature range 700–900 °C, deposition of sulphates starts which leads to reaction between sodium chloride and sulphur compounds in the gas phase nearby the metals (Hancock 1987).

According to Shih et al. (1989) metals and alloys repeatedly experience an enhanced oxidation at higher temperature gas atmospheres when enclosed with a thin film of liquefied salt. This type of oxidation is generally regarded as hot corrosion. Hot corrosion is a severe damage of metals and/or an alloy due to the oxidation which is badly caused by liquid salt deposits, largely Na_2SO_4. The main source of Na_2SO_4, in aircraft engines is due to reaction between NaCl in swallowed air and sulphur in fuel as per the following reactions (Khajavi and Shariat 2004).

$$2NaCl + SO_2 + 1/2\,O_2 + H_2O \rightarrow Na_2SO_4 + 2HCl \tag{2.1}$$

$$2NaCl + SO_3 + H_2O \rightarrow Na_2SO_4 + 2HCl \tag{2.2}$$

To safe guard the turbine engines against high-temperature corrosion attack caused by impurities such as Na, S and V, thermal sprayed coatings need to be placed over the hot section parts of turbine engines and boiler tubes (Uusitalo et al. 2004).

2.1 *Physical Characteristics of Hot Corrosion*

High-temperature hot corrosion (Type I) is the form of hot corrosion usually arises above the melting point of sodium sulphate (884 °C), where the salt is clearly a liquid state. Goebel et al. (1973) extended the fluxing theory to explain the acidic fluxing of protective scale in Cr_2O_3 and Al_2O_3 forming alloys which contain Mo, W and V. It is observed that Al_2O_3 can be fluxed as cationic species attached to the metal surface, which is acidified by refractory metal oxides, such as MoO_3, WO_3 and V_2O_5. Further, a prolonged layer of Al_2O_3 forms on the alloy surface by using the oxygen present in the salt. This increases the sulphur activity in the salt, it increases to such an extent that the sulphides of aluminium are formed as particles in the metal substrate.

Due to the formation of sulphides of aluminium in the substrate, the key element (Al) for protecting the alloy surface gets depleted in the alloy, once sulphur is removed from the salt, the oxygen activity in the salt increases, the local basicity of salt increases to such an extent that Al_2O_3 dissolves in the basic salt at the salt/oxide interface and get reprecipitated at the gas/salt interface. This reaction continues until the sodium sulphate remains on the alloy surface and increases the rate of hot corrosion due to fluxing of shielding oxide scale. Low-temperature hot corrosion (Type II) is one of the forms of hot corrosion that occurs below melting point of Na_2SO_4, where the salt is supposed to be a solid. Higher corrosion rate during the beginning stages were attributed to the rapid sulphation of cobalt oxide or Co (at scale/metal interface) which forms liquid eutectic melt followed by the dissolution and precipitation of cobalt oxide at the gas/salt interface by countertransport of Co^{2+}/Co^{3+} ions during the propagation stage. Thus, fluxing action of cobalt oxide prevents the formation of protective layer of Cr_2O_3, as the temperature increases, the partial pressure of SO_3 decreases, which is not sufficient to form liquid eutectic mixture. Hence, the corrosion rate at high temperature is much less than at low temperatures (Goebel et al. 1973).

2.1.1 High-Temperature Hot Corrosion (HTHC) Type I

It is beaning observed since the 1950s and it is a tremendously rapid form of oxidation attack takes place in the temperatures range between 815 and 926 °C in the existence of pure Na_2SO_4 (m.p 886 °C) (Khajavi and Shariat 2004). HTHC starts with the accumulations of bonded alkali salts (Na_2SO_4) on the component surface; the most significant source of sodium is marine, industrial atmosphere as well as fuel. During the combustion of fuels, sodium from air and sulphur from the fuel combine to form a sodium sulphate (Eliaz et al. 2002). Na_2SO_4 formation lies basically in the reaction

$$SO_2 + 2NaCl + O_2 \rightarrow Na_2SO_4 + Cl_2 \tag{2.3}$$

Hot corrosion (Type I) is analysed by a macroscopically uniform corrosion rate, which involves an internal oxidation layer which comprises internal sulphides and carbides. The exterior oxide is not shielding and is composed of the base metal oxides (nickel or cobalt); and the oxides of the other ingredients, such as chromium and aluminium (Stringer 1998).

The hot corrosion mechanism depends on temperature as shown in Fig. 1. With the increase in temperature, the attack changes from low-temperature attack (Type II) to high-temperature attack (Type I). Type I hot corrosion was first met in gas turbines of aircraft. When a gas turbine used for marine propulsion, additional type of hot corrosion was detected and it was found that it is necessary to have SO_3 present in the gas. It has been established that SO_3 should be present to cause hot corrosion attack a sum of experiments were conducted between 650 and 950 °C temperature range using oxygen–SO_2 gas mixtures. At temperatures from 650 to 750 °C, low-temperature (Type II) corrosion attack was detected when SO_3 gas pressures present in the mixture.

2.1.2 Low-Temperature Hot Corrosion (LTHC) Type II

Low-temperature hot corrosion (LTHC) was identified in the 1970s as a distinct tool of corrosion attack (Khajavi and Shariat 2004). Low-temperature hot corrosion mainly witnessed within the 650–800 °C temperature range and needs a substantial high partial pressure of SO_3, for cobalt-based superalloys. The formation of

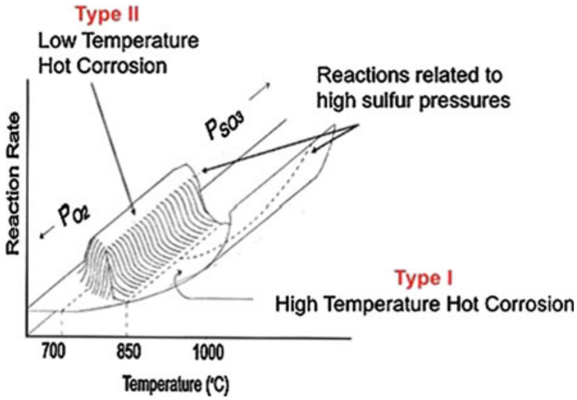

Fig. 1 Schematic to demonstrate the different hot corrosion attack as a role of temperature and SO_3 partial pressure. Various hot corrosion reaction rate surface processes are presented (Pettit 2011)

low-melting eutectic compounds occurs due to the mixture of sodium sulphate and cobalt sulphate (melting temperature of the $Na_2SO_4 \pm CoSO_4$ eutectic is 540 °C) (Eliaz et al. 2002). The formation of $Na_2SO_4 + NiSO_4$ eutectics at 671 °C has been reported for nickel-based superalloys, the morphology of attack is pitting when the LTHC takes place, low temperature corrosion characteristically shows no denuded zone, little inter-granular attack, and a layered type of corrosion scale with no subscale sulfide particles (Misra 1986). Chromium (25–40 %) and silicon are most useful in coatings for safeguarding against Type II hot corrosion. Type I or Type II hot corrosion attack mainly classified based on the morphology, and not on the temperature. Type II, or low-temperature hot corrosion is considered by a pitting attack (Stringer 1998).

2.2 *Degradation of the Superalloys*

The hot corrosion decay of superalloys typically involves two distinct phases of attack (Pettit and Meier 1985; Pettit and Giggins 1987), namely an initiation (incubation) stage and propagation stage. Such conditions are represented schematically in Fig. 2.

2.2.1 The Initiation Stage

There is no alloy developed till now which offers resistant against hot corrosion forever whereas some alloy mixtures that involve an extended beginning times before the hot corrosion attack starts from the beginning stage to the transmission stage. Hot corrosion beginning periods, degradation rate of superalloys, are similar to those in the non-existence deposits of molten salts. Different metals when oxidised movement of electrons from metallic atoms to the degradable materials propagates under the molten salts deposit. Subsequently, the oxide layer below the

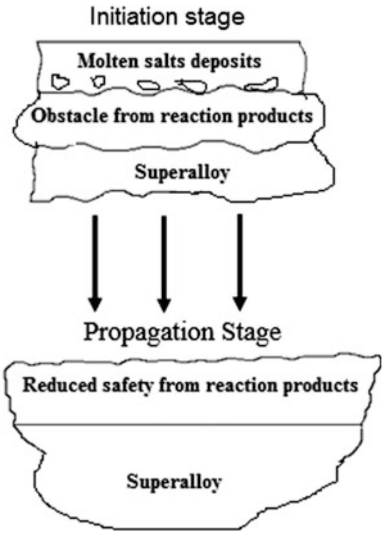

Fig. 2 Graphical diagram showing the situations that progress during the initiation and propagation of hot corrosion attack

molten salts deposit acts as a barricade on the surface of alloys (Pettit and Giggins 1987). The travel of initiation to propagation stage of hot corrosion process depends on several reasons that disturb with the time as shown in Fig. 2. In the propagation stage, the kind of corrosive species that are produced depends on the above aspects.

