

AN OVERVIEW OF Na_2SO_4 AND/OR V_2O_5 INDUCED HOT CORROSION OF Fe- AND Ni-BASED SUPERALLOYS

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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 superalloys 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. In this paper the hot corrosion phenomenon has been described in detail with a special reference to Fe- and Ni-based superalloys with the help of a survey of the available literature related to the hot corrosion of the superalloys, in the environments constituting mainly of Na_2SO_4 and/or V_2O_5 .

1. INTRODUCTION

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 nonprotective 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]).

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 com-

bustion 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]). Apart

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from Na_2SO_4 , V_2O_5 is a commonly-found high-temperature corrosion promotor in these applications. Due to high cost of removing these impurities, the use of these low grade fuels is usually justified. Sodium vanadyl vanadate ($\text{Na}_2\text{O}\cdot\text{V}_2\text{O}_4\cdot 5\text{V}_2\text{O}_5$), which melts at the relatively low temperature of 550 °C, is found to be the most common salt deposit on boiler superheaters, (Barbooti *et al.*, [5]). Similarly, the predominant species in the salt deposits forming on gas turbine surfaces are also expected to be Na_2SO_4 , V_2O_5 , and $\text{Na}_2\text{V}_2\text{O}_6$ (Luthra and Spacil, [6]).

Due to the depletion of high-grade fuels and for economic reasons, use of residual fuel oil in these energy generation systems is well known. Residual fuel oil contains sodium, vanadium, and sulphur as impurities, as well as salt (NaCl) contamination from entrained brine. Sodium and sulphur form Na_2SO_4 (melting point 884 °C) by reactions in the combustion system. During combustion of the fuel, vanadium reacts with oxygen to form an oxide V_2O_5 (melting point 670 °C). Thus V_2O_5 is a liquid at gas turbine operating temperatures. These compounds (known as ash) deposit on the surface of the materials and induce accelerated oxidation (hot corrosion) in energy generation systems. When considering coal-gasification processes, hot corrosion is expected to be a problem because the gas environment generally may contain sulphur and chloride compounds and low oxygen activities, and the feedstock also contains substantial amount of salts, (Natesan, [7]).

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]).

Power plants are one of the major industries suffering from the severe corrosion problems resulting in the substantial losses. For instance, the steam temperature of boilers is limited by corrosion and creep resistance of boiler components, which affects the thermal efficiency of the boilers. Consequently, the thermal efficiency is reduced and hence the rate of electricity production is reduced (Uusitalo *et al.*, [9]). According to a survey [10] conducted over a period of 12 years, encompassing 413 investigations, overheating was listed as the

cause of 201 failures or 48.7% of those investigated. Fatigue and corrosion fatigue were listed as the next most common causes of failure accounting for a total of 89 failures or 21.5%. Corrosion, stress corrosion and hydrogen embrittlement caused a total of 68 failures or 16.5%. In another case study of a coal fired boiler of a power plant in north western region of India, Prakash *et al.*, [11], reported that out of 89 failures occurring in one year, 50 failures were found to be due to hot corrosion and erosion by ash.

A superalloy is an alloy developed for elevated-temperature application, usually based on group VIIIA elements, where relatively severe mechanical stress is encountered, and where high surface stability is frequently required. Iron and nickel base superalloys are the commercial alloys commonly used for the high temperature applications e.g. manufacture of components used in aggressive environments of gas turbines, steam boilers, *etc.* The superior mechanical performance and good corrosion resistance of the superalloys, and especially of the nickel-base superalloys at high temperature, make them useful materials for components that are subjected to high temperature service environments (such as blades or vanes) in industrial gas turbines and other energy conversion systems. However, the presence of combustion gases constitutes an extreme environment and hot corrosion is inevitable when alloys are used at high temperatures for long periods of time, (Goebel *et al.*, [12]).

2. 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 °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 Ni- and 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.

2.1. 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]).

2.2. Low temperature (Type II) hot corrosion (LTHC)

Low temperature (Type II) hot corrosion (LTHC) occurs well below the melting point of pure Na_2SO_4 . 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 sulphide 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.

3. 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 sulphide 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]).

Numerous factors affect the time at which the hot corrosion process moves from the initiation stage into the propagation stage as shown in Fig. 1. These factors also play the dominant role in determining the type of reaction product that is formed in the propagation stage. This fact is responsible for a variety of hot corrosion processes that have been observed when superalloys are exposed to different environments (Pettit and Meier, [15]).

The propagation stage of the hot corrosion sequence is the stage for which the superalloy must be removed from service since this stage always has much larger corrosion rates than for the same superalloy in the initiation stage (Pettit and Meier, [15] and Pettit and Giggins, [16]). The pertinent mechanism behind this mode of hot corrosion has been summarised 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.

As per the views of Yoshida, [17], Ni-based superalloys are well known to be susceptible to hot

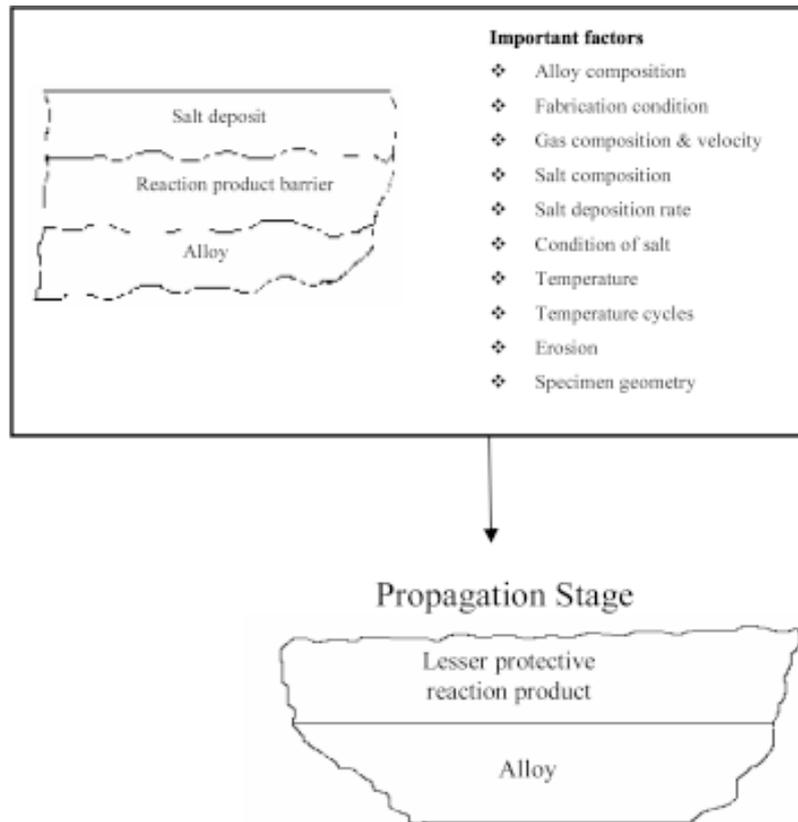


Fig. 1. Schematic diagram illustrating the conditions that develop during the initiation and the propagation of hot corrosion attack and to identify the factors that determine the time at which the transition from the initiation to the propagation stage occurs (see [15]).

corrosion associated with combined reaction processes such as sulphidation-oxidation and occasionally together with chlorination. In practice, it is a serious problem for such alloy systems when used for hot section components of various heat engines such as gas turbines subjected to corrosion-induced strength degradation.

4. MECHANISMS OF THE HOT CORROSION

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.

Goebel and Pettit [22] also interpreted the hot corrosion of pure nickel in terms of basic dissolution and reprecipitation of NiO in the fused salt film. Goebel *et al.* [12] extended this mechanism to include acidic fluxing and oxide re-precipitation to account for the catastrophic oxidation caused by pure Na_2SO_4 for alloys containing strong acid components such as vanadium or molybdenum. The next important contribution in the fluxing model was made by Rapp and Goto [23]), who proposed that if the gradient in solubility of the protective oxide with distance into the salt layer becomes negative at the oxide/salt interface, accelerated attack could be sustained. Sodium vanadyl vanadate ($\text{Na}_2\text{O}\cdot\text{V}_2\text{O}_4\cdot 5\text{V}_2\text{O}_5$), which melts at a relatively low temperature 550°C is found to be the most common salt deposit on boiler superheaters. Addition of Na_2O to liquid V_2O_5 causes an increase in the basicity of the melt with a corresponding increase in corrosivity with respect to the acidic oxides. Moreover, Na_2O has also been reported to de-

