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# The Importance of Hot Corrosion and Its Effective Prevention for Enhanced Efficiency of Gas Turbines

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I. Gurrappa, I.V.S. Yashwanth, I. Mounika,  
H. Murakami and S. Kuroda

Additional information is available at the end of the chapter

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## 1. Introduction

Advanced gas turbine engines essentially need novel materials to exhibit forever-greater efficiency by increasing their operating temperatures. Higher operating temperatures lead to high temperature corrosion of the components and thereby reduce their life significantly. The blades in modern aero, marine and industrial gas turbines are manufactured primarily from Ni - based superalloys. Oxidation and hot corrosion are the two important factors (under high temperature corrosion), which determine the life of gas turbine engine components. The rate of degradation is slow under oxidation conditions, while it is significantly fast under hot corrosion conditions and catastrophic failures are imminent if proper materials in association with appropriate coatings are not used. Hot corrosion is major problem for marine and industrial gas turbines while aero gas turbines experience it while they move across the sea. Assessment of current status on hot corrosion problems in different gas turbine engines is imperative in order to improve their life by selecting advanced hot corrosion resistant materials and coatings. This process helps in highlighting the issues that need to be addressed not only for enhancing the efficiency of gas turbine engines but also to avoid failures during service.

A section of a typical gas turbine engine is shown in Fig.1 [1]. It is important to note that hot section components of the engine are manufactured from Ni-based superalloys. Advances in processing of Ni-based superalloys have allowed evolution of microstructures from equiaxed structures about three decades ago to directionally solidified (DS) multi-grain and single crystal (SC) components today. With added capability from compositional flexibility coupled with advances in processing over that time period, high-pressure turbine blade temperatures have increased marginally and metal surface temperature at the hottest locations approach 1150<sup>o</sup> C in state-of-the-art gas turbine engines. The most severe combinations of stress and

temperature in the present engine designs correspond to bulk average metal temperatures approaching  $1000^{\circ}\text{C}$  using the first generation single crystal alloys.

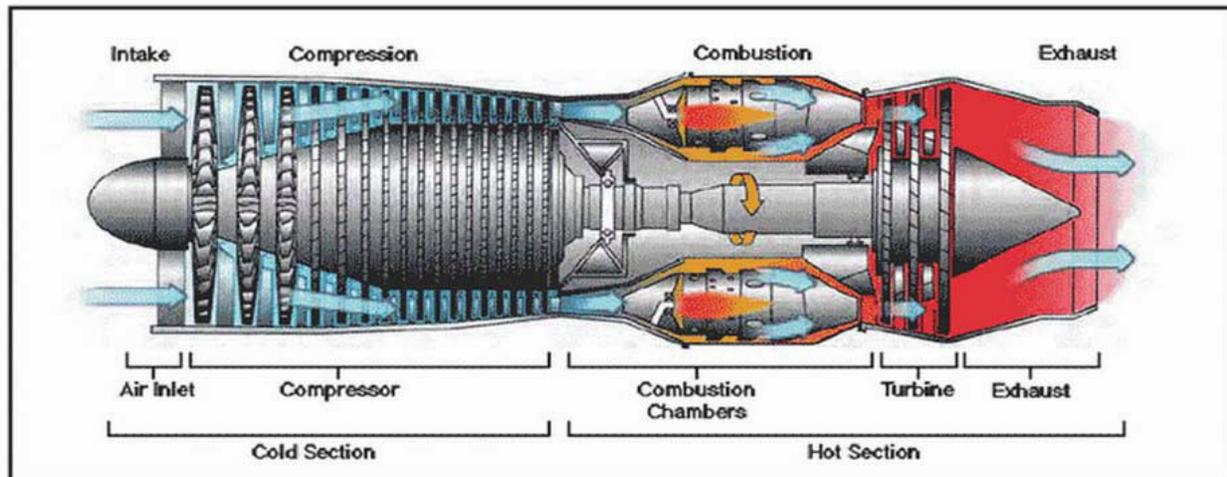


Figure 1. Gas turbine engine showing the usage of superalloys and titanium based materials [1]

One of the most critical components in the engine is the gas turbine blade. The high-pressure turbine blade operates under the most arduous conditions of temperature and stress than any component in the engine. Not only does the blade experience high temperature and direct stress, it also experiences rapid temperature transients at various points during the engine cycle. The hot gases surrounding the blade are highly oxidizing and contain high levels of contaminants like sulphur and chlorine if low-grade fuels are used. An ideal superalloy / coating should be able to survive this harsh corrosive environment.