The above-mentioned reason accountable for multiple hot corrosion developments is detected once superalloys are left open to diverse corrosive atmospheres (Pettit and Meier 1985).

2.2.2 The Propagation Stage

Hot corrosion transmission stage of any alloy must be detached from service because it has travelled much longer corrosion time than that of initiation stage (Pettit and Meier 1985; Pettit and Giggins 1987). Superalloys contain some components that attract oxygen; we can find oxygen distribution along the deposition (Pettit and Giggins 1987).

3 Mechanisms of Hot Corrosion

From the literature review, it has been observed that there are varieties of conditions which can be considered for hot corrosion degradation of the superalloys. Researchers have proposed number of mechanisms for this type of degradation such as failure of oxide scale, sulphidation–oxidation and salt fluxing, oxide solubility, and effect of vanadium (Eliaz et al. 2002; Stringer 1987; Rapp and Goto 1981; Pettit and Meier 1985; Goebel and Pettit 1970a, b; Beltran and Shores 1972; Otsuka and Rapp 1990).

These mechanisms can be observed in relation to each other rather than as completely different and unconnected corrosion process. The molten salt dissolution kinetics initially projected by Goebel and Petit (1970a, b). According to them, protective and safe surface oxide film vanished as a result of dissolution oxide layer under the influence of molten salt environment. This dissolution caused grouping of O^{2-} with oxides that form anions (basic fluxing) or by disintegration oxides to equivalent cations and O^{2-} (acidic fluxing) (Goebel et al. 1973).

It is has been observed that absorption of oxygen ions for dissolution is restricted by the quantity of deposition existing on the superalloy surface. As opposed to the basic dissolution, the acidic dissolution can be self-supporting (Stringer 1987; Pettit and Meier 1985). Therefore, acidic fluxing is more severe as compared to basic fluxing. In overall, the hot corrosion of the superalloys stated to arise due to basic dissolution kinetics and also because of high concentration of Al and Cr.

Hot corrosion dissolution process creates a (−)ve solubility inclination whereby the oxide on the surface of an alloy liquefied in the melted deposit at the oxide-scale/deposit interface, but precipitated out in the deposit where the solubility was lesser as an intermittent scale, as depicted in Fig. 3a. The solubility of a sum of oxides in Na_2SO_4 as a purpose of the activity of Na_2O in the Na_2SO_4 displayed that the solubilities could be streamlined via reactions with the Na_2O or SO_3 components in Na_2SO_4, Fig. 3b.

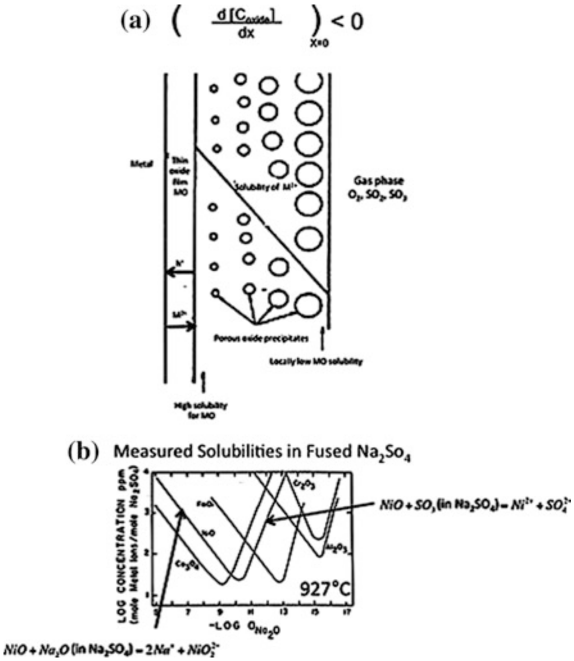

Fig. 3 **a** Sketch describing the negative solubility gradient where an oxide dissolves and reprecipitates out in the Na_2SO_4. **b** Solubilities of oxides in fused Na_2SO_4 with reactions describing the dissolution process (Pettit 2011)

With high amounts of tungsten, molybdenum and vanadium in superalloys frequently conveyed that hot corrosion follows the acidic dissolution mechanism (Eliaz et al. 2002), and these components oxidised with the existence of Na_2SO_4 and deposit on alloys causing disastrous self-supporting hot corrosion (Pettit and Meier 1985). Stott et al. (1994) suggested that sulphur-containing elements, piercing through limited paths in the oxide, which creates sulphide channels from the scale–metal border to the scale–gas border. The sulphide channels deliver easier circulation paths for the base metal ions through the oxide to the surface and finally allow more fast development of sulphide lumps above the oxide.

However, Natesan (1985) described that no passage of sulphur into the oxide, or sulphide channel development was necessary to form immense mixed iron and chromium sulphides at the oxide–gas border. Established on the experimental analysis of sulphidation–oxidation of Incoloy 800, he reported that adsorption of sulphur by the oxide scale accelerates the movement of cations such as Fe and Ni from the base metal to the scale–gas interface.

For base metal sulphidation, the partial pressure of sulphur in the gas should be more in off for the transport cations with sulphur to form sulphides as an outer scale. Hot corrosion in vanadate, sulphates and chloride atmosphere of a Ni-based superalloy is informed by Deb et al. (1996). Mass gain readings were taken in air without coated molten salts and with coated molten salts in air. Internal sulphidation of the superalloy beneath the external oxide layer is caused due to the presence of sulphur in the form of sulphates.

Rapp and Goto (1981) anticipated that shielding scales on alloy become non-shielding if negative dissolution gradients formed on the oxides in the presence of liquefied molten salts, due to possibility of continuous dissolution and reprecipitation of oxide. On the basis of oxide solubilities measurement in liquefied Na_2SO_4 as an occupation of the acidity of the molten salt, they suggested a (−)ve gradient of the solubility of the shielding oxide in the salt layer. Without any sulphide-developing reaction local deviation of sodium oxide activity and oxygen partial pressure along molten salt film was observed because of the fluxing, above-mentioned mechanism explains enhanced corrosion attack by the dissolution of the shielding oxide film (Stringer 1987).

Different research workers have examined the effect of vanadium on high-temperature hot corrosion of metals and alloys. Bornstein et al. (1973) and Goebel et al. (1973) recommended that self-supporting acidic degradation of shielding chromium and aluminium oxide scales could take place in the presence of vanadium salt layer. Zhang and Rapp (1987) further proposed that in the presence of vanadate every oxide forms an acidic solute with much higher solubility which promotes more faster attack by mixed vanadate–sulphate fluxes on oxides and further by sulphate flux.

3.1 Chemistry of Salts

3.1.1 Sulphate Chemistry

As described by Rapp and Mehl (2000) and Rapp (2002), an acid/base atmosphere is shown by oxy-anion melts of hydroxides, sulphates, etc., where in the acid constituents reflected as NO_2 (g), CO_2(g), H_2O(g) or SO_3(g), correspondingly. While the use of the Lux-Flood collection of NO_3^-, CO_3^{2-}, OH^- and SO_4^{2-} as the basic elements is collective for such fused salts, the oxide ion can otherwise be chosen as the Lewis base in common for all of these salts. For a melt of pure Na_2SO_4 (m.p 884 °C), there exists an equilibrium as given below:

$$Na_2SO_4 \rightarrow Na_2O + SO_3(g) \tag{2.4}$$

According to Rapp and Mehl (2000), chromium oxide is the best oxide for the protection of alloys from the attack by bonded sodium sulphate. Figure 4 presents the superposition of the Ellingham phase constancy plot for Cr–S–O onto the Na–S–O phase constancy diagram to examine the suitability of Cr_2O_3 in fused Na_2SO_4 at 1200 K. The chromium oxide can melt as two acidic solutes (Cr_2 $(SO_4)_3$ and CrS) and two basic solutes (Na_2CrO_4 and $NaCrO_2$) (Rapp and Mehl 2000).