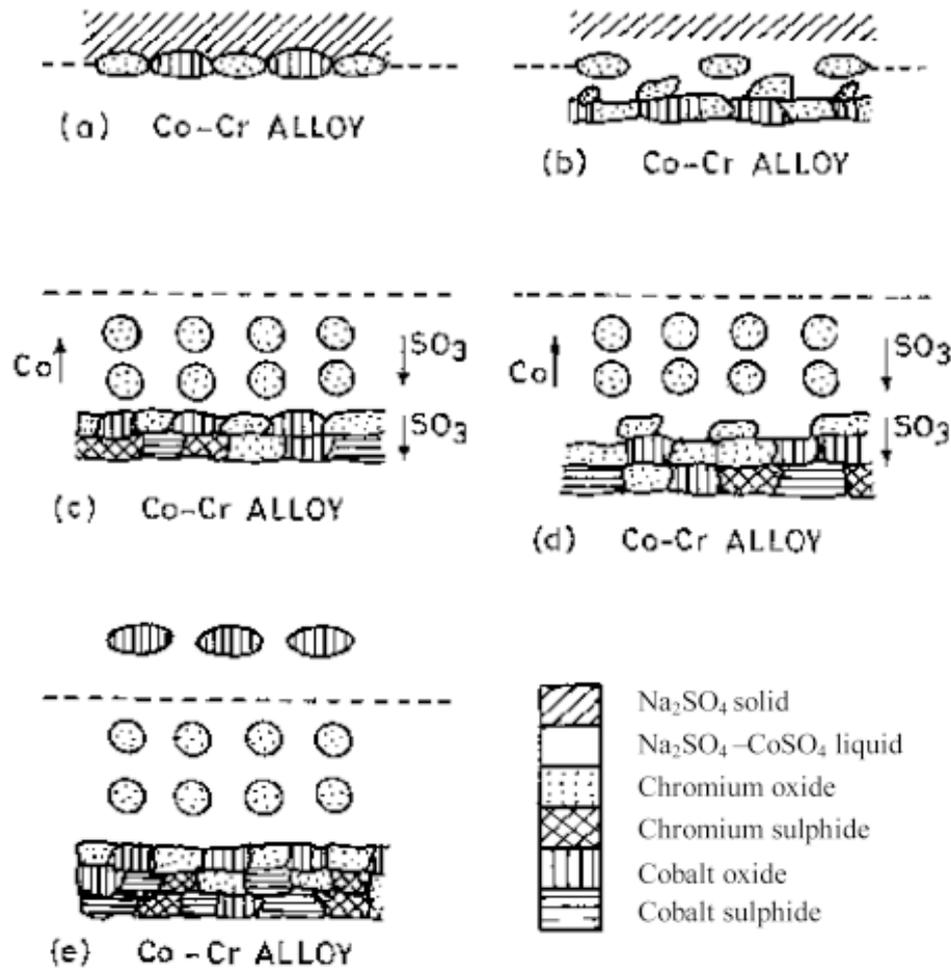


Fig. 2. Schematic representation of the reaction sequence during low-temperature hot corrosion of a Co-30%Cr alloy exposed to O_2 - SO_2 - SO_3 environment where Na_2SO_4 - CoSO_4 liquid and Co_3O_4 are stable. At higher concentration of SO_3 , where Co_3O_4 is unstable at the gas-salt interface, the outward migrating cobalt will form CoSO_4 (s) or Co_3O_4 and CoSO_4 (s) (see, e.g. [29]).

crease the viscosity. Therefore the protective oxides become porous and non-adherent. The formation of binary and tertiary low melting eutectics increases the surface attack thereby reducing the useful life of the component.

Several mechanisms have been proposed to describe the phenomenon of hot corrosion (Goebel and Pettit [4,22,24], Rapp and Goto, [23], Pettit and Giggins [16], Stringer [18], Otsuka and Rapp, [25], and Zhang *et al.*, [26]). Eliaz *et al.* [8] briefed in their review on failures of turbine materials that the initiation of high temperature hot corrosion (HTHC) is often attributed to failure of the protective oxide layer, which allows the molten salt to access di-

rectly the substrate metal. This failure may result from erosion, thermal stresses, erosion-corrosion, chemical reactions, *etc.* The mechanisms proposed for the HTHC propagation stage are the sulphidation-oxidation mechanism and the salt fluxing mechanisms (Stringer, [25]). The salt fluxing mechanism was firstly proposed by Goebel and Pettit [22,24]. According to this model, the protection efficiency of the surface oxide layer might be lost as a result of fluxing of this layer in the molten salt. This fluxing may be either due to combination of oxides with O^{2-} to form anions (basic fluxing) or by decomposition of the oxides into the corresponding cations and O^{2-} (acidic fluxing). As compared to

basic fluxing, acidic fluxing causes more severe oxidation. The acidic fluxing takes place when the O^{2-} activity in the molten salt is markedly lowered. In contrast to basic fluxing, the acidic fluxing can be self-sustaining because the displacement of the salt from the stoichiometry does not become progressively more difficult as the reaction proceeds (Stringer, [25]). In general, the hot corrosion of superalloys with high contents of aluminium and chromium is often reported to occur according to the basic fluxing mechanism, whereas the hot corrosion of alloys with high contents of tungsten, molybdenum, and vanadium has been reported to follow the acidic fluxing mechanism.

Rapp and Goto [23] measured the oxide solubilities in molten Na_2SO_4 as a function of the acidity of the salt. They suggested on the basis of these measurements that a negative gradient of the solubility of the protective oxide in the salt film at the oxide/salt interface should lead to oxide dissolution at this interface and to precipitation of a non-protective oxide away from the interface, where the solubility is lower. In this case fluxing arises only because of the local variation of sodium oxide activity and/or oxygen partial pressure across the salt film, without any necessity of sulphide-forming reactions. This mechanism can explain a self-sus-

taining process of dissolution of the protective oxide to maintain an accelerated corrosion attack (Stringer, [25]).

The effect of vanadium on HTHC has also been studied by different researchers. Bornstein *et al.* [21] and Goebel *et al.* [12] opined that a self-sustained acidic dissolution of the protective Cr_2O_3 or Al_2O_3 scales could take place when the salt film contains vanadium, because V_2O_5 is a strong acidic oxide. Further, Zhang and Rapp [28] believed that every oxide should form an acidic solute with much higher solubility in the presence of vanadate, which should contribute to the more accelerated attack of oxides by mixed sulphate-vanadate melts than by a pure sulphate melt.

The phenomenon of LTHC was explained by Luthra [29] with the help of a common model, according to which LTHC follows two stages. In the first stage liquid sodium-cobalt sulphate is formed on the surface, whereas in the second stage propagation of the attack takes place, refer Fig. 2. The propagation is suggested to occur via migration of SO_3 and cobalt inward and outward, respectively, through the liquid salt.

Some of the hot corrosion studies conducted by various investigators in the Na_2SO_4 and V_2O_5 environments are summarized in Table 1.

Table 1. A summary of hot corrosion studies on some Fe- and Ni-base alloys in the Na_2SO_4 and V_2O_5 environments.

Material	Environment	Brief Details
Na_2SO_4 Induced Hot Corrosion		
Pure Iron and Fe-5Cr Alloy, and Fe-13Cr Alloy	1 atmosphere of oxygen, 900 °C	Pure iron did not undergo accelerated oxidation, which has been attributed to the thickening of the scale too rapidly for sulphur to penetrate the oxide and interact directly with the metal. Authors further reported an immediate acceleration in oxidation rate of Fe-5Cr alloy in the presence of Na_2SO_4 deposits this was attributed to sulphide formation mechanism which initially restricted spinel formation (Trafford and Whittle, [30]). In their study conducted on Fe-13% Cr alloy, Na_2SO_4 coating markedly enhanced the oxidation rate and resulted in the formation of thick, compact and stratified scales. They postulated that formation of sulphides in the alloy substrate and mechanical failure of scale was responsible for the enhanced oxidation (Trafford and Whittle, [31]).

Pure iron, chromium and manganese, and chromium	Gas mixture, containing O_2 (3.6%), SO_2 (0.25%) and N_2 (bal), 600-800 °C	The enhanced corrosion phenomenon was interpreted in terms of low melting liquid sulphate formation. Further the corrosion rate of pure chromium was not appreciably affected by the salt deposit (Nanni <i>et al.</i> , [32]).
Pure iron	Simulated combustion gas containing SO_3 , 600-800 °C	The accelerated reaction observed in the presence of Na_2SO_4 deposits was attributed to the formation of a liquid salt solution between Na_2SO_4 and the sulphates of the corroded metal with the production of duplex scales consisting of a mixture of metal oxides and sulphides (Gesmundo and Viani, [33]).
Iron	In oxygen, 750 °C	The accelerated oxidation of iron in the presence of deposits of Na_2SO_4 was attributed to the formation of abundant sulphide which had a highly defected lattice and allowed rapid diffusion of a liquid phase. The liquid phase was a eutectic melt of Na_2SO_4 and Na_2O . Further it was concluded that the accelerated oxidation had most of the characteristics common with usual low temperature hot corrosion except that it occurred under basic conditions developed by the removal of sulphur from the sulphate deposits instead of the usual acidic conditions established by the SO_3 in the atmosphere (Shi, [34]).
Pure iron and Fe-Al Alloys	Na_2SO_4 deposit, O^{2-} -rich atmospheres containing SO_2 - SO_3 at 650 –700 °C	The accelerated oxidation of pure iron beneath Na_2SO_4 deposit was believed to be induced by the formation of eutectic melt of Na_2SO_4 -iron sulphate. The growth of oxide has been reported to predominate although fluxing contributed a little to the corrosion. In alloys containing Al, fluxing proceeded at a considerable rate in the early stages due to the different oxygen pressure at the oxide/melt interface. Reduction of SO_3 released SO_2 , which caused the formation of sulphides in the scale. Sulphides were supposed to contribute considerably to the acceleration due to their high defect concentration (Shi <i>et al.</i> , [35]).
Pure Ni and Al and Fe-Cr, Ni-Cr and Fe-Al alloys	In oxygen and air, 750 °C	Shi [36] studied the possibility of Na_2SO_4 - Na_2O eutectic melt formation on the metals deposited with Na_2SO_4 . In the case of Ni, Co, Al, Cr, and their alloys he could not detect formation of Na_2SO_4 - Na_2O . In the case of iron-based alloy with high Cr or Al content, where Cr_2O_3 or Al_2O_3 were formed, again Na_2SO_4 - Na_2O eutectic was not observed. However, at lower Cr or Al content, this eutectic melt was suggested to be the possible cause for accelerated rate of corrosion.
Pure iron	Na_2SO_4 , Na_2SO_4 + NaCl , Na_2SO_4 + V_2O_5 , combustion gas, 600 °C	Iron suffered low temperature hot corrosion in the presence of salt deposits at 600 °C. The additions of NaCl and V_2O_5 to Na_2SO_4 changed the corrosion kinetics significantly and modified the scale structure (Li <i>et al.</i> , [37]).
Binary iron aluminide (Fe_3Al)	In pure oxygen, 827, 952, and 1057 °C	The faster kinetics observed in the initial stages of oxidation was related to the formation of θ - Al_2O_3 and slower kinetics in the later stages of oxidation to the formation of α - Al_2O_3 . The overall rate of hot corrosion was higher than that of oxidation at all temperatures. The presence of α - Fe_2O_3 in addition to alumina was indicated by XRD.