The efficiency of a gas turbine is proportional to firing or turbine inlet temperature. Increase in engine operating temperature has meant that the traditional corrosion resistant turbine blade alloys such as IN 738 and IN 939 are no longer strong enough to last the expected 25,000 hours minimum life [2]. It implies that higher strength alloys like Mar M247, CM247 LC, single crystal alloys, CMSX-4, CMSX-10 etc. are required for creep strength. Progress in aero and industrial gas turbine blade materials is illustrated in Fig.2 [2]. During the last one decade, dramatic competition in the power equipment industry has boosted technology to the levels achieved in the aviation turbines just years before. Latest industrial gas turbines use single crystal, rhenium containing Ni-based superalloys and directionally solidified blades and vanes. These alloys have relatively poor hot corrosion resistance and hence have to rely on advanced protective coatings to prevent severe and potentially life limiting damage.

The majority of Ni - based superalloy development efforts has been directed towards improving the alloy high temperature strength with relatively minor concern being shown to its hot corrosion resistance. Further, it is not always possible to achieve both high temperature strength and hot corrosion resistance simultaneously because some alloying elements help to improve hot corrosion resistance while some may help to improve high temperature strength. It is rare that an alloying element leads to enhancement both in high temperature strength and

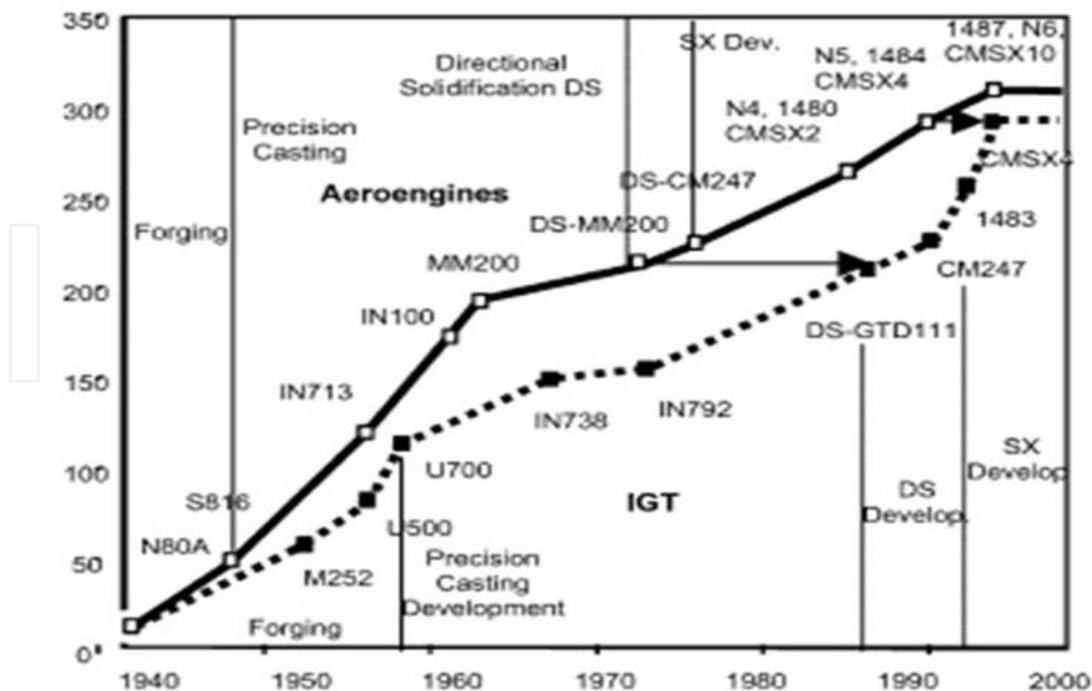


Figure 2. Progress in aero and industrial gas turbine blade superalloys [2]

the hot corrosion resistance. This is further complicated for marine applications by the aggressivity of the environment, which includes sulphur and sodium from the fuel and various halides contained in seawater. These features are known to drastically reduce the superalloy component life and reliability by consuming the material at an unpredictably rapid rate, thereby reducing the load-carrying capacity and potentially leading to catastrophic failure of components [3-5]. Thus, the hot corrosion resistance of superalloys is as important as its high temperature strength in gas turbine engine applications. Recent studies have shown that the high temperature strength materials are most susceptible to hot corrosion and the surface engineering plays a key role in effectively combating the hot corrosion problem [6-7]. Therefore, the two materials (base and coating) must be considered as an integral system and the interface between them is also equally important as it can often be the limiting factor.