3.1.2 Vanadate Chemistry

Among the transition metals, vanadium is unique; in that, it forms a low-melting oxide V_2O_5. This low melting temperature (670 °C under 1 atm of oxygen) results from the peculiar crystal structure of the compound in which vanadium is 5, coordinated with oxygen and in which there occur four different vanadium–oxygen bond lengths (Suito and Gaskell 1971).

The phase constancy diagram for the Na–V–S–O system at 900 °C has been shown in Fig. 5. The hot corrosion field is very much conscious that vanadates are most corrosive constituents in bonded salts, e.g., as a solute in bonded Na_2SO_4. The difficulty is vanadates lower the liquidus of the melt, and another problem is tendency of these strong acids to complex oxide ions, according to the following equilibria (Rapp and Mehl 2000). The dashed lines in the salt solution represent isoactivity lines of vanadate species (Hwang and Rapp 1989).

$$Na_2SO_4 \rightarrow Na_2O + SO_3 \tag{2.5}$$

$$Na_3VO_4 \rightarrow Na_2O + NaVO_3 \tag{2.6}$$

$$2NaVO_3 \rightarrow Na_2O + V_2O_5 \tag{2.7}$$

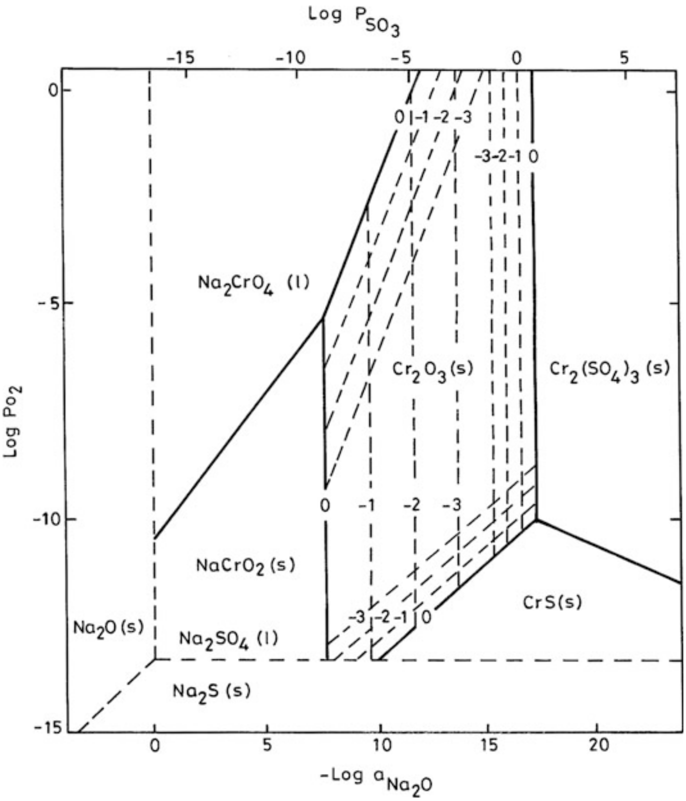

Fig. 4 Na–Cr–S–O phase constancy diagram for 1200 K (Rapp and Mehl 2000)

The stability percentage of vanadium species differs constantly with melt basicity. Na_3VO_4 is a leading compound in the melt at basicity less than 8.2, and V_2O_5 is leading at basicity larger than 16.3. For basicity between 8.2 and 16.3, $NaVO_3$ is vital vanadium solute (Hwang and Rapp 1989).

3.2 Hot Corrosion in Liquefied Salt Atmospheres

3.2.1 Liquefied Salt (Na_2SO_4–60 %V_2O_5) Atmosphere-I

Kolta et al. (1972) studied the mechanisms of reactions between Na_2SO_4 and V_2O_5. They established that reaction rate predominantly depends on temperature range between 600 and 1300 °C at molar ratios of Na_2SO_4 and V_2O_5. These researchers revealed with the reaction time increase greater than 30 min; the reaction rate goes on decreasing and finally touched zero order. The decrease in reaction time

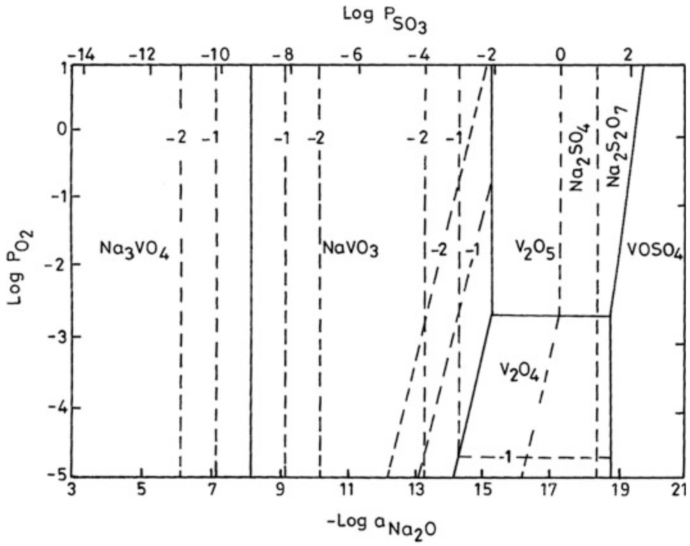

Fig. 5 Diagram showing phase stability of Na–V–S–O system at 900 °C (Rapp and Mehl 2000)

attributed with the development of vanadous sulphate mixtures such as $(NaV_3O_8)_2$. Na_2SO_4 and $(NaVO_3)_2.Na_2SO_4$, which are disintegrated at high temperatures obtaining meta- and pyrovanadates correspondingly.

The consequence of enhanced oxidation by sodium and vanadium on the nickel-base alloys is conveyed by Bornstein et al. (1975), between V_2O_5 and alloy substrate, they witnessed oxidation rate was rapid in the early stages. Inter-metallic Ni_3Al and NiAl were predominantly found to be liable to V_2O_5 corrosion. As reported by them, the composition of the melt altered by sulphidation attack and produces extra ions of oxide, i.e. $M + SO_4^- = MS + O^- + 3/2O_2$. Harshness of attack is found to be reduced by increasing early oxide ion concentration.

Hot corrosion performance of Cr_3C_2–NiCr coatings on superalloys in molten salt atmosphere at 900 °C was studied by Kamal et al. (2008). Thermogravimetry method was used by authors to know the high-temperature hot corrosion conduct of bare and Cr_3C_2–NiCr-coated superalloys in liquefied salt atmosphere (Na_2SO_4–60 % V_2O_5) at a temperature 900 °C for hundred cycles. The corrosive species were examined to disclose their compositional topographies for revealing the corrosion mechanisms. It has been observed that resistance to hot corrosion is because of development of necessary topographies such as low porosity, even fine grains and the plane splat structures.

Kofstad (1988) has anticipated that in burning, the vanadium impurities are reacted to the upper-valence vanadium oxides (V_2O_4 and V_2O_5) which react with sodium salts to form low-melting-point sodium vanadates (lowest m.p 535 °C) such as $(Na_2O)_xV_2O_4(V_2O_5)_{12-x}$, $(Na_2O)_5(V_2O_4)_x(V_2O_5)_{12-x}$, $NaVO_3$, $Na_4V_2O_7$ and Na_3VO_4. Vanadates in the oxides of metal offend and destroy eutectic temperatures and m.p (melting point), he has established that sodium sulphate and sodium vanadates deposit as a slag on valves of diesel engines and they have melting point 400 °C. Hwang and Rapp (1989) studied the solubility of oxides in the mixed sodium sulphate–vanadate solution containing 30 mol% vanadates. They reported that the basicity of the melt, oxygen, partial pressure and proportion of V^{5+} and V^{4+} states of vanadate in the sulphate–vanadate solution decide the solubilities of oxides.