Ferritic steels containing Cr, Al, and Ti	Fused salt mixture containing Na_2SO_4 at 927 °C and gas mixture CO , CO_2 , CH_4 , H_2O , H_2 and H_2S at 600 °C	Cross-sectional microscopy revealed that the metal scale interfaces were pitted in hot corrosion conditions and the pits contained aluminum sulphide. Sulphides were also detected along grain boundaries in the inter metallic near the scale-metal interface (Das <i>et al.</i> , [378]). The presence of Ti with 12% Cr and 3% Al increased the proportion of Fe, which diffused to the outer layer of the scale. The excellent behavior of steels at temperatures above 600 °C was explained by the increase in Al diffusion coefficient with temperature (Coze <i>et al.</i> , [39]).
310 Stainless steel	Various ratios of $\text{Na}_2\text{SO}_4/\text{NaCl}$ deposit, in air at 750 °C	The weight gain kinetics in simple oxidation was found to follow a steady state parabolic rate law after 3 hours, while the kinetics with the salt deposits displayed multi stage growth rates. The most severe corrosion took place with 75% NaCl mixtures. Uniform internal attack was the morphology of NaCl-induced hot corrosion, while the extent of intergranular attack was more pronounced as the content of Na_2SO_4 in the mixture was increased (Tsaor <i>et al.</i> , [40]).
Pure nickel and Udimet 700	In a high velocity burner rig, 900 °C	Corrosion of Ni in the burner rig produced a relatively compact NiO scale along with some internal grain boundary corrosion. Corrosion of Udimet 700 was observed to occur in two stages. During the first stage, the corrosion proceeded by the reaction of Cr_2O_3 scale with the Na_2SO_4 and evaporation of the Na_2CrO_4 reaction product from the surface of the corroding sample. Cr depletion in the alloy occurred and sulphide particles were formed in the Cr depletion zone. Extensive sulphidation occurred during the second stage of corrosion and a thick scale was formed (Misra, [41]).
Pre-oxidised nickel	In an $\text{SO}_2\text{-O}_2$ gas atmosphere at 900 °C	Chromate anion suppressed the sulphidation of Ni probably by precipitating solid Cr_2O_3 from the melt. Vanadate anions enhanced the onset of the hot corrosion and sulphidation probably via rapid dissolution of the protective oxide scale at cracks/defects or grain boundaries (Otsuka and Rapp, [26]).
Pure nickel	Under $\text{SO}_3 + \text{SO}_2 + \text{O}_2$ gas mixture & SO_2 and O_2 atmospheres, 900 °C	The corrosion loss in mixed atmosphere containing SO_3 was reported to be larger than those observed in pure SO_2 and O_2 atmospheres. The corrosion loss was found to correspond to the thickness of the oxide layers. High corrosion losses were attributed to the fact that SO_3 strongly acted as an oxidizing agent for the corrosion process (Hara <i>et al.</i> , [42]).
Ni-23.1 Nb-4.4Al and Ni-19.7Nb-6.0 Cr-2.5Al	Dean rig test, 900 °C and 1100°C	Below the outer layer, mainly of NiNb_2O_6 , a high proportion of Al_2O_3 has been reported to be present. Internal oxidation of the metal producing Al_2O_3 and Cr_2O_3 was believed to occur before the development of external Al_2O_3 layer. In some isolated regions the alloy was found to be much more severely attacked, the pit contained NiNb_2O_6 , NbCrO_4 , and Ni. At 1100 °C, more uniform corrosion was observed, the outer layer was mainly NiCr_2O_4 and beneath it a layer of Cr_2O_3 containing particles of NbCrO_4 was observed. Internal ox-

Ni-30Cr and Co-30Cr	600-900 °C	ides were mainly Al_2O_3 and there were massive Ni-rich sulphides ahead of oxidation front (Johnson <i>et al.</i> , [43]). The rapid rate of attack was explained on the basis of sulphation of the transient surface oxides (Ni or Co oxides) and the dissolution of these transition metal sulphates into Na_2SO_4 to yield a liquid phase (Luthra and Shores, [44]).
B-1900	Na_2SO_4	Na_2SO_4 interacted with the alloy to form sodium and sulphur compounds, rapid removal of sulphur from Na_2SO_4 by unretarded diffusion of sulphur and precipitation of Cr-rich sulphide phases promoted the formation of Na_2O . The catastrophic oxidation observed during sulphidation was due to interactions between Na_2O and the substrate (Bornstein and DeCrescente, [45]).
Ni-base superalloys and seven binary Ni-base alloys	Pure O_2 , 825-1000 °C	Based upon the results, it was concluded that the reduction of the oxide ion content of Na_2SO_4 was a necessity, but not sufficient condition for sulphidation inhibition. The addition of Mo or V to nickel imparted sulphidation resistance in it because their oxides reacted with and decreased the oxide ion content of Na_2SO_4 . The disagreement in the literature regarding the effect of Molybdenum on hot corrosion was suggested to be largely due to differences in testing techniques and differences in whether the investigators have been more concerned with the initiation or with propagation modes of hot corrosion (Bornstein <i>et al.</i> , [21]).
Ni- base superalloys	1 atm O_2 , 650-1000 ° C (Goebel <i>et al.</i> , [12]), O_2 , 750-950 ° C (Misra, [46])	The alloys underwent catastrophic corrosion. The, accelerated oxidation occurred as a result of the formation of a liquid flux based on Na_2SO_4 which dissolved the normally protective oxide scales. Catastrophic or selfsustaining rapid oxidation can occur in alloys which contain Mo, W or V because solution of oxides of these elements with Na_2SO_4 decrease the oxide ion activity of the molten salts, producing melts which are acidic fluxes for oxide scales (Goebel <i>et al.</i> , [12], and Misra, [46]). The evaporation rate of MoO_3 from $\text{Na}_2\text{Mo-MoO}_3$ melts has been reported to decrease considerably [46] (1986) when dissolved in Na_2MoO_4 .
Ni-based industrial superalloys	Static deposits of Na_2SO_4 or NaCl or both in still air, 850-1000 °C	The susceptibility to hot corrosion was found to be correlated to the type of scale produced during simple oxidation. Alloys forming an Al_2O_3 scale were found to be susceptible to Na_2SO_4 deposits, independent of their Cr content. The quantity of the Na_2SO deposits dictated the nature of attack and under certain conditions, the refractory element alloy additions appeared to play an essential role. Alloys containing Cr_2O_3 or TiO_2 in the simple oxidation scale proved to be sensitive to NaCl attack (Bourhis and John, [47]).
Ni-15Cr-Mo (Peters <i>et al.</i> , [48]), Fe-, Ni- and Co-based alloys	900 °C (Peters <i>et al.</i> , [48]), 600 °C and above (Pettit and Meier, [15]), 975 °C in oxygen	The effect of Mo on the hot corrosion of superalloys has also been reported by Peters <i>et al.</i> [48], Pettit and Meier [15], and Fryburg <i>et al.</i> [48]). The alloy containing Mo suffered catastrophic degradation. It has been re-