This chapter explains the critical issue of hot corrosion of superalloy components in gas turbine engines and methodologies to select appropriate materials and coatings for its prevention. It is followed by an assessment of current status of coatings, coating techniques and finally, some of the critical areas that need to be addressed for development of more efficient and smart coatings.

## 2. Hot corrosion

Hot corrosion became a topic of important and popular interest in the late 60s as gas turbine engines of military aircraft suffered severe corrosion during the Vietnam conflict during

operation over seawater. Metallographic inspection of failed components showed sulphides of nickel and chromium and hence the process was named 'sulphidation'. However, the process has subsequently been renamed "hot corrosion" because corrosion by a thin electrolyte film bears some common features with 'atmospheric corrosion' by an aqueous film at room temperature.

Break down of protective oxide layers by chemical interaction with certain aggressive species contained in the combustion environment can produce accelerated attack on the underlying metal. This process is known as hot corrosion. Hot corrosion takes place mainly because of high concentrations of sulphur, vanadium and sodium in the fuels, which may be as high as 4, 0.05 and 0.01% (all are in wt%) respectively. Chlorides and sulphates enter the engine with the air; sulphur, vanadium and sodium oxidize during combustion and mostly volatile compounds such as  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NaOH}$ ,  $\text{NaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{VO}(\text{OH})_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{V}_2\text{O}_4$  are formed. These compounds condense at 500 to 900<sup>o</sup> C and build up deposits depending on the fuel.  $\text{Na}_2\text{SO}_4$  is the main component of deposits in engines running on high sulphur and low vanadium fuel. Table I summarizes the main contaminants likely to be formed in working environment for three types of gas turbine engines i.e. aero, marine and industrial gas turbines [8]. Table II provides the composition of slag actually formed on first stage vanes in gas fired stationary gas turbine during operation [9]. Table III provides the relevance and importance of hot corrosion in various energy fields and the associated contaminants, which are responsible for degradation of components during the service [10].

Engine application	Contaminants
Aero	Na, Cl, S, Ca ( All low)
Marine	Na, Cl, S, Mg (All high)
Industrial	Na, V, S, Pb, Cl

**Table 1.** Contaminants in gas turbine fuel and air [8]

$\text{Na}_2\text{SO}_4$	4.3
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	22.7
$\text{Fe}_2\text{O}_3$	22.3
$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	20.6
$\text{K}_2\text{SO}_4$	10.4
$\text{MgO}$	2.8
$\text{Al}_2\text{O}_3$	6.5
$\text{SiO}_2$	10.4

Temperature : 850<sup>o</sup> C

Atmosphere : Air containing 0.015 vol-% $\text{SO}_2$  -0.015 vol-% $\text{SO}_3$

Flow rate: 60 l h<sup>-1</sup>

**Table 2.** Composition of slag (all are in wt%) [9]

Energy systems	Mixed oxidant reactions	Hot corrosion
Batteries and Fuel cells	SO <sub>2</sub> , SO <sub>3</sub> , O <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> S and H <sub>2</sub> O attack of alloys	Fused halides and carbonate cells
Coal conversion and combustion systems	CO, CO <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> S and H <sub>2</sub> O attack of alloys	Slag films, residue films, fly ash films, salt films in MHD*, salt film assisted coal combustion
Solar energy and energy storage	-	Salt spillage or leakage from thermal storage tanks
Nuclear Energy	H-O-C in HTGR Steam reactions with Zircaloy	Fission product, salt condensation on cladding
Gas Turbines	SO <sub>2</sub> , SO <sub>3</sub> and O <sub>2</sub> attack of alloys	Na <sub>2</sub> SO <sub>4</sub> , NaV <sub>x</sub> O <sub>y</sub> , NaCl attack of alloys
Gas and Oil recovery and Magma Energy	H <sub>2</sub> , H <sub>2</sub> S and H <sub>2</sub> O attack of alloys	-

\* Magneto Hydrodynamic

**Table 3.** Relevance and importance of hot corrosion in energy systems [10]

## 2.1. Types

Two different forms of attack have been identified, types II hot corrosion, and I, which occur over different temperature ranges; 600-750<sup>0</sup> C and 800-950<sup>0</sup> C respectively. Type I results from a fluxing process where modification of the sodium sulphate deposit chemistry permits ingress of sulphur into the underlying metal; this produces localized depletion of protective elements and progressive internal attack occurs. The net process of type I hot corrosion produces a characteristic of attack which includes a porous oxide scale, an irregular metal / scale interface and internal attack with preceding metal sulphides.