Kofstad (1988) revealed that the dissolution of oxides of metal is greater and they totally rely on the Na/V ratio. Dissolving capacity of Cr_2O_3 and Fe_2O_3 is the highest ($\approx$50 mol%) at Na:V ratios near to 5:12. For NiO, and the dissolving capacity is about 60 mol% at Na:V = 3:2 which declines to 55 mol% at Na:V = 5:12. The presence of acidic V_2O_5 reacts with extra basic oxides to form equivalent vanadates.

3.2.2 Liquefied Salt (Na_2SO_4–25 %K_2SO_4) Atmosphere-II

Shih et al. (1989) observed the performance of K_2SO_4 + Na_2SO_4-coated aluminium diffusion coatings on a pure iron substrate with aluminium concentrations of 28–51 % at the top most surface of the coatings at 600 °C in O_2-SO_2–SO_3 gases atmosphere. Entire coating undergone submelting point hot corrosion, but the corrosion rates are lesser than pure iron, and there is a development of a liquid phase.

Wang et al. (2004) tested the hot corrosion performance of arc ion plating NiCoCrAlY (SiB) coatings sprayed on Ni-based superalloys DZ 125 and DSM 11, in liquefied 75 Na_2SO_4 + 25K_2SO_4 (wt%) at 900 °C in air for 90 h. The coating developed hot corrosion resistance of DZ125 and DSM11 superalloys. The authors established that the additions of silicon and boron can improve oxidation resistance of the coating by the formation of an unbroken oxide scale in the beginning of corrosion stage and improve the adherence of the outer scale to the coating in the succeeding hot corrosion process.

Kamal et al. (2009) assessed the cyclic hot corrosion performance of Cr_3C_2–25 %NiCr coatings on Ni- and Fe-based superalloys. The cyclic hot corrosion experiments were analysed on without coated as well as coated superalloys in the presence of different molten salts. Weight gain method is used to create the mechanism of hot corrosion of without coated and coated superalloys. It was witnessed that Cr_3C_2–NiCr-coated superalloys displayed higher hot corrosion resistance than the without coated superalloys as a result of the formation of unbroken and shielding oxides of chromium, nickel and their spinel.

A nanocrystalline NiCrAlY coating was sprayed on a Ni-based superalloy by magnetron sputtering (Ren and Wang 2006). Sputtered coating was post-aluminising for better performance. The isothermal oxidation behaviour at 1000–1100 °C and hot corrosion behaviour in the presence of 75 wt% Na_2SO_4 + 25 wt% K_2SO_4/NaCl thin layer at 900 °C of the sputtered coating with and without aluminising have been investigated. They observed that the sputtered

NiCrAlY coating obsessed outstanding oxidation resistance at 1000 °C due to the presence of huge amount of Cr and maximum percentage of Al. But the coating lost its protection at 1100 °C because of the extreme consumption of Al in the coating. Aluminised NiCrAlY coating exhibited improved resistance to hot corrosion in comparison with sputtered coating due to the development of an uninterrupted and protective Al_2O_3 scale (Ren and Wang 2006).

Zheng et al. (2006) reported that an original gloss-Al_2O_3 composite coating with a thin layer of NiCoCrAlY bond coat was deposited on K38G superalloy. They showed that this combined coating performed much better oxidation resistance at high temperature between 900 and 1000 °C and hot corrosion resistance in melted sulphate salts (75 wt% Na_2SO_4 + 25 wt% K_2SO_4) at 900 °C, much better than solo NiCoCrAlY coating and uncoated K38G. The protection kinetics of this compound coating was different from those of old metallic coatings. Further, it was reported that it has not been oxidised longer period during tests and acted as an obstacle to successfully delaying the corrosive species from penetrating into substrate.

Guo et al. (2006) studied the corrosion mechanism of the substrates coated with 0.5 mg (Na_2SO_4 + K_2SO_4 20 wt% salt mixture)/cm^2 at 900 °C. For bare DSM 11 alloy, he has observed substantial weight gain due to rapid hot corrosion attack of the alloy during the first 20 h, followed by variation due to the struggle of oxide-scale formation and spallation. After 80 h, the weight gain diminishes abruptly due to a higher amount of oxide spallation.

3.2.3 Hot Corrosion of the Nickel-Based Alloys

Bornstein et al. (1975) have observed the consequence of sodium and vanadium on the enhanced oxidation of the Ni-based superalloys. Liquid vanadium pentoxide has been observed to be a brilliant flux and cool path for oxygen penetration. They observed between V_2O_5 and Ni-based superalloys; oxidation rate is rapid during the initial stages. They determined that the sulphidation attack can be reduced if melt is prohibited from increasing concentration of oxide ion in the early stages.

Weight gain describes concurrent vanadate- and sulphate-encouraged corrosion at 650–800 °C studied by Seiersten and Kofstad (1987). Mixtures of sodium vanadate and sodium sulphate initiated corrosion by intricate kinetics. Otero et al. (1987) investigated the hot corrosion behaviour of IN657 (46.5 Cr, 1.32 Nb, bal-Ni) at 635 °C in a liquefied salt atmosphere of 60:40 V_2O_5:Na_2SO_4 (mol%). They characterised the morphology and chemical compositions of the corrosion products and found that the occurrence of oxide and sulphur promotes the development of isolated portions with outward morphology. Penetrability of these portions eased the access of oxygen; hence, protective oxide scale was lost, vanadium and its oxidised mixture with change in morphology produce various compounds which increases the protective nature of the scale as described by the author.

Otero et al. (1990) again studied the hot corrosion performance of the same alloy IN657 in same molten salt atmosphere 60 %V_2O_5–40 %Na_2SO_4. They observed that for duration less than 100 h, the corrosion rate increased with temperature when the temperature was less than 727 °C. For temperatures greater than 727 °C, corrosion rate decreased. An increase in corrosion rate with temperature witnessed during the early stages of exposure was related to the higher volatility of the liquefied salt mixture. At temperatures greater than 727 °C, once the suitable fluidity was attained, the corrosion rate decreased due to the decrease in the oxygen solubility in the liquefied salt.

Otsuka and Rapp (1990) examined the influence of vanadate and chromate anions on hot corrosion of nickel by bonded Na_2SO_4 film in an SO_2–O_2 gas atmosphere at 900 °C. The results indicate that the standby of sulphidation may be due to the dissolution of solid Cr_2O_3 which partly seals/plugs the cracks and voids of protective oxide film. Further, they found that vanadate anions enriched the inception of the hot corrosion and sulphidation; this may be via fast degradation of protective oxide layer at cracks and voids.

The oxidation and hot corrosion studies of Ni-based superalloys in Na_2SO_4-60 %V_2O_5 environment at 700 °C were carried out by Lambert et al. (1991) to investigate the effects of Si addition. On the outer surface of the alloy, they found a thin layer of NiO whereas on the Si-enriched alloy, a thin $A1_2O_3$ scale formed. They attributed that distinctly increase in oxidation rate of Ni-based superalloys due to highly corrosive condensed vanadates and sodium.

According to them, the continuous regeneration of protective oxide obstruction was significantly affected by the corrosive resistant coating, particularly in the Si-enriched alloy. They identified Ni, Cr, Al and Si complex oxides in the inner oxide layer.

Gurrappa (1999) studied the hot corrosion behaviour of Ni-based superalloy in sodium sulphate and mixture of sodium sulphate + sodium chloride. He has witnessed that the superalloy got rigorous corrosion attack in just 4 h, whereas it is entirely corroded in 70 h when examined in 90 %Na_2SO_4 + 10 %NaCl. When the same alloy studied in 90 %Na_2SO_4 + 5 %NaCl + 5 %V_2O_5 atmosphere at 900 °C, in just 2 h superalloy lost its entire strength.

Gitanjaly and Prakash (1999) analysed the hot corrosion performance of some Ni-, Fe- and Co-based superalloys in an atmosphere of Na_2SO_4 + 60 %V_2O_5 at 900 °C. In general, the author observed significant corrosion degradation in all the superalloys. However, the Ni-based superalloy Sn 75 exhibited lowermost rate of corrosion related to Superco 605. The presence of $Ni(VO_3)_2$ in the coating represented as a diffusion barricade for the oxidising corrosive species which improves corrosion resistance of Ni-based superalloy.