	(Fryburg <i>et al.</i> , [50])	ported that MoO_2 reacted with Na_2SO_4 to produce an acid (SO_2 -rich) salt, leading to acidic fluxing. MoO_3 incorporated into the Na_2SO_4 via the formation of compounds such as Na_2MoO_4 , $\text{Na}_2\text{MoO}_4 \cdot \text{MoO}_3$, and $\text{Na}_2\text{MoO}_4 \cdot 2\text{MoO}_4$. All these phases were liquid and left a high solubility for Al_2O_3 and Cr_2O_3 . Peters <i>et al.</i> [48] added that there is a threshold amount of molybdenum below which catastrophic attack is not encountered, e.g. for Ni- 15% Cr threshold has been reported to be between 3-4%.
Ni-based superalloys, B-1900 and NASA-TRW IVA	In pure O_2 , 900 °C	After an induction period of little corrosion, local basic fluxing attack of the $\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3$ scale spread to cover the surface and generated catastrophic linear kinetics. During catastrophic attack of B-1900, the sulphate ions reacted to release SO_2 and formed sulphides in the alloy and salt was converted to Na_2MoO_4 (Fryburg <i>et al.</i> , [50]).
Fe-, Ni- and Co-based alloys	Atmospheres containing O_2 , N_2 , and SO_2 , 729-1076 °C	The corrosion rate was lowest when the chromium content of the alloy was highest. Further Mo and Cu were found to increase the corrosion rate. The main corrosion products formed in air were NiO and Cr_2O_3 . In hot corrosion tests NiS and Cr_5S_8 were found (Pehkonen <i>et al.</i> , [51]).
Ni and Ni-based Alloy EI 867 with the Aluminide and Cr-Al Diffusion Coatings	Pure Na_2SO_4	Low alloyed aluminide and Cr-Al coatings showed very poor resistance to oxidation. After 24 hrs, these had been almost completely removed. Modification of highly alloyed aluminide coatings with Cr resulted in uniform and relatively slow degradation of the coating. Cr enriched zone is supposed to act as a barrier to the oxidation of refractory metals such as Mo, W, and V thus preventing the onset of catastrophic corrosion (Godlewski and Godlewska, [52]).
Ni-16Cr-2Nb, IN738, Ni-16Cr, and Superalloy 537	900 and 1000 °C	Na_2SO_4 coated coupons of Ni-16Cr-2Nb and Ni-16Cr developed dense, protective oxide scales and exhibited good hot corrosion resistance. Alloys 537 and IN 738 experienced a shift from basic fluxing to acidic fluxing and as the temperature was increased, the rate of attack increased significantly (Zho <i>et al.</i> , [53]).
Inconel 600 and Incoloy 825	Ar +1% O_2 , 940 °C	Inconel 600 was able to form a protective layer of chromia in Ar +1% O_2 with or without a thin layer of Na_2SO_4 at a temperature of 940 °C, whereas Incoloy 825 was not able to form chromia in the same environment. This was attributed to the formation of nickel and chromium molybdates due to 3.22% Mo present in the alloy. When O_2 content was only 300 ppm, sodium sulphate layer strongly enhanced the corrosion of Inconel 600 and Incoloy 825 (Santorelli <i>et al.</i> , [54]).
Review (Shih, [55])	Low-temperature hot corrosion	Some superalloys containing molybdenum are subjected to sub-melting point hot corrosion when covered with a sulphate, which is associated with the formation of a molybdenum-containing melt resulting from the reaction of MoO_3 with the sulphate (Shih, [55]).

Superalloys HA-188, S-57, IN-617, and TD-NiCrAl	Mach 0.3 burner rig at various temperatures, sea salt concentrations and salt compositions.	Accelerated corrosion of the specimens has been reported in the temperature zones above the calculated dew points of Na_2SO_4 . It was believed that the corrosion occurred by small amount of salt deposit on those temperature zones during heat-up following each cooling cycle or by small amounts of salt migrating from deposits at cooler zones via a wetting action. Large deposits of salt appear to inhibit corrosion that is why less corrosion was noticed at 900 °C when the flame was doped with 10 ppm sea salt than when it was doped with 5 ppm sea salt (Santoro, [56]).
Nimonic 105	900 °C	Hot corrosion did not seem to be very detrimental towards the superalloy. It was concluded that SO_3 pressures below $5 \cdot 10^{-3}$ atm did not affect the electrokinetic behaviour, but pressures greater than $5 \cdot 10^{-3}$ atmospheres produced higher corrosion rates which was attributed to the acid fluxing by the sulphate melt. Addition of NaCl to the molten Na_2SO_4 resulted in increased dissolution of Nimonic 105 (Sequeira and Hocking, [57]).
Nimonic 105, 75, 80A and 90	With and without $\text{Cr}_2(\text{SO}_4)_3$, NiSO_4 or CoSO_4 additions, 650-1000 °C	Up to 800 °C, the lower oxidation rates for Na_2SO_4 coated alloys were attributed to a scale morphology consisting of inner scales of Cr_2O_3 acting as a protective oxide film and external scales of NiO. This morphology was observed to be maintained at high temperatures (Malik and Ahmad, [58]).
Alloys B1900 and IN 100 (Al_2O_3 -formers), Inconel 600, 690, Incoloy 800, IN 738, Nimonic 80A, 100, and 105 (Cr_2O_3 -formers)	In the presence of Na_2SO_4 (s) and NaCl (s) separately, and in combination, air, 850 and 1000 °C	The Cr_2O_3 formers got attacked more aggressively by NaCl (s) than Na_2SO_4 (s). Al_2O_3 -formers and to some extent NiO-formers were more resistant to NaCl attack than Cr_2O_3 formers. While Na_2SO_4 induced corrosion preceded by fluxing and sulphidation reactions, the NaCl induced corrosion was observed to follow a reaction path of fluxing, chloridation and oxidation. The Na_2SO_4 -NaCl induced corrosion involved combination of reactions occurring in the presence Na_2SO_4 and NaCl separately (Malik <i>et al.</i> , [59]).
Single-crystal Ni-based superalloys and DS Mar M 200	704 and 900 °C	All the alloys were severely degraded at 900 and 704 °C. There was no significant difference between the hot corrosion of these alloys when tested in air or in oxygen with SO_3 , provided a liquid deposit was present in both cases. It was concluded that all the superalloys under study require a coating if they were to be exposed to any of the hot-corrosion conditions at temperatures of 704 °C or higher (Levy <i>et al.</i> , [60]).
Inconel 740	850 – 1000 °C	The kinetics curves of the alloy at 950 °C without Na_2SO_4 deposit and at 850 °C with Na_2SO_4 deposit obeyed the parabolic law, whereas the uniform parabolic growth behaviour of oxide was not followed at 1000 °C without Na_2SO_4 deposit and at 950 °C with Na_2SO_4 deposit due to oxide spallation at 1000 °C and the evaporation of Na_2CrO_4 melt at 950 °C, respectively. The oxide scales were found to be consisting of Cr_2O_3 , (Ni, Co) Cr_2O_4 , TiO_2 , and Al_2O_3 and internal oxide scales at all temperatures. The internal sulphidation was suggested to

		take place due to the existence of Na_2SO_4 deposit. The complex layered structure of the oxide scales was reported to be in favor of the resistance to oxidation. The accelerated oxidation of the alloy in the presence of Na_2SO_4 deposit was attributed to the dissolution of Cr_2O_3 induced by basic fluxing in molten Na_2SO_4 (Zhao <i>et al.</i> , [61]).
Co-Cr, Co-Al, and Co-Cr-Al Alloys	In O_2 - SO_2 - SO_3 , 600 to 750 °C	Co-Cr and Co-Cr-Al alloys reacted non-uniformly, usually in the form of pits and Co-Al alloys suffered broad frontal attack. Under all conditions, a thin sulphur-rich band containing sulphides was observed at the alloy/scale interface and cobalt dissolved near the interface and formed Co_3O_4 /or CoSO_4 (S) (Luthra, [62]).
Co-Cr, Co-Al, and Co-Cr-Al Alloys	In O_2 -0.15% (SO_2 + SO_3), 750 °C	Accelerated oxidation tests at 750 °C showed that the corrosion resistance of binary Co-Cr and Co-Al alloys increased with the Cr and Al content of alloys. This protection was offered by the rapid growth of CoCr_2O_4 / Cr_2O_3 and CoAl_2O_4 / Al_2O_3 oxides in comparison to CoO and Co_3O_4 . At high enough Cr (=40%) and Al (=15%) concentrations, the growth rates were so fast that liquid did not even form; consequently the corrosion rates were very low. Tests on Co-Cr-Al alloys indicated that simultaneous presence of Cr and Al was deleterious to the resistance against low temperature hot corrosion (Luthra, [63]).
Metal oxides such as Co_3O_4 , NiO , Al_2O_3 , Cr_2O_3 , Fe_2O_3 , and SiO_2	627-927 ° (Malik and Mobin, [64]) and 827-927 °C (Mobin <i>et al.</i> [65]) in O_2	The interaction of the metal oxides with Na_2SO_4 has been studied. As suggested, the high temperature reaction products usually contain 3-phase structures namely, $\text{Na}_2\text{O-MO-M}_2\text{O}_3$ and metal sulphide and or metal sulphate. The formation of $\text{Na}_2\text{O-M}_2\text{O}$ was further reported to be dependent upon the solid state solubility of metal oxide in the molten salt at high temperature and under limited solubility conditions $\text{Na}_2\text{O-M}_2\text{O}$ was invariably formed, but as soon as conditions relaxed the oxide M_2O_3 precipitated and was observed to form a separate phase (Malik and Mobin [63], and Mobin <i>et al.</i> , [64]).

V_2O_5 Induced Hot Corrosion

Gas-turbine alloys	750 °C and above	Vanadium pentoxide coatings had a deleterious effect throughout the useful temperature range of all the alloys up to 1120 hrs in 70-hr cycles. The effect was reported to be more pronounced for iron based alloys at temperatures above 750 °C (Harris <i>et al.</i> , [66]).
Review	- - -	Oxidation of pure Cr in V_2O_5 occurs with a very rapid diffusion rate and so only the initial stages of the oxidation curve were supposed to be more important. Later slowing down of the oxidation rate could be attributed mainly to the effect of scale thickening. Loose and spongy appearance of the scale was observed at the beginning of the process; V_2O_5 was present in excess and did dissolve the products of oxidation. At the same point the liquid was saturated with the oxide which sub-