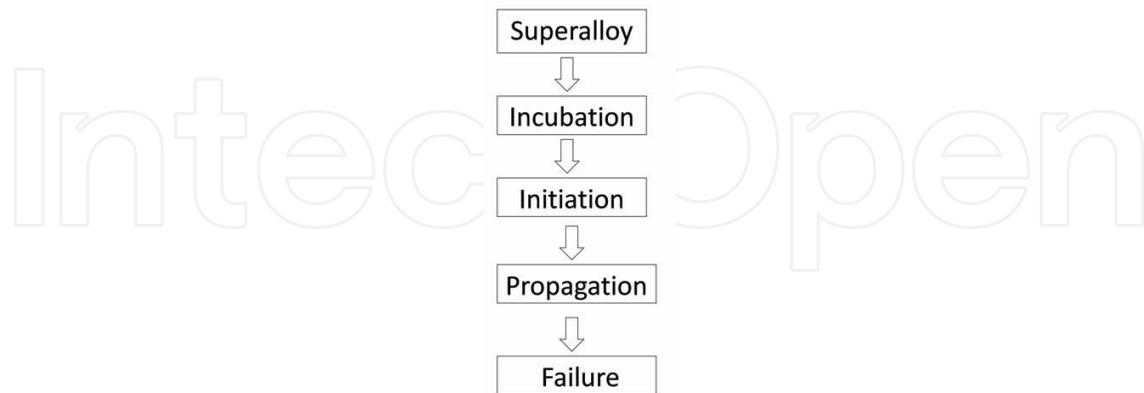
On the other hand, type II hot corrosion requires sodium sulphate and sufficient sulphur trioxide to maintain low melting deposit, which readily fluxes the surface oxide. Thermodynamics favour sulphur trioxide formation in the lower temperature range. The associated attack is normally localized, producing pits with a lamellar scale rich in sulphur through progressive fluxing action of the deposits; sulphur generally does not enter the alloy to form internal sulphide with this type of attack [6, 11].

## 2.2. Mechanism

Many mechanisms have been proposed for hot corrosion. All the mechanisms involve deterioration of the reaction product barrier that forms on the alloys when the deposits are not present. Basically, the hot corrosion process proceeds in three stages (Fig.3);

- a. An incubation stage during which the reaction proceeds at a rate essentially similar to that of normal oxidation
- b. An initiation step during which the corrosion is accelerated

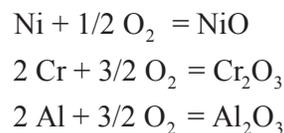
- c. A propagation stage during which rapid corrosion takes place and
- d. Ultimate failure of a component



**Figure 3.** Various stages of hot corrosion processes, which lead to catastrophic failures of superalloy components

### 2.2.1. Incubation Period

During this period, the alloy undergoes normal oxidation similar to that observed in the absence of salt deposit. Initially, the oxides of most of the alloying elements are formed as given below:



Due to the reaction with oxygen in the initial stages, rapid weight gain of the alloy takes place. At the end of incubation stage, thermodynamically stable oxides such as  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  (depending on the composition) are formed as a dense oxide scale on the surface of alloys. This oxide scale acts as a diffusion barrier for the ingress of deleterious species such as oxygen and sulphur.

### 2.2.2. Initiation stage

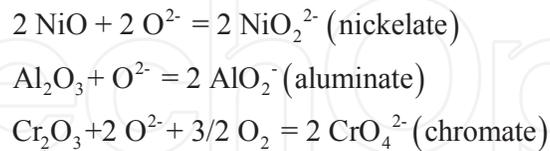
Cracking or spalling of oxide scale occurs in this stage due to the stresses developed during oxide growth. Thus, fresh alloy surface, which is depleted of scale forming alloying elements, is exposed to the action of deposit as shown below:



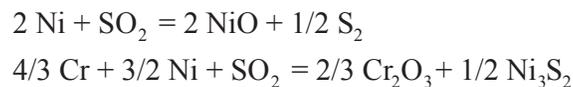
$\text{SO}_2$  will be in the form of dissolved gas.