Tzvetkoff and Gencheva (2003) reviewed the kinetics on the development of corrosion films on Ni and Ni-based alloys in molten salts containing oxyanions. They reported that catastrophic hot corrosion failure due to rapidly induced fluxing of the protective oxide scale in the presence of acidic oxides such as those of V and Mo.

The chromate oxide layers were identified as useful for the repassivation of the surfaces which lost due to molten salt fluxing. Further, they reported that the molten sulphate mixtures are violent towards Ni-based superalloys. In such atmospheres, they additionally detected the presence of sulphides at oxide/metal boundary which do not suggest probable protection except for a positive role of MoS_2 developed on Ni-based alloys having substantial quantity of Mo.

Author has investigated the hot corrosion behaviour of NiCoCrA1YTa coatings sprayed on the superalloys (specifically Sn 75, Sn 718 and Sf 800H) exposed to Na_2SO_4–25 %K_2SO_4. Better protection attributed to the formation of thick and adherent of Cr and Al oxide scale on coating. In the subscale region, these oxides formed across the periphery of Ni-rich splat borders performed as diffusion obstacles to the internal dissemination of corrosive species which moderately minimise the mass gain. Graphics of projected oxidation mechanism of the detonation-gun-coated NiCoCrAlYTa on Sf 800H at 900 °C in Na_2SO_4–25 %K_2 SO_4 after 100 cycles are shown in Fig. 6.

Singh et al. (2005) studied hot corrosion behaviour of a nickel-base superalloy in molten salt atmosphere at 900 °C under repeated settings for 50 cycles of one hour each. They used thermogravimetric technique to estimate the mechanism of corrosion. They revealed that superalloy Superni 601 revealed that extreme spalling of oxide scale and the mass gain, including the spalled scale, was huge during the hot corrosion studies in the given rigorous atmosphere. They reported non-stop increase in the mass of the superalloys, but the rate of increase was more during the early period of exposure. They revealed that $NaVO_3$ formed due to the reaction of Na_2SO_4–60 %V_2O_5 acts as a reagent and assists as an oxygen transporter to the metal. The chromium has great attraction for oxygen to form Cr_2O_3, which rapidly increase mass gain in the initial stages of hot corrosion.

Prakash et al. (2005) witnessed the hot corrosion performance of another Ni-based superalloy under the same conditions and at same temperature. They reported that the superalloy suffered a catastrophic hot corrosion attack which leads

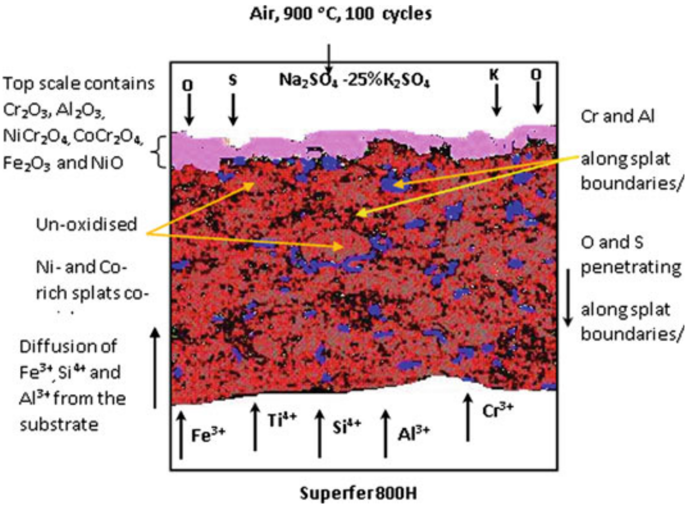

Fig. 6 Schematic of the proposed oxidation mechanism of the NiCoCrAlYTa-coated superalloy Superfer 800H at 900 °C in Na_2SO_4–25 %K_2 SO_4 after 100 cycles

to extreme spalling and sputtering of the scale. They concluded this behaviour with the existence of Mo in the alloy, as oxides of Mo cause an alloy-induced acidic fluxing. Ravindra et al. (2007) also reported the hot corrosion and oxidation performance of a directionally solidified Ni-based superalloy.

3.2.4 Hot Corrosion of Iron-Based Mixtures

Fairman (1962) reported severe corrosion of some metal pieces in an ash blend (V_2O_5 + 10 % Na_2SO_4) atmosphere in air. Greatest corrosion attack was established where the percentage of O_2 and V_2O_5 was higher, proposing the movement of oxygen atoms or ions on the metal surface: $2V_2O_5 \rightarrow 2V_2O_4 + 2O\downarrow$. He reported that the enhanced oxidation is a diffusion controlled process of the absorption of flaws into the oxide scale. He further suggested that the kinetic of enhanced attack could be more reasonably clarified by the catalytic action of V_2O_5 operating with the growth in the fault concentration of the scale.

Kerby and Wilson (1972) revealed that the fluxing of protective oxide layers rise the corrosion speed of metals by liquid vanadates present on the alloy surface and acted as a source of oxide ion for the corrosion reaction. The electrical conductivity enhanced with increase in temperature and with reducing oxygen pressure.

Valdes et al. (1973) studied AISI 446 stainless steel under V_2O_5 and $Na_2O.6V_2O_5$ atmosphere in the range 700–900 °C in air and established the presence of Cr_2O_3 scale with little oxides of vanadium which performed as a reasonable obstacle to corrosion. Above 850 °C in V_2O_5, a breakaway corrosion reaction occurred. No Cr_2O_3 barricade was present, but there was an uninterrupted oxide scale that consisting of Cr_2O_3, Fe_2O_3 and V_2O_5 at the metal/oxide interface from which a region of crystals grew. They suggested that the addition of Na_2O to V_2O_5 enhanced the oxide ion (O^{2-}) in the melt and made it extra destructive to acidic oxides such as Cr_2O_3.

Shi et al. (1992) studied the effect of K_2SO_4 added to a Na_2SO_4 on the low-temperature hot corrosion performance of iron aluminium alloys. He concluded that K_2SO_4 preservative increased the low-temperature hot corrosion of Fe–A1 alloys affected by Na_2SO_4 deposit in the environment containing O_2, SO_2 and SO_3, but the kinetics of corrosion remained unaffected. In the initial period, degradation/precipitation of Fe_2O_3 proceeded at a substantial rate; at a longer time, growth of a compact iron oxide conquered the enhanced hot corrosion caused by K_2SO_4 stabiliser was not ascribed to the formation of intricate sulphates. The equilibrium phase diagram for changing composition of Na_2SO_4 and K_2SO_4 is shown in Fig. 7.

Tiwari and Prakash (1996, 1997) and Tiwari (1997) have stated hot corrosion studies on high-temperature-resistant superalloys in range of 700–900 °C in the atmospheres consisting of Na_2SO_4, Na_2SO_4–15 %V_2O_5 and Na_2SO_4–60 %V_2O_5. They detected very high rates of corrosion in the atmosphere having Na_2SO_4–60 % V_2O_5. Due to the low melting point of this compound (550 °C), the corrosive environment of this mixture is huge. Tiwari and Prakash (1997) additionally

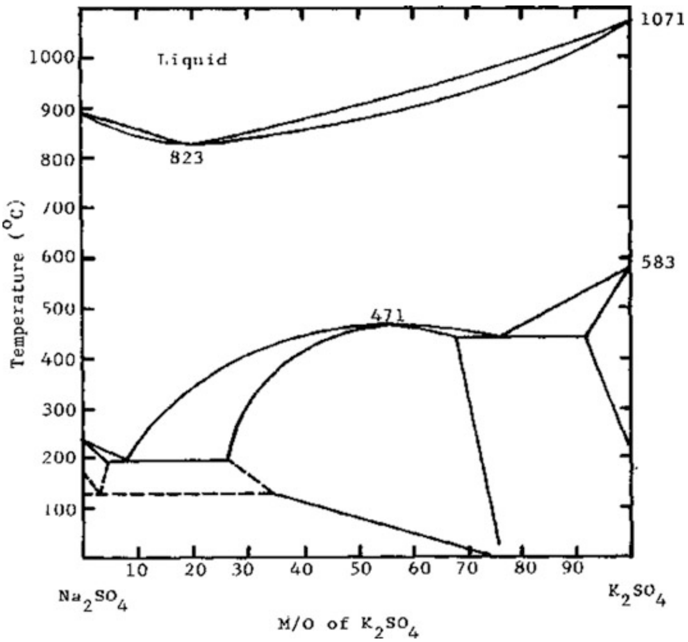

Fig. 7 Phase diagram of Na_2SO_4 and K_2SO_4 system (Shi et al. 1992)

exposed that in Na_2SO_4–60 %V_2O_5 molten salt, precipitation found with the presence of cracks in the defensive scale due to degradation by the molten salt for Sf 800H and Superco 605. Greater precipitation was observed due to the presence of tungsten in the form of Na_2WO_4–WO_3 mixture. Tewari (Tiwari 1997) determined that Co-based alloy has lower corrosion protection than Ni-based superalloy in Na_2SO_4–60 %V_2O_5 atmosphere at 900 °C.