<p>Technical note (Fairman,[68]) Review (Pantony and Vasu [69])</p>	<p>- - -</p>	<p>sequently could get precipitated. The presence of various phases in a thin layer of scale would impose such severe strain on the film that cracking and exfoliation could be expected. This would permit liquid phase to reach the metal surface again and the conditions to form a spongy scale were seen to prevail. This mechanism would apply only to iron base alloys, which are susceptible to the catastrophic corrosion (Sachs, [67]).</p>
<p>Pure metals such as iron, cobalt, nickel, molybdenum, titanium, tungsten, and 99.5% vanadium rods, and single crystals of chromium</p>	<p>Immersion in the melt, in O_2</p>	<p>Fairman [68] reported that the accelerated oxidation due to V_2O_5 is most likely to be the consequence of the catalytic action of vanadium pentoxide. It results in splitting the oxygen molecule at the metal surface, so cause rapid corrosion. Pantony and Vasu [69] concluded from the theoretical survey of fireside corrosion of boilers and gasturbines that in residual fuel ash, V_2O_5 can be the most serious cause of "catastrophic" corrosion.</p>
<p>Iron, nickel, and several alloys containing iron, nickel, and chromium</p>	<p>Crucible and rotating disk testing</p>	<p>A diffusion controlled corrosion process given by equation below hold good for the initial stages of vanadic corrosion of all metals under study except nickel and chromium. $\Delta w = Kt$, where Δw is the weight change per cm^2 at time t, and K is the velocity constant. Whereas nickel obeyed a logarithmic rate law. The velocity constant was found to be inversely proportional to the depth of melt. On the basis of comparison of activation energies of the various rate processes, a single mechanism underlying the corrosion processes of iron, cobalt, vanadium, titanium, tungsten, and molybdenum was suggested, which involves an inward diffusion of oxygen (or other active species) and a sequential outward diffusion of the corrosion products. In case of nickel and chromium, the existence of a coherent corrosion layer separating the slag from nickel and chromium was revealed, which was named as protective barrier for these metals and was found to be absent for other metals under study (Pantony and Vasu, [70]). The stainless steels and particularly 440 stainless steel (25 wt.% Cr) showed the best corrosion resistance to liquid V_2O_5. The rate of corrosion of Armco iron by liquid V_2O_5 has been reported to be controlled initially by the diffusion of oxygen across the metal oxide-liquid vanadate interface. As the available oxygen ions got depleted from the melt, the rate controlling mechanism was observed to be changed to the sorption of oxygen at the liquid vanadate gas phase interface. Whereas in case of nickel, Inconel 600 and the iron alloys, the rates of corrosion were found to be affected by the formation and dissolution of the protective metal oxide layers. They concluded that the presence of Fe and Na in the vanadate melts did not alter the rate controlling process of oxygen diffusion and oxygen sorption, but it increased the non stoichiometry and hence increased the oxygen diffusion. The rate of corrosion was reported to be af-</p>

High temperature alloys	- - -	<p>ected by temperature, oxygen partial pressure and rotational speed, volume of liquid vanadate, composition of the metal and composition of the liquid vanadates. According to them, Inconel showed better corrosion resistance than stainless steels (Kerby and Wilson, [71]).</p> <p>Vanadate-induced corrosion of high temperature alloys has been studied by thermogravimetry in laboratory furnaces (using a limited amount of vanadate deposit), in burner rigs (where small amounts of vanadates are continually being deposited on the surface), or by immersion of specimens in crucibles with molten salt. The reaction products formed during exposure in laboratory furnaces and in burner rigs were qualitatively the same, but the kinetics and reaction rates were differing considerably. The mechanisms were found to be complex (Beltran and Shores, [4]).</p>
50Cr-50Ni alloy	In pure V_2O_5 and sodium vanadates, 750-950 °C in a rotating disk apparatus	<p>In pure V_2O_5 at 810 °C, a Cr_2O_3 scale has been observed on the alloy which subsequently got dissolved slowly into the liquid melt and was thus proposed as a barrier layer by them. In the case of NV6, this barrier layer was not observed. The increased basic character of the melt and its consequently greater fluxing ability toward acidic oxides was thought to be a more important part process than the increased ionic conductivity of NV6 over V_2O_5 at this temperature. At 950 °C the corrosion in terms of both dissolution rate and corrosion rate was reportedly greater in V_2O_5 than in NV6 (Dooley and Wilson, [72]).</p>
Superalloys	700 °C	<p>The relationship of the high temperature corrosion of superalloys with contaminants has been reported by Hancock [73]. It was proposed that to compare contaminant conditions the contaminant flux rate (CFR) rather than the contaminant level in the fuel or environment should be considered. He further suggested that at temperatures above 700 °C where vanadates cause fluxing of the protective oxide scales, corrosion could be determined by the CFR and temperature rather than by material selection.</p>
Nickel base superalloy	In air, 700 °C	<p>Vanadium, present as vanadium pentoxide, attacked the alloy severely at the temperature of investigation. Study of ternary oxide system and spot tests showed that two low melting eutectics, namely, $NiO-V_2O_5-Cr_2O_3$ melting at 550 °C and $V_2O_5-Cr_2O_3-Fe_2O_3$ melting at 480 °C, were formed. The formation of these liquid eutectics and the presence of corrosive V_2O_5 caused severe damage to the superalloy (Iyer <i>et al.</i>, [74]).</p>
Nickel base superalloys Nimonic 80A, Hastelloy C-276, and Superni 600	In air, 650, 700, and 750 °C	<p>The hot corrosion kinetics obeyed a parabolic law with two regions at 700 and 750 °C, the corrosion rate falling with the formation of a solid $Ni_3V_2O_8$ layer. The acid-base fluxing mechanism and a second mechanism by which nickel vanadate was precipitated from a nickel vanadium compound located in the short circuit diffusion path has been assumed to be occurring in the growing oxide. The corrosion rate for these alloys got decreased with the formation of a compact solid vanadate layer (Swaminathan <i>et al.</i>, [75]).</p>

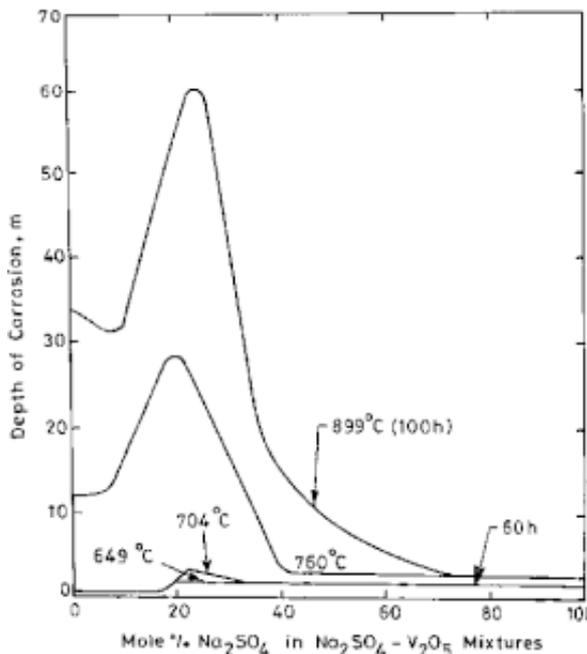


Fig. 3. Corrosion rate of Type 304 stainless steel in different mixtures of Na_2SO_4 - V_2O_5 (see [7]).

5. STUDIES RELATED TO Na_2SO_4 - V_2O_5 INDUCED HOT CORROSION

The kinetics of the reactions between Na_2SO_4 (X) and V_2O_5 (Y) as studied by Kolta *et al.* [76] revealed that the rate of reaction depended both on the temperature (600-1300 °C) and the molar ratios of X:Y. They further found that with increase in the reaction period (>30 min.), there was a decrease in reaction rate which finally reached to zero order. This decrease in the reaction rate has been attributed to the formation of vanadosulphate complexes such as $(\text{NaV}_3\text{O}_8)_2 \cdot \text{Na}_2\text{SO}_4$ and $(\text{NaVO}_3)_2 \cdot \text{Na}_2\text{SO}_4$ which get decomposed at higher temperatures giving the meta- and pyro-vanadates respectively.

Kofstad [77] proposed that during combustion, the vanadium contaminants are oxidized to the higher valence vanadium oxides (V_2O_4 and V_2O_5) and sodium vanadates are formed by the reaction of vanadium oxides and sodium salts, e.g. Na_2SO_4 . Accordingly the composition of the vanadates may be presented in a simplified form as $(\text{Na}_2\text{O})_x \text{V}_2\text{O}_5$, but the detailed compositions of the individual vanadates may be more complex as part of the vanadium may be in the +IV state. The solid compounds comprise $(\text{Na}_2\text{O})_x \text{V}_2\text{O}_4 (\text{V}_2\text{O}_5)_{12-x}$ (often termed

β -bronze), $(\text{Na}_2\text{O})_5 (\text{V}_2\text{O}_4)_x (\text{V}_2\text{O}_5)_{12-x}$ (K bronze), NaVO_3 (sodium metavanadate), $\text{Na}_4\text{V}_2\text{O}_7$ (sodium pyrovanadate) and Na_3VO_4 (sodium orthovanadate). A notable feature of the vanadates is that they have relatively low melting points, which extend from 535 °C upwards. Furthermore, metal oxides dissolved in the vanadates may suppress the melting points and eutectic temperatures even further. He further reported that the slags developed on valves in diesel engines consist predominantly of sodium sulphate and sodium vanadates and have melting points as low as 400 °C.

Molten vanadates flux oxide ceramics. The solubilities of metal oxides may be high and are dependent on the Na:V ratio. The solubilities of Cr_2O_3 and Fe_2O_3 are highest at Na : V ratios close to 5 : 12 and amount to about 50 mol.%. For NiO the solubility is about 60 mol.% for Na : V = 3 : 2 and decreases to about 55 mol.% for Na : V = 5 : 12. As V_2O_5 is acidic, it will in general react with more basic oxides to form the corresponding vanadates.