### 2.2.3. Propagation stage

The propagation stage during hot corrosion is substantially different from the behaviour of the alloy in the absence of a deposit. It is accompanied by a very severe attack of the alloy as a result of fluxing of oxides as shown below:



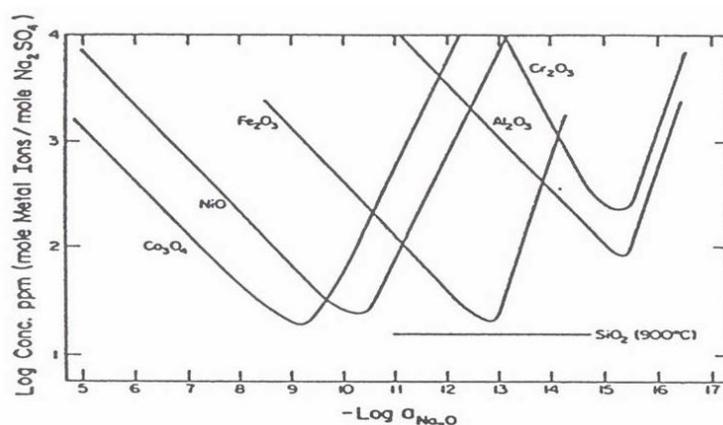
The dissolved sulphur dioxide formed during initiation period can react with the alloying elements to produce oxides, sulphides and sulphur.



The relationship between the initiation and propagation stages and the factors that are important in preconditioning the alloy during the initiation stage are explained by Pettit and Meurer [12].

If the deposits contain chloride ions, it can selectively remove certain elements such as chromium or aluminium from the alloy. This process involves the formation of highly volatile gaseous chlorides inside the pores of the alloy and thereby metal chlorides diffuse out from the alloy. As a result, mechanical properties of the alloy reduce significantly as the cracks are formed on the alloy surface. The metallic components of these chlorides convert to oxides eventually but these oxides form as particles and not as continuous layers. Hence, severe attack of the alloy can take place.

The mechanisms have been explained based on acidic and basic fluxing of protective oxide scales depending upon the conditions. The protective oxide scale, for example  $\text{Cr}_2\text{O}_3$  is fluxed either as acidic solutes such as  $\text{Cr}_2(\text{SO}_4)_3$  or  $\text{CrS}$  or as basic solutes such as  $\text{Na}_2\text{CrO}_4$  and  $\text{NaCrO}_2$ . As a result, the oxide scale can become non-protective. Such non-protective scales can be formed by dissolution of the oxide near the alloy surface and re-precipitation as discontinuous particles from the molten deposit. It is important to emphasise that there are other means by which an oxide scale can become non-protective via a fluxing process. For example, the fluxing reaction may cause a certain element to be removed from the alloy, which in turn gives rise to a non-protective scale on the surface of the alloy. Rapp and his group [13-14] carried out extensive studies pertaining to hot corrosion fluxing mechanisms, different oxide solubilities and electrochemical evaluation methods for hot corrosion resistance. Kinetic studies of various materials at high temperatures under hot corrosion conditions were reported by the earlier workers [15-16]. Natesan et al [17-18] have studied the high temperature corrosion of Ni-based superalloys in coal conversion environments.



**Figure 4.** Measured solubilities for different oxides in fused pure sodium sulphate at 1200 K [13]

As fluxing of the protective scale is important in hot corrosion attack, the selection of alloys or coatings for hot corrosion resistance should be based on the solubility of protective oxides. For a given deposit and environmental conditions, the most favoured oxide is the one that has the least solubility and can form a protective scale in the presence of salt film. Fig.4 presents the measured solubilities of various oxides in fused  $\text{Na}_2\text{SO}_4$  at 1200 K [13]. The difference of six orders of magnitude in basicity between minima for the most basic  $\text{Co}_3\text{O}_4$  to the acidic  $\text{SiO}_2$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  is striking and is consistent with important known alloy systems and coatings under hot corrosion conditions. Cobalt based alloys and coatings are more vulnerable to acidic fluxing than Ni-based alloys and coatings.  $\text{Cr}_2\text{O}_3$  is resistant to acidic fluxing because the minimum in its solubility curve corresponds approximately to the acidity of gas turbine environments.