Kamachi Mudali et al. (2004) reported that the stainless steels are susceptible to corrosion in the presence of violent corrosive atmosphere and also in aqueous, high temperature, axial or compressive stress and other service constraints. Under such situations, proper care is to be taken by preparing exclusively diverse surface morphology by forming corrosion-resistant thermal spray coatings.

Singh et al. (2005) investigated the hot corrosion performance of an iron-based superalloy in melt (Na_2SO_4–60 %V_2–O_5) atmosphere at 900 °C under cyclic situations for 50 h and found that the superalloy underwent severe exfoliation and crackling and the mass gain was massive during the course of study.

Sidhu et al. (2006) reported that iron-base superalloy Superfer 800H underwent intense spalling, sizzling of scale along with cracking sound during cooling and detaching of the protective oxide scale in an violent atmosphere of Na_2SO_4–60 % V_2O_5 at 900 °C. During the cyclic study for 50 h, the mass gained by the superalloy was enormous. It was found that the weight increased uninterruptedly, during the early period of exposure. The rate of increase in weight gain was ascribed mainly due to the formation of $NaVO_3$ complex compound. Slower increase in mass gain after early mass gain was due to the instantaneous growth and degradation of oxide scale in the molten salt due to the following reaction. This Na_2CrO_4 vaporised as a gas

$$Cr_2O_3 + 4NaVO_3 + 3/2O_2 \rightarrow 2Na_2CrO_4 + 2V_2O_5. \tag{2.8}$$

Sidhu et al. (2006a, b) reported that the behaviour of HVOF sprayed Cr_3C_2–NiCr coatings on an iron-based superalloy in Na_2SO_4–60 %V_2O_5 atmosphere at 900 °C in repeated conditions. The thermogravimetric measurements were used to study the kinetics of corrosion. The coating has effectively imparted resistance to molten salt-induced hot corrosion. The Cr_3C_2–NiCr-coated alloys offer corrosion resistance with the development of phases such as Cr_2O_3, NiO and $NiCr_2O_4$ in the protective oxide scales.

4 Some Studies on Power Plant Environments

Different researchers informed that accumulation/reduction of low-melting-point molten salts (present in the gases) on the thermal power plant tubes used for superheaters and reheaters in coal-fired boilers is an original reason for the massive damage of tube materials. At the operating temperatures of boiler tubes molten salts consisting sulphates of sodium and potassium, they simply liquefy and cause rigorous hot corrosion of boiler tubes (Rapp and Mehl 2000; Nelson et al. 1959; Backman et al. 1987; Salmenoja et al. 1996).

Boilers and other steam power plant equipment are subjected to a wide variety of failures involving one or more of several mechanisms. Overheating is described as main root cause damage in steam generators. A survey compiled by one laboratory over a period of 144 months, covering 413 inquiries, listed excess heating damage causes 201 failures or 48.7 % of those examined. Defective or improper material has been cited as the cause of most of the remaining failures (13.3 %). Although “defective material” is often blamed for a failure, this survey indicates that statistically it is one of the least likely causes of failure in power plant equipment (Handbook 1975).

Moujahid (1987) observed severe ash corrosion, mechanical deformation and cracks on the cast iron chains of moving grate used to air burning of coal. Liquid coal ash at 1300 °C is strongly acidic and dissolves spinel layers which formed on the chains at elevated temperature. The fused ash embeds coal particles and also reduces the thermal efficiency of the equipment. Drastic enhancement in ash corrosion rate has been attributed to the mechanical damages. Kamal et al. (2010) incorporated rare earth oxide (CeO_2) in NiCrAlY coating and investigated hot corrosion resistance. The coatings revealed distinctive splat spherical dendritic phases. Cerium oxide dispersed along the boundaries of splats, while Al lines scattered non-uniformly. On the coated superalloys a thick oxide film observed which represents shielding phases such as NiO, Cr_2O_3, Al_2O_3, $NiCr_2O_4$ and Ni Al_2O_4 formed on the surface which offers resistance to hot corrosion, some of the oxides of iron and silicon moved to the top surface during initial period of exposure. Graphical drawing showing projected hot corrosion kinetics of the NiCrAlY + 0.4 wt% CeO_2-coated superalloy Superfer 800H at 900 °C in Na_2SO_4 + 60 % V_2O_5 after 100 cycles is shown in Fig. 8 (Kamal et al. 2010).

Iyer et al. (1987) witnessed the hot corrosion behaviour of Nimonic 80A under tension using combustion gases environment at 600–700 °C and reported the presence of NiO, Cr_2O_3, $Ni(VO_3)_2$ and $NiO.Cr_2O_3$ on the surface of the corroded alloy. Accelerated oxidation was observed, and the scale was reported to be spongy. They observed that the lowest melting liquid was formed even at 550 °C. They suggested that the presence of stresses enhanced the damage due to spalling, allowing fresh surface to be exposed to hot corrosion. They proposed that as vanadium content increases, some of the vanadium participates as vanadates and, therefore, increase in vanadium above certain level is not so violent. This critical level was found to be around 20 ppm vanadium.

Prakash et al. (2001) observed failure of boiler tube in the pulverised coal-fired boiler in India, a case study conducted for the period of one year. They observed total 89 failures, out of which 50 failures were caused to the hot corrosion and erosion by fly ash lumps. Under detailed investigation of five (5) samples of failed boiler tubes, they reported major cause of tube failures is overheating.

Coal is an abandoned cheep fuel available with its low price related to its worldwide obtainability and due to the forthcoming deficiency of other fossil fuel assets such as heavy oil and natural gas. But burning of coal generates very corrosive environment near the superheater boiler tubes. Hot corrosion of boiler tubes

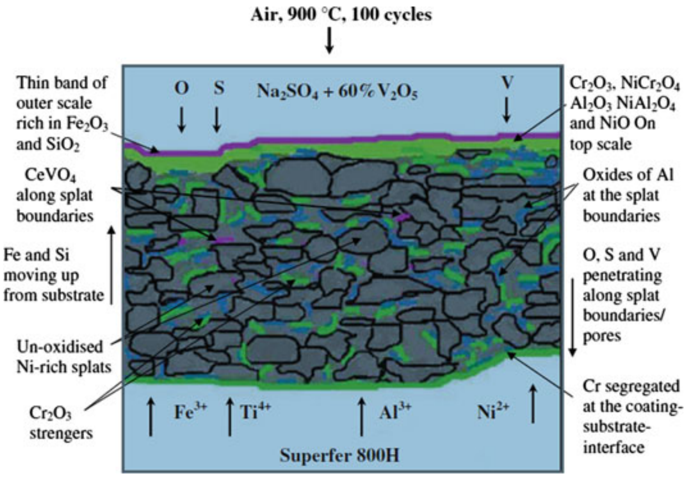

Fig. 8 Graphical drawing showing projected hot corrosion kinetics of the NiCrAlY + 0.4 wt% CeO_2-coated superalloy Superfer 800H at 900 °C in Na_2SO_4 + 60 % V_2O_5 after 100 cycles (Kamal et al. 2010)

is considered as a more demanding aspect, which results in tube wall thinning and catastrophic failure. Efforts have been made to decrease the maintenance costs of these tubes that have increased interest in protecting them with protective thermal spray coatings (Sidhu et al. 2006).