5.1. Iron and iron-based alloys

Natesan [7] reported that the fuels containing only 50 ppm vanadium can cause severe attack on stainless steels. Fig. 3 shows the corrosion rate of Type 304 stainless steel in different V_2O_5 - Na_2SO_4 mixtures at temperatures between 790 and 900 °C, as has been presented by him. At temperatures below the melting point of ash, the rate of attack of stainless steel is low and follows the normal oxidation rate. It was concluded that all stainless steels and other common engineering alloys are severely attacked by fuel ash that contain vanadium with or without sulphates.

Fairman [68] studied some metal specimens in an ash mixture (V_2O_5 +10% Na_2SO_4) environment in air. The corrosion was found to be severe at the ash/air or ash/atmosphere interface. The intensity of attack, however, was still higher at the locations where the concentration of oxygen and vanadium pentoxide was greatest, suggesting the transfer of oxygen atoms or ions by the pentoxide to the metal surface: $2\text{V}_2\text{O}_5 \rightarrow 2\text{V}_2\text{O}_4 + 2\text{O} \downarrow$. He opined that the mechanism of accelerated attack could be most satisfactorily explained by the catalytic action of V_2O_5 operating with an increase in the defect concentration of the scale.

Valdes *et al.* [78], in a study of AISI 446 stainless steel under V_2O_5 and $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ environment in the temperature range 700-900 °C in air, found that the oxide scale was mainly Cr_2O_3 with some vanadium oxide which acted as a moderate bar-

rier to corrosion. Above 850 °C in V_2O_5 , a breakaway corrosion reaction occurred. No Cr_2O_3 oxide barrier was present but there was a continuous oxide that comprised of Cr_2O_3 , Fe_2O_3 , and V_2O_5 at the metal/oxide interface where the crystals grew. It was suggested that the addition of Na_2O to V_2O_5 increased the oxide ion (O^{2-}) content of the melt and made it more aggressive to acidic oxides such as Cr_2O_3 .

Tiwari ([79-81] have reported hot corrosion studies on some industrial superalloys in temperature range 700-900 °C in the environments comprising of pure Na_2SO_4 , Na_2SO_4 -15% V_2O_5 , and Na_2SO_4 -60% V_2O_5 . Very high corrosion rates were observed in the environment having Na_2SO_4 -60% V_2O_5 composition. The extremely corrosive nature of this composition was attributed to its low melting point i.e. 500 °C. Tiwari *et al.* [80] further revealed that in Na_2SO_4 -60% V_2O_5 melt, the degradation was due to the cracking of the protective scale under the influence of the fluxing action of the melt for both Fe-base alloy Superfer 800H and Cobase alloy Superco 605. The enhanced degradation was reported to be due to the presence of tungsten in the form of Na_2WO_4 - WO_3 compound. No oxidation and sulphidation into the substrate was observed in Co-base alloy. Tiwari [81] concluded that the Co-base alloy has inferior corrosion resistance than the Ni-base alloy in Na_2SO_4 -60% V_2O_5 environment at 900 °C.

Almeraya *et al.* [82] carried out electrochemical studies of hot corrosion of steel AISI-SA-213-TP-347H in 80 wt.% V_2O_5 + 20 wt.% Na_2SO_4 at 540 °C–680 °C and reported the corrosion rate values of around 0.58-7.14 mm/year. They observed an increase in corrosion rate with time. However, the corrosion potential was observed to be decreasing with increase in temperature from 540 to 680 °C. Almeraya *et al.* [83] further conducted similar studies on type 347H stainless steel under the same environment and temperature range, and revealed the fact that with change in temperature from 540 to 680 °C the corrosion potential decreased.

Cuevas-Arteaga *et al.* [84] used both LPR (Linear Polarisation Resistance) and weight loss techniques, in their hot corrosion study on alloy 800 in Na_2SO_4 -20% V_2O_5 , and reported slightly higher corrosion rate at 900 °C than at 700 °C. They further reported that in both the techniques, corrosion rates increased in the beginning of the experiment but decreased later on until steady values were reached.

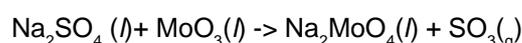
Singh [85], during his studies on the hot corrosion of GrA1, T11, and T22 boiler steels in an envi-

ronment of Na_2SO_4 -60% V_2O_5 at 900 °C, observed that the Mo containing T22 steel showed least resistance to the hot corrosion attack. This was attributed to the formation of a low melting point MoO_3 phase, which reacted with molten salt resulting in formation of Na_2MoO_4 . This low melting point oxide was suggested to cause the acidic fluxing of the protective scale.

The hot corrosion behavior of some Ni- superalloys viz Superni 75, Superni 600, Superni 601, and Superni 718, and an Fe-based superalloy; Superfer 800H was evaluated by Singh [86] in air, as well as, molten salt environment of Na_2SO_4 -60% V_2O_5 at 900 °C under cyclic conditions. In general the superalloys indicated accelerated oxidation in Na_2SO_4 -60% V_2O_5 environment at 900 °C in comparison to that in air. The Fe-base superalloy Superfer 800H showed a least resistance to the hot corrosion amongst the Superalloys Superni 75, 600, 601, and Superfer 800H. The weight gain values for the fifth superalloy Superni 718 could not be compared with the rest of cases, as data was available for 20 cycles only for this superalloy. This superalloy showed intensive spallation of its scale in the molten salt environment, such that weight gain data could be obtained for 20 cycles only. On the basis of cumulative weight gain data for 50 cycles, corrosion rate of the superalloys under study could be arranged in the following order:

Superfer 800H > Superni 601 > Superni 600 > Superni 75

The superior corrosion resistance shown by Ni-base superalloys, Superni 75, and 600 was attributed to the formation of Cr_2O_3 and nickel vanadate in the oxide scales. Further, it was observed that all the superalloys under study obeyed parabolic rate law of oxidation up to 50 cycles, except Superni 718. In the latter case, the superalloy followed a parabolic rate law upto 20 cycles only. The accelerated hot corrosion of Superni 718 was ascribed to the presence of higher amount of molybdenum (3.05%) in it. Singh [86] suggested that the molybdenum might have resulted in the formation of MoO_3 , which according to Peters *et al.* [48] may react with Na_2SO_4 to form a low melting point phase Na_2MoO_4 by the following reaction:



This might have caused alloy induced acidic fluxing, subsequently giving rise to accelerated spalling of the scale. Identical findings have also been reported by Bourhis and John [46], Pettit and Meier [15], Misra [46], and Shih *et al.* [55]. Fig. 4

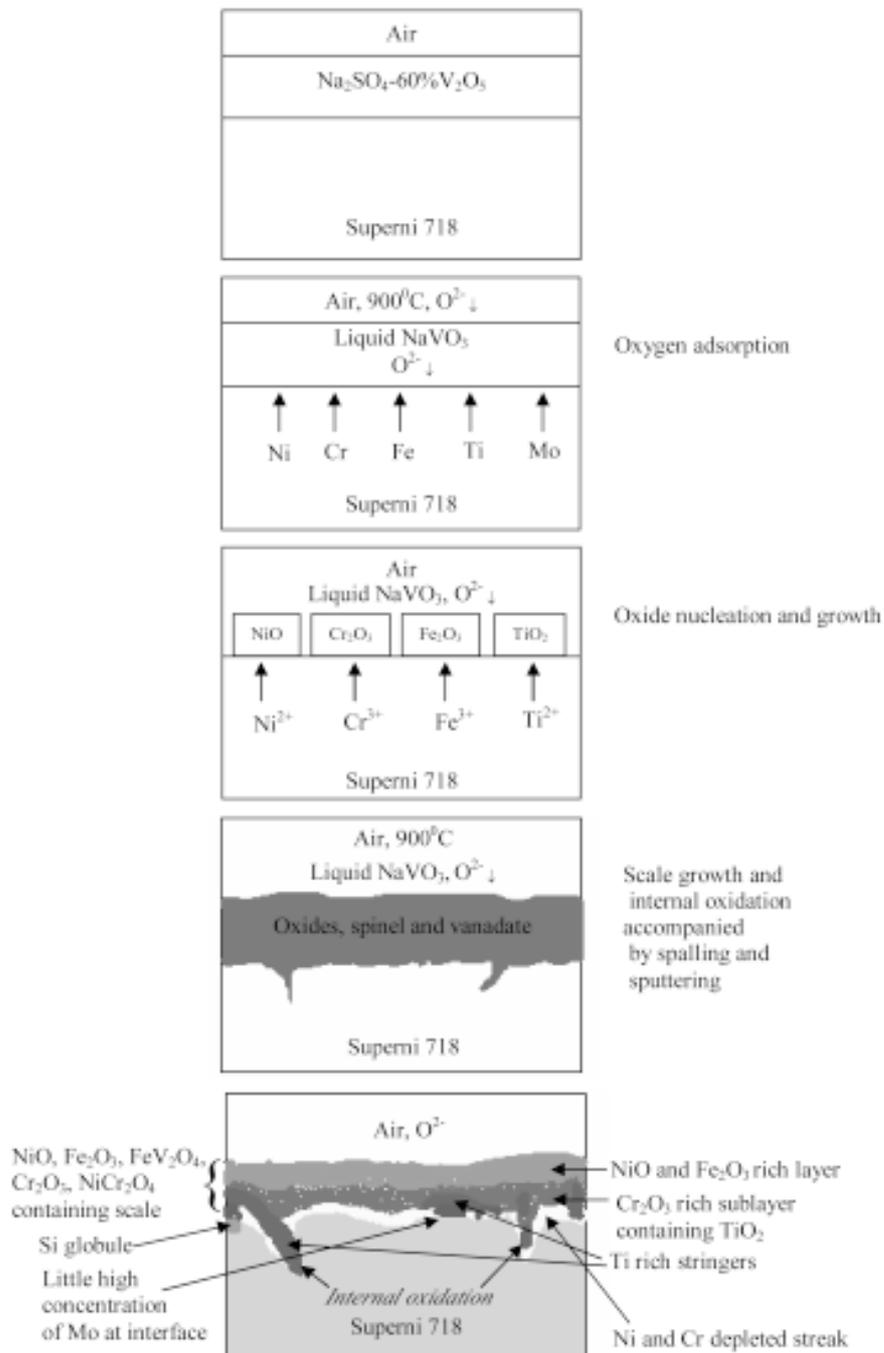


Fig. 4. Schematic diagram showing probable hot corrosion mechanism for the uncoated superalloy Superni 718 exposed to Na_2SO_4 -60% V_2O_5 at 900 °C for 50 cycles (see [86]).

shows the plausible mechanism governing the corrosion process for superalloy Superni 718 in an environment of Na_2SO_4 -60% V_2O_5 as has been suggested by Singh [86].