It is very essential to assess the materials / coatings in the laboratory under simulated engine conditions for testing their performance, since it is not feasible to test each material directly in the engine. A satisfactory test should yield a prediction of service performance, with an estimation of component life as a desirable objective. The next section covers different techniques, which are used for evaluation of various materials / coatings for hot corrosion resistance.

### 2.3. Assessment techniques

The following laboratory hot corrosion techniques are in use for assessing a variety of materials /coatings for gas turbine engine applications:

- i. Burner rig test
- ii. Furnace test
- iii. Crucible test
- iv. Thermo gravimetric test
- v. Electrochemical methods

### 2.3.1. Burner Rig test

This test simulates the operating conditions in gas turbine engines, the gas composition, pressure, velocity and temperature. In this test, rigs are composed of a combustion chamber from a small turbine, supplying air from compressors and burning fuel in the usual way. Salt can be sprayed into the combustion chamber. The hot exhaust gases are brought into the sample chamber, where several specimen coupons are placed and rotated in the gas stream. Here, the test variables (such as gas pressure, velocity, sample temperature, salt concentration and fuel-to-air ratio) can be selected to simulate aero, marine and land based gas turbine engine's operation. This test was used extensively for evaluation of coated and uncoated materials for hot corrosion resistance [19-22]. It was also established that the materials tested showed generally similar behaviour during service. Therefore, this test is more appropriate for testing the materials as well as coatings to get comparable results with the service conditions of gas turbine engines.

### 2.3.2. Furnace test

In this test, a furnace having two zones, whose temperature can be controlled independently is employed. The specimen is placed in one zone and a crucible containing the test salt is placed in the other. Using a carrier gas, the vaporized salt is carried from one zone into the other where it deposits on the specimen. In this manner, the deposition of salt per unit time can be strictly controlled. In modified method known as 'Dean Test', the corrosion conditions can be controlled from very mild to very severe, by simply altering the temperature differential within the two zones. This test was used mainly to study kinetics of various materials in different environments.

### 2.3.3. Crucible test

This method involves direct immersion of the sample to half its length in molten salt in air atmosphere and measurement of weight change to monitor the reaction rate. Gas may be bubbled through the melt or passed over it to provide oxidizing or reducing environments. This test was used by Simons et al [23] for the first time followed by other researchers for evaluation of a number of bare and coated materials for hot corrosion resistance. The corrosion test conditions are severer than that in normal operating condition of the engines, but it is a simple and helpful test for screening of different materials and coatings [24-34].

### 2.3.4. Thermo gravimetric test

It is also called "Salt coated test". In this test, a coupon of the material is coated with saturated salt solution, then dried, weighed and placed in a heated furnace. The coupon weight is continuously recorded. In most cases, the weight increases as oxidation proceeds, as the vaporization rate is small compared with the oxidation rate. This method was adopted by many researchers for determining the hot corrosion kinetics because the experimental parameters such as gas composition, temperature and salt loading can be controlled very easily and precisely.

### 2.3.5. Electrochemical methods

This method involves measurement of corrosion current as a result of oxidation-reduction reaction continuously and provides instantaneous corrosion rates. The net reaction is the oxidation of metal to form oxide scales and the reduction of  $\text{SO}_4^{2-}$  to a lower oxidation state. Generally, corrosion is accelerated only when the salt film is molten such that the material and the gas are physically separated by the ionically conducting fused salt. Fused sodium sulphate is a dominant ionic ( $\text{Na}^+$ ) conductor like in normal solutions. Thus, the reaction must involve electrochemical steps and hence this method is most ideal for assessing materials / coatings for hot corrosion resistance.

The electrochemical polarization of alloys in molten salts can cause corrosion attack which is qualitatively similar to that found for a thin salt film in a combustion- product environment. In addition, the 600 hours burner rig test results are well comparable with 4 hour electrochemical test method. It proves that electrochemical techniques are extremely helpful in evaluating the materials / coatings at a faster rate compared to other tests developed so far and hence this method was used extensively by the researchers for the above purpose as well as to study reaction mechanisms and on line monitoring of corrosion rates in the actual plants [35-37]. The advantages and disadvantages of each technique are presented in Table IV. It is important to mention here that no established ISO standard testing procedure is available till now for evaluation of materials and coatings for their hot corrosion resistance and hence the need to establish such standards in near future. In fact, it is an important issue that needs special attention by all researchers in the field.