Kamal et al. (2009) and Sidhu et al. (2006c, d, e, f) carried out various tests in the laboratories and in the actual coal-fired boiler environments in order to estimate the hot corrosion damage, all the coatings deposited on Ni-based superalloy imparted better hot corrosion resistance than the uncoated one. The Stellite-6-coated superalloy did well than the NiCrBSi-coated alloy in the given environment.

5 Preventive Measures Against Hot Corrosion

The corrosion control in highly aggressive applications requires careful selection of materials. Nickel-based superalloys have better physical properties and superior corrosion resistance at higher temperatures and are used as base materials for hot section components in turbines. However, the hot corrosion is unavoidable when used at higher temperatures for longer duration of time in an extreme environment (Goebel et al. 1973).

Heath et al. (1997) proposed a number of countermeasures corresponding to the variety of corrosive environments including the following:

- Proper selection of alloy,
- Optimum design of components,
- Use of chemical additives to neutralise the corrosive components in the flue gases,
- Shielding the substrate and
- Protective coatings.

The important factors that influence hot corrosion are as follows: (a) alloy composition, (b) alloy fabrication condition, (c) deposit composition, (d) amount of deposit on superalloy, (e) gas composition and velocity, (f) temperature, (g) temperature cycles and (h) erosion (Gurrappa 1999). Eliaz et al. (2002) also, in their review of hot corrosion in gas turbine components, suggested several approaches to control the hot corrosion, which include appropriate selection of physically high-strength alloys, thermal spray coatings on hot section components, regular cleaning of hot section parts, air filtering and governing of both fuel hygiene and composition.

Hot corrosion can prevent by thermal spray coating the substrate alloy with a preventive film. This is the favoured method, even when comparatively less hot corrosion-resistant substrate alloys are used (Eliaz et al. 2002). For sufficient corrosion protection of an alloy in the given destructive atmosphere, compatible techniques and proper selection of materials are more important. Adding organic inhibitors such as pyridines, pyrimidines, quinolines is enough to diminish hot corrosion of alloys in many corrosive atmosphere, although inhibitors have partial success due to solubility and/or thermal instability at high-temperature, intense salt solutions (Priyantha et al. 2003).

6 Role of Thermal Spray Coatings

The coatings at high temperature develop a shielding oxide film on the metal surface to limit loss of metal by oxidation. Generally, these protective oxides (e.g. $A1_2O_3$, Cr_2O_3 and SiO_2) diminish the penetration of gaseous or liquid corrosive mixture towards the substrate alloy and equally prevent substrate elements diffusion towards the external surface where they could react with the coated elements. Moreover, there should be minimum inter-diffusion phenomenon between coating and substrates as far as the quality of the coated constituent are concerned (Mevrel 1989).

Premature failure of the thermal power plant components regularly arises due to the rigorous reactions between the substrate alloy and the violent combustion atmosphere. Degradation mechanism at high temperature by distinctive molten salt film should be clearly understood, so as to reduce the tube material failure by emerging more defensive structural alloys and coatings (Li et al. 2005).

To enhance the life or enrich the performance of alloys, thermal spray coatings are contributing substantial part in today's aero- and industrial turbine engines; about 75 % of all the components in jet engines are coated (Zheng et al. 2006; Gurrappa 2000). MCrAlY-type metallic coatings regularly used in the hot segment of turbine engines, which is precisely designed and developed to meet the violent environmental operating conditions (Guo et al. 2006).

6.1 *Advantages of Thermal Spray Coatings*

Nearly all types of superalloys and boiler steels with enhanced strength, the requirements of defensive coatings demand have recently increased, because of high-temperature corrosion difficulties become major problems for these superalloys with growing working temperatures of current heat engines (Yoshiba 1993). Further, Porcayo-Calderon et al. (1998) have reported the use of protective coatings for the superheater/reheater parts of boiler, where the alloys rigorously undergo fireside hot corrosion. To prolong the life of alloys to work at the higher end of their performance abilities, only coatings offer a way, by permitting the mechanical properties of the substrate materials to be maintained while defending them against wear or corrosion (Sidky and Hocking 1999).

Unfortunately, it is well known in the literature that it is not always possible to develop an alloy that will be resistant to hot corrosion as well as possess good high-temperature strength by the addition of alloying elements. Some alloying elements may help to improve the mechanical properties, while others may improve the hot corrosion resistance, but generally both properties are not improved simultaneously. Tremendous increase in mechanical properties can offer with the presence of tungsten, vanadium and molybdenum while their existence makes the alloy highly prone to hot corrosion (Gurrappa 1999).

The need for better-quality performance, higher operating temperature, prolonged component life and higher efficiency power plant places high demands on the construction materials used in a high-temperature plant. Consequently, a large number of components worked at high temperature are coated or surface treated (Nicholls 2000). According to Taylor and Evans (2001), for fossil power plants few previous efforts made on the thermal sprayed defensive coatings, however, thermal spray process is comprehensively used for gas turbine engine components.

Furthermore, improvement in the conventional steam-raising plants, substitute power supply systems, for example, combined with cycle plants, wherein a gas and steam turbine, are coupled, suggesting greater thermal efficiencies, as the inlet temperatures of gas turbine are 1200 °C and above (Nickel et al. 2002). According to them, components operated at high temperatures prone to increase oxidation rates; hence, defensive coatings with higher temperature abilities are necessary. Therefore, an alternative is to go for protective coatings for hot corrosion resistance; it is essential to cultivate appropriate coatings to enhance the operational life of the components. Although corrosion problems cannot be completely eradicated, nevertheless, 25–30 % of corrosion associated costs can be saved with the use of best corrosion anticipatory and control policies (Priyantha et al. 2003; Koch et al. 2002).

6.2 Requirement of High-Temperature Coatings

Preventive surface preparations are extensively used at low temperature, but largely limited use of these at elevated temperature applications. A huge ultimatum exists to grow and apply these coating for high-temperature applications (Stroosnijder et al. 1994). Consequently, all components working at high temperature are coated (Nicholls 2000). Superalloys have been developed for high-temperature applications; however, protective coatings are applied to improve their lifespan for use in corrosive atmospheres as they are not able to meet the requirement of high-temperature asset and high-temperature corrosion protection concurrently (Liu et al. 2001).

6.3 Coating Deposition Techniques

Nicoll (1984) reported that from manufacture point of view, chemical vapour deposition (CVD), physical vapour deposition (PVD) and thermal spray techniques (metal spraying) are used extensively. Since CVD process is a non-line-of-site technique, appropriate covering and tool requirements is the foremost design deliberations and it is expensive. Additional limitation of the CVD process is the insertion of package particles in the coating which can lead to coating damage.

Variety of coating deposition methods are available in the market, and selecting the best coating methods depends on the useful requirements, flexibility of the coating material to the selected coating method, field of application required (size, shape of coating powder and metallurgy of the substrate), and accessibility of the powder and cost of the coating equipment such as HVOF, Detonation-gun and Plasma spray.

6.3.1 Thermal Spray Techniques

In the year nineteen hundreds, a young Swiss inventor named Dr. Max Schoop designed thermal spray method, after watching his son playing with his toy. Dr. Schoop observed that the hot lead particles were projected out of the cannon, held nearly any surface, which gave him the idea that if the molten metal projected in a spray-like manner, then a surface will be built up with that material. A variety of engineering problems have been solved using thermal spraying applications. Thermal spray technique is used across many engineering processes, from the locomotive to the space craft industry (Nicoll 1984). Thermal spraying is the most resourceful method offered for the application of coating materials used to protect parts from abrasive, adhesive, erosive wear and erosion corrosion (Marceau and Adjorlolo 1995).

Thermal spraying is a generic coating technique whereby droplets of molten or partially molten material are generated and projected at a surface to form a coating. The droplets undergo little interaction with the substrate, merely adhering to the roughened surface through physical means to form an “overlay” coating. Variety of techniques has been designed for this process, varying in the manner in which they heat the material, the operating temperature and the velocity to which the droplets are accelerated. Through the range of operating conditions generated, any material that does not undergo sublimation or degradation upon heating can be applied as a coating.