5.2. Nickel and nickel-based alloys

Thilakan *et al.* [87] studied hot corrosion of nickel free austenitic stainless steel, Cr-Ni stainless steel and Inconel in oxygen atmosphere at different tem-

peratures with vanadium-sodium slags of varying composition. They justified the use of saturated solution of Na_2SO_4 as the liquid medium because of its low gas solubility, vapor pressure and viscosity. Threshold temperature was found to lie between 700 and 800 °C. Above the threshold temperature the extent of attack initially increased but with increasing temperature either it became constant (as observed for Inconel) or decreased (for other alloys). Increase in the amount of Na_2SO_4 in sodium sulphate-vanadium pentoxide mixtures first increased and then decreased the rate of oxidation at the temperature of 820 and 870 °C. At 950 °C, all Na_2SO_4 additions to V_2O_5 decreased its corrosive effect. The fluidity of slag was observed to be important in allowing diffusion of oxygen. According to an interesting observation of their study, nickel free stainless steel was found to have a high resistance to attack against V_2O_5 - Na_2SO_4 mixture, and under the experimental conditions showed a resistance superior to that of even Inconel at temperatures above 850 °C especially in 70% V_2O_5 -30% Na_2SO_4 environment.

Bornstein *et al.* [21] investigated the relationship between vanadium oxide and Na_2SO_4 accelerated oxidation for nickel-base superalloy B-1900 and seven binary nickelbase alloys. It was established that the corrosion attack commenced by dissolution of the normally protective oxide scale into the fused salt. The dissolution was suggested to occur by a reaction between oxide ions present in melt and the oxide scale. They further opined that the sulphidation attack can be inhibited by decreasing the oxide ion content of the fused salt. In another study, Bornstein *et al.* [88] reported the effect of vanadium and sodium on the accelerated oxidation of nickel base alloys. The initial rapid rate of oxidation between V_2O_5 and metal substrate was attributed to the reduction of V_2O_5 by the substrate. According to them, intermetallics Ni_3Al and NiAl were particularly susceptible to V_2O_5 corrosion. It was further concluded that the sulphidation attack can be attenuated if the initial oxide ion content of the melt is prevented from increasing. Oxides such as Cr_2O_3 have been reported to react preferentially with oxide ions.

A 50Cr-50Ni commercial alloy was corroded in pure V_2O_5 and in vanadate melts containing sodium sulphate and chloride in the temperature range 750 to 950 °C in a rotating disc apparatus by Dooley *et al.* [72]. The study reported the formation of chromium rich oxide scale in pure V_2O_5 which dissolved only slowly into the liquid melt and thus observed to act as a barrier layer. In $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$,

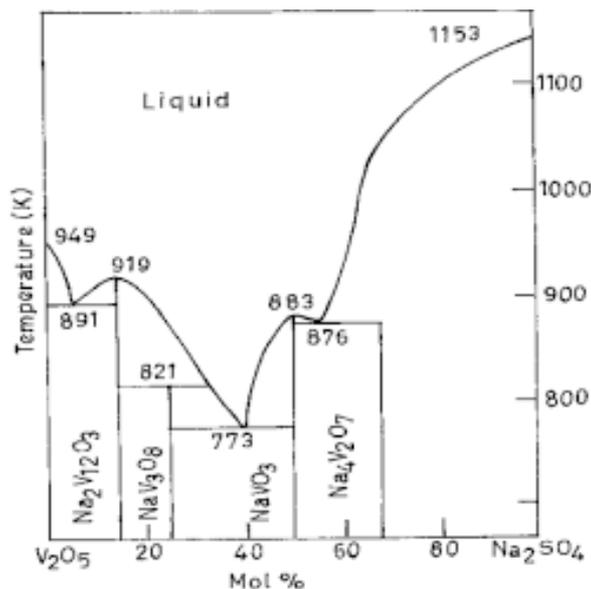


Fig. 5. Phase Diagram for Na_2SO_4 - V_2O_5 system (see [91]).

this barrier layer was not observed. Marked internal oxidation of the Cr-rich α -phase was noticed in chloride containing melts throughout the temperature range 750-950 °C.

Thermogravimetric studies which delineate the conditions for simultaneous sulphate and vanadate induced corrosion at 650 to 800 °C have been carried out by Seiersten and Kofstad [89]. They found that the corrosion caused by sodium sulphate/sodium vanadate mixtures have a complex mechanism. Samples coated with sodium vanadate were exposed to $\text{O}_2 + 4\% \text{SO}_2$ and the initial reaction was observed to be the same as that observed in pure oxygen. After an incubation period, the duration was found to decrease with increasing temperature and sufficient SO_3 got dissolved in the molten vanadate which resulted in formation of a mixture of NiSO_4 and Na_2SO_4 near the metal. When a molten NiSO_4 - Na_2SO_4 solution containing small amounts of vanadate was formed as an intermediate layer, the reaction reportedly proceeded as sulphate-induced hot corrosion. The corrosion mechanism was observed to change from initial vanadate-induced to essentially sulphate induced hot corrosion when the sulphur trioxide pressure was high enough to form sodium sulphate.

Sidky and Hocking [90] investigated the mechanisms of hot corrosion by molten sulphate-vana-

date deposits for Ni-10Cr, Ni-30Cr, Ni-20Cr-3Al, Ni-21Cr-0.3Si, Ni-20Cr-5V alloys, and IN738 superalloy. The effect of adding Cr to Ni was found to be beneficial in the Na_2SO_4 melt, however, on increasing the VO_3 - concentration in the melt, this effect diminished, becoming harmful in pure NaVO_3 due to the formation of the non protective CrVO_4 . According to them, alloying element Al was found to be harmful in Na_2SO_4 - NaVO_3 melts. Cr depletion was observed in rich VO_3 - melts but internal corrosion was more obvious in the SO_4^{2-} rich melts. Corrosion in rich VO_3 - melts was aggressive due to the fluxing action of the salt, which takes place along internally sulphidised areas. According to their study, IN738 suffered tremendous internal attack due to its γ precipitates which became sulphidation prone areas, and were fluxed by the VO_3 - melt.

The presence of sulphur and its oxidized compounds favor the formation of isolated lobes with radial morphology (Otero *et al.*, [91]) during the hot corrosion of IN657 at 635 °C in molten salt environment. These lobes had great permeability which facilitated the access of oxygen; therefore the protection character of the scale was reduced. They further reported that the presence of vanadium and its oxidized products generate compounds with aciculate morphology, which is not very much covering and contribute to reduce the protective character of the scale. The equilibrium diagram for varying composition of Na_2SO_4 is shown in Fig. 5 and the mixture of Na_2SO_4 -60% V_2O_5 is seen to be the lowest eutectic temperature.

The effects of chromate and vanadate anions on the hot corrosion of Ni by a thin fused Na_2SO_4 film in SO_2 - O_2 gas atmosphere at 900 °C were investigated by Otsuka and Rapp [26]. Their results showed that the inhibition of sulphidation may result from the precipitation of solid Cr_2O_3 from the melt and thereby partially sealing/plugging the crack defects and grain boundaries of the original protective oxide layer. They proposed that vanadate anions enhanced the onset of the hot corrosion and sulphidation probably via rapid dissolution of the protective oxide scale at cracks/defects or grain boundaries.

Lambert *et al.* [92] studied the oxidation and hot corrosion of Ni-17Cr-6Al-0.5Y and Ni-16Cr-5.7Al-0.47Y-5Si alloys at 700 °C in Na_2SO_4 -60% V_2O_5 to ascertain the effect of addition of Si. They observed an outer layer of NiO developed on the surface of the Ni-17Cr-6Al-0.5Y alloy whereas a thin Al_2O_3 oxide scale formed on the Si-enriched alloy. They further opined that the condensed vanadates of

sodium are highly corrosive and can markedly increase the rate of oxidation of nickel base superalloys.

In the same aggressive environment (Na_2SO_4 -60% V_2O_5), the hot corrosion behaviour of Superalloy IN-657 at 727 °C has been investigated by Otero *et al.* [93,94]. They reported that corrosion rate of the alloy in contact with molten salt mixtures was reduced by approximately one order of magnitude over exposure times of 210 hr when the amount of molten salt was kept constant. During the initial stages of the exposures the corrosion rate increased with the temperature up to 1273 °C and decreased for still higher temperature. After 100 hr of exposure, it was observed that the temperature scarcely influenced the corrosion kinetics.