Materials ranging from polymers to metals, cermets and ceramics are regularly sprayed. In the generalised thermal spray process, the coating material in rod, wire or powder form is fed into a high-temperature heat source, where it is heated close to, or in excess of, and its melting temperature. A high-velocity accelerating gas or combustion gas stream accelerates the droplets of material to the substrate, where they impact and spread across the surface to form a “splat” (Matthews 2004). The oxidation time during thermal spray coating is short typically less than 0.01 s and can occur in either the solid or molten state. The oxidation of coatings is not always harmful, it is equally important to control and understand the different aspects of oxidation of coatings; therefore, it is important to find an optimum level for oxidation of coatings (Herman 1988; Korpiola and Vuoristo 1996; Nerz et al. 1992). Commonly, any material, which does not decay, boil, transfer or dissociate on heating, can be thermally sprayed. Subsequently, a wide range of metallic and non-metallic materials (such as metals, alloys, ceramics, cermets and polymers) can be easily deposited by thermal spraying. Metals, carbides and cermets are the more extensively used as a coating material; also polymer deposition has been investigated (Kawase and Nakano 1996). High-temperature corrosion protection can be obtained by the deposition of metallic coating on the substrate metal with the use of thermal spray process and are listed below, summarised by Heath et al. (1997).

- Flame spraying with a powder or wire,
- Electric arc wire spraying,
- Plasma spraying,
- Spray and fuse,
- HVOF spraying and
- Detonation-Gun
  The technology continued, but expanded in the 1970s due to development of the thermal plasmas and the increasing demand of high-temperature and wear-resistant materials and coating systems (Knotek 2001).

Table 1 shows some of the significant parameters linked with these thermal spray techniques (Bhushan and Gupta 1991; Sobolev et al. 2004; Wagner et al. 1984). Speed of powder particles, flame temperature and spray environment are the main constraints which differentiate the various spraying methods. Porosity, bond strength and oxide content of the coating are the properties depended on the coating process. Also, Kuroda et al. (2008) show the grouping of numerous thermal spray processes in terms of particle temperature and velocity. Similarly, Gledhill et al. (1999) proposed the schematic diagram showing unmelted particles, splats, voids and in coming particles with unmelted.

6.4 *Nanostructured Coatings*

Nanostructured coating (Khana and Jha 1998) is the collection of crystalline/amorphous blends. It has newly attracted necessary research and engineering applications, because of the producing, a surface safety film with exceptional physiochemical properties that are frequently not achieved in the bulk coating. Nanostructured coating is a new class of manufacturing materials with superior properties and physical length between 1 and 100 nm. Broad range of engineering applications that needed resistance to abrasive wear, erosion, hot corrosion, cracking and spallation, better properties can be incorporated with nanostructured ceramic coatings produced by plasma-sprayed processes are being developed recently.

Bansal et al. (2003) compared commercial coarse-grained and the nano-Al_2O_3–13 wt% TiO_2 ceramic coatings by plasma spray on steel substrate. These nanocoatings enhanced resistance to wear and had a good bond strength which is

Table 1 Comparison of characteristics for various thermal spray processes (Bhushan and Gupta 1991; Sobolev et al. 2004; Wagner et al. 1984; Stokes and Looney 2001; Hao et al. 2005)

Deposition technique	Heat source	Material feed type	Spray gun temp. (°C)	Coating materials	Porosity level % volume
Electric arc	Arc between electrodes	Wire	6000	Ductile materials	8–15
Plasma arc spraying	Plasma arc	Powder	16,000	Metallic, ceramic, plastic and compounds	2–5
Low-pressure plasma spraying	Plasma arc	Powder	16,000	Metallic, ceramic, plastic and compounds	<5
Spray and fuse	–	Powder	–	Fusible metals	<0.5
Flame spraying	Oxyacetylene/oxy-hydrogen	Powder	3000	Metallic and ceramics	10–20
Detonation-gun spraying	Oxygen/acetylene/nitrogen gas detonation	Powder	4500	Metallic, ceramic, plastic and compounds	0.1–1
High-velocity oxy-fuel (HVOF)	Oxy-propylene/hydrogen/propane/LPG	Powder/ire	3000	Metallic and ceramic	0.1–2

twice higher than that of coarse coatings, representing “nano” coatings scientifically most usefully. Shaw et al. (2000) observed the reliance of microstructure and properties of nanostructure Al_2O_3–13 wt% TiO_2 coating by wear test. It has been observed that nanocoating performed better wear resistance than the coarse coatings. Ding et al. (2003) have conducted the wear resistance test for nanostructured zirconia coatings and coarse-grained zirconia coating by plasma-spray, coarse-grained coating shows much lesser wear resistance than their nanostructured zirconia coating. The greater properties of nanostructured coatings include improved microhardness and microstructure phases responsible for higher wear resistance.

Leblanc (2003) observed from commercial coarse-grained and nanostructured powders, he has assessed sliding wear, abrasion wear and microstructural properties of Al_2O_3–13TiO_2, Cr_2O_3–5SiO_2–3TiO_2 and TiO_2. Efficiency and features of VPS-deposited coatings are normally higher or equal to those of APS-deposited coatings. Thermal spray process for nanostructured powder coating is established to be more delicate, as compared to commercial coarse-grained powders. VPS delivers a better atmosphere for applying nanostructured coatings, as related to APS retained nanostructure in the applied coating shows the greater properties. Plasma spray produced reconstituted nanostructured alumina–titania coatings using improved processes with optimised plasma spray parameter (Jordan et al. 2001).

Kim et al. (2006) have magnificently obtained WC-Co wear-resistant nanostructured coatings by thermal spray process and the results showing substantial resistance wear when it is compared with conventional counterparts. Well-established nanostructured feedstock powder coating effectively resolved microstructural non-similarity of conventional Cr_2O_3-based solid lubricant coatings. The deposition of commercial coarse-grained and nanostructured zirconia coatings by atmospheric plasma spraying was tested for thermal shock resistance of as-sprayed coating by the water quenching method (Liang and Ding 2005). The outcomes exhibited that the nanostructured as-sprayed coating exhibited much improved thermal shock resistance than the commercial coarse-grained coating. This is due to the modification in microstructure and microstructural changes happening during thermal shock cycling. During the thermal shock cycle, the development of vertical cracks, inter-granular fracture and tetragonal monoclinic transformation on the coating surface contributed to the improved thermal shock resistance of the nanostructured zirconia coatings.

Soltani et al. (2003) have effectively deposited Y_2O_3–PSZ-nanostructured coatings. The results of wear test revealed that the nanostructured coating had a lower coefficient of friction and higher wear resistance under discontinuous testing conditions in comparison with commercial coarse-grained coatings. Lin et al. (2004) have examined that the effects of temperature between 600 °C and room temperature on the tribological properties of atmosphere plasma-sprayed nanostructured and commercial coarse-grained Al_2O_3–3 wt% TiO_2 coatings against silicon nitride ball were tested. The results revealed that wear resistance of the nanostructured coating was found better at high temperature as compared to their conventional counterpart.

7 Conclusions

1. Failure of different parts of gas turbine hot sections for ships, aircrafts, boilers, industrial waste incinerators is attributed because of high-temperature hot corrosion. For high-temperature applications, superalloys were developed, but they failed in meeting both requirements such as desired strength at high temperature and hot corrosion resistance at high temperature concurrently.
2. Thermal sprayed coatings seem to be an alternative and are extensively observed with respect to hot corrosion resistance. Hot corrosion is a serious problem and cannot be totally inhibited, but it can be identified at an initial stage to avoid disastrous failure.
3. An extensive research undertaken to assess the feasibility of various coatings in natural air environments, but additional research methods are required to test different types and combination of coating powders in more destructive corrosive atmospheres, either replicated in the laboratory or in real practical conditions.
4. While extensive perception has been collected on kinetics of hot corrosion, whereas, it has not been completely understood the reaction mechanism and further extensive analysis are required, further life of the coating has to be forecasted against hot corrosion behaviour in actual industrial environmental situations as well as by mathematical modelling which simulate the actual environment.
5. Investigators extensively tested several factors of different thermal spraying process. More ever, additional examinations need to optimise numerous coating process parameters, with distinct importance to estimate their performance of coating on hot corrosion behaviour.

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