Swaminathan and Raghvan [95] reported that cracking and fluxing of the protective scales together with easier crack nucleation and growth at grain boundaries in the presence of liquid deposits of sodium metavanadate and sodium metavanadate plus 15 wt.% sodium sulphate at 650-750 °C accounted for the enhanced creep rates and reduced rupture life for Superni-600. During a similar study on Superni-C 276 in the same temperature range, they have reported that eutectic NaVO_3 + 15 wt.% Na_2SO_4 mixture was more severe in degrading the creep properties (Swaminathan and Raghavan, [96]). The corrosives were found to reduce the rupture life through enhanced creep deformation. They further opined that the degradation of the alloy in case of NaVO_3 melt was due to the cracking of the protective scales under the influence of the applied stress and the fluxing action of the melt. The addition of sodium sulphate to sodium metavanadate increased the corrosivity of the deposit by lowering the melting point and by formation of molten Ni-Ni₃S₂ eutectic which initiates a self-sustaining hot corrosion. It was suggested that the additional presence of molybdenum compounds Na_2MoO_4 - MoO_3 caused enhanced degradation.

Oxidation and hot corrosion in sulphate, chloride and vanadate environment of a cast nickel base superalloy have been reported by Deb *et al.* [97]. Weight gain studies were carried out in air for the uncoated samples and coated with 100% Na_2SO_4 , 75% Na_2SO_4 + 25% NaCl, and 60% Na_2SO_4 + 30% NaVO_3 + 10% NaCl. The presence of sulphur in the form of sulphates has been reported to cause internal sulphidation of the alloy beneath the external oxide layer. They observed the formation of volatile species by chlorides which

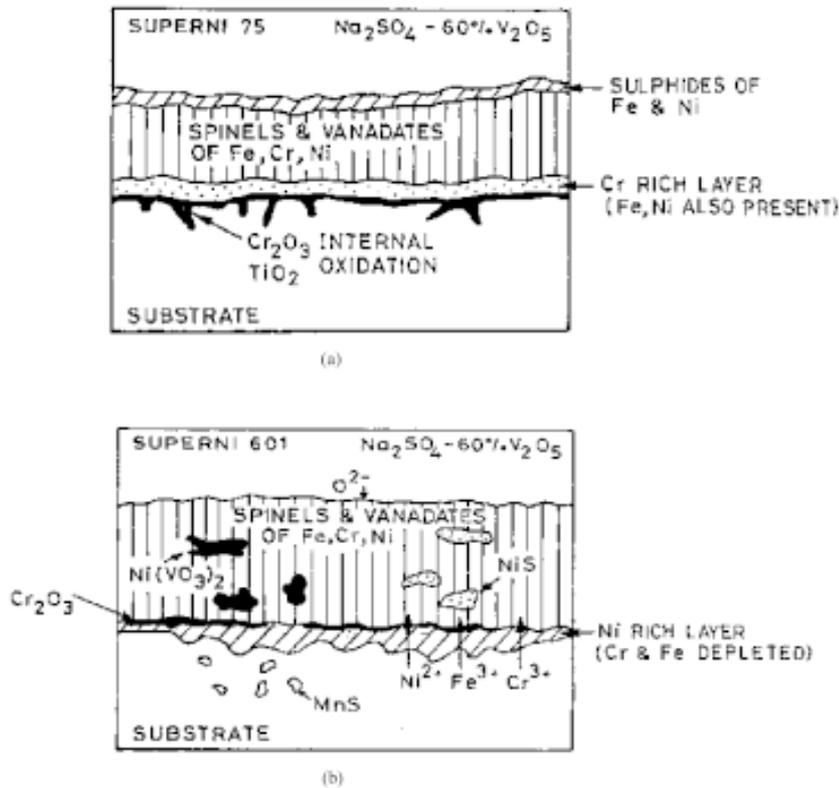


Fig. 6. Schematic diagram showing probable hot corrosion mechanism in $\text{Na}_2\text{SO}_4 - 60\% \text{V}_2\text{O}_5$ after exposure for 50 cycles at 900°C for alloys (data from [100]) (a) Superni 75 (b) Superni 601.

further led to formation of voids and pits at grain boundaries. These voids and pits were suggested to provide an easy path for flow of corrodents. It was proposed that the presence of vanadate in conjunction with sulphate and chloride provided additional fluxing action, which destroyed the integrity of the alloy and weakened its mechanical properties.

Gurrappa [98] during hot corrosion studies on CM 247 LC Superalloy in Na_2SO_4 and $\text{Na}_2\text{SO}_4 + \text{NaCl}$ mixtures at 900°C observed that the superalloy CM 247 LC got severely corroded in just 4 hr, while it was completely consumed in 70 hr when tested in $90\% \text{Na}_2\text{SO}_4 + 10\% \text{NaCl}$ at 900°C . The life of the superalloy, however, further decreased to just 2 hours in $90\% \text{Na}_2\text{SO}_4 + 5\% \text{NaCl} + 5\% \text{V}_2\text{O}_5$ at 900°C .

Lee and Lin [99] carried out studies on the molten salt-induced oxidation/sulphidation on nickel aluminide intermetallic compound (Ni_3Al) in the $1\% \text{SO}_2/\text{air}$ gas mixtures. Their observations on hot-corroded specimen tested at different time periods

showed the formation of only NiO at 605°C , and NiO and NiAl_2O_4 at 800 and 1000°C . EDAX analysis revealed the presence of AlS_x and/or NiS_x beneath the oxide scale at all the temperatures. Based on the experimental studies, a hot corrosion mechanism was proposed by the investigators, according to which NiO oxide formation consumed the oxygen in the molten salt, which locally reduced the oxygen and increased the sulphur partial pressure in the molten salt. Stability diagram was used to represent this partial pressure change of sulphur. They suggested that as the increased partial pressure of the sulphur reaches the equilibrium partial pressure region of NiS_x and/or AlS_x , NiS_x and/or AlS_x will form at the salt/alloy interface through sulphidation reaction. The consumption of sulphur will balance out the sulphur, and oxygen partial pressure increases in the molten salt. This will force NiO to form. This process confirmed the simultaneous formation of NiO , NiS_x , and/or AlS_x . They further opined that as the sulphides are thermodynamically unstable when the oxygen partial

pressure increases, it is possible for sulphide to convert into oxides NiO , Al_2O_3 , and NiAl_2O_4 through necessary reactions. Two possibilities have been pointed out for the formation of spinel phase, either through the reaction of Al and Ni with oxygen in the molten salt or through the evolution of sulphides.

Gitanjaly [99] has conducted hot corrosion studies on some Ni-, Fe-, and Co-based superalloys in an environment of $\text{Na}_2\text{SO}_4+60\%\text{V}_2\text{O}_5$ at 900 °C. Whilst the observed corrosion rate was significant in all the superalloys, Ni-base superalloy Superni 75 showed the lowest rate of corrosion and the Co-base superalloy Superco-605 the highest. Better corrosion resistance of Ni-base superalloys was attributed to the presence of refractory nickel vanadate $\text{Ni}(\text{VO}_3)_2$ which acted as a diffusion barrier for the oxidizing species. The proposed hot corrosion mechanisms of this study for the superalloys Superni 75 and Superni 601 have been schematically shown in Fig. 6.

Tzvetkoff and Gencheva [101] presented a review on the mechanism of formation of corrosion layers on nickel and nickel-based alloys in melts containing oxyanions. The molten sulphate mixtures are stated to be particularly aggressive towards Ni superalloys. In such environments, the formation of Cr-rich passive films such as spinel-type oxides could be protective to some extent. They further revealed that at metal/oxide interface, sulphides are detected which do not offer plausible protection except for a possible positive role of MoS_2 formed on Ni alloys containing significant amounts of Mo. Furthermore, acidic oxides such as those of V and Mo have been reported to induce rapid fluxing of the oxide scale and therefore catastrophic hot corrosion. Whereas, the chromates were stated to be beneficial for the re-passivation of the surfaces following fluxing of the oxide scale by the molten salt.

6. CONCLUDING REMARKS

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, etc. present in the coal or in fuel oil used for combustion in the mentioned applications. In some situations, these impurities may be inhaled from the working environment, for instance NaCl in marine atmospheres. There is a general agreement that

condensed alkali metal salts notably, Na_2SO_4 , are a prerequisite to hot corrosion [4]. Due to the high cost of removing these impurities, the use of these low grade fuels is usually justified.

Although natural gas has also been considered as an alternative to these traditional fuels for generation of electricity in combined cycle power plants, still there remains strong interest in the development of clean, high efficiency coal-based systems for power generation (Saunders *et al.*, [102]). This might be due to anticipated saving of high grade energy such as natural gas. Similarly, in coal conversion processes, which are known to produce clean environmentally acceptable fuels, technical problems arise from the interaction of sulphur and ash in the coal with plant construction materials at high temperatures and pressures (Natesan, [103]).

For the reason that hot corrosion of the components in aforesaid high temperature environments is inevitable, the phenomenon has maintained its relevance from the last more than 60 years. Hot corrosion often increases the corrosion loss of heat resisting alloys by over hundred times, in comparison to that incurred by simple oxidation (Shinata *et al.*, [104]).

The use of Ni-, Fe- and Co- based superalloys in the high temperature applications such as gas turbines, boilers, etc. is well known and many more applications are still to be explored, where these alloys may have tremendous potential. Although the superalloys have adequate mechanical strength for such high temperature applications, yet they are prone to degradation by high temperature oxidation/corrosion during long term exposures. Therefore, the superalloys need to be protected, however the protection system must be practical, reliable and economically viable.

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