Technique	Advantages	Disadvanges / limitations
Burner Rig Test	Simulates gas composition, pressure, velocity and temperature of gas turbine engines	Complex process and requires long running time. Difficult to control all the parameters accurately
Furnace Test	Corrosion conditions can be controlled depending upon the requirements i.e. severe or mild corrosion	Difficult to maintain salt deposition rate for longer times
Crucible Test	Most simple and highly useful for preliminary screening of the materials and coatings	Corrosion is severe for alloys or coatings having low or intermediate resistance to hot corrosion
Thermo-gravimetric Test	Precise weight gain measurement possible under different test conditions i.e. gas composition, temperature, salt composition etc.	Not useful for predicting the life of materials and coatings
Electrochemical Test	Fast and useful for ranking the materials and coatings based on oxidation-reduction Phenomenon	Yet to be established fully

**Table 4.** Comparison of hot corrosion evaluation techniques

## 2.4. Influence of superalloy composition

Different superalloys of varied categories namely forged alloys such as Nimonic 75, Nimonic 105, Inconel 718 etc., conventional casting (CC) alloys like Inconel 713, Inconel 100 etc., and directionally solidified alloys such as CM 247 LC, MAR-M200, MAR-M247 etc. were reported for their hot corrosion resistance in different environments. Single crystal superalloys of different generations such as first generation namely CMSX-2, TMS-12, TMS-26, PWA1480, Rene N4 etc., second generation with up to 3 mass % rhenium (CMSX-4, Rene N5, TMS 82+ etc.), third generation with up to 6 mass % rhenium (CMSX-10, TMS-75, TMS 80+ etc., and fourth generation with rhenium and ruthenium (TMS-138 etc.) have been developed recently. The 3<sup>rd</sup> and 4<sup>th</sup> generation superalloys contain large amount of rhenium (Re) as mentioned above and less amount of chromium, exhibits good hot corrosion resistance but susceptible to oxidation. As one of the directionally solidified (DS) superalloys, CM 247 LC alloy exhibits comparable properties as the single crystal alloys. Table V presents different superalloys for which hot corrosion characteristics have been reported in the literature [6, 32, 38-44]. Advancements in superalloys as well as processing techniques have permitted the hot gas path components now to operate in modern gas turbine firing at increased temperatures for significantly increased duration (many thousands of hours) under severe conditions of centrifugal, thermal and vibratory stresses.

Few superalloys have been designed and developed based on phase stability and utilizing predictive techniques by balancing the levels of critical elements (Cr, Mo, Co, Al, W and Ta) in order to maintain good hot corrosion resistance at higher strength levels. One among them is IN 738 superalloy. Therefore, IN 738 is notable as being one of a very small class of modern superalloys that has an outstanding combination of elevated temperature strength and hot corrosion resistance. The balance of these two properties was optimal for heavy-duty gas turbine applications. It was significantly designed for application in land-based gas turbine, as opposed to aircraft use. This alloy was first developed by the international nickel company and subsequently modified its chemistry to improve its castability. This work enabled the successful application of IN 738 over the past 20 years in General Electric gas turbines. Indeed this alloy is now used throughout the entire heavy-duty gas turbine industry with platinum aluminide coatings. Developmental efforts were focused on single processing and advanced DS alloy development. Single crystal airfoils offer the potential to further improve component high temperature materials strength and by control crystal orientation, can provide an optimum balance of properties. In single crystal material, all grain boundaries are eliminated from the material structure and a single crystal with controlled orientation is produced in an airfoil shape. By eliminating all grain boundaries and the associated grain boundary strengthening additives, a substantial increase in the melting point of the alloy can be achieved, thus providing a corresponding increase in high temperature strength. The transverse creep and fatigue strength is increased compared to equiaxed or DS structures. The advantages of single crystal alloys compared to equiaxed and DS alloys in low cycle fatigue (LCF) are shown in Fig. 5. The single crystal alloys (2<sup>nd</sup> generation) have been in use in gas turbine engines since 1995. Together with improved protective coatings, the new materials like third and fourth generation alloys will provide enhanced growth capability for gas turbine engines in the years to come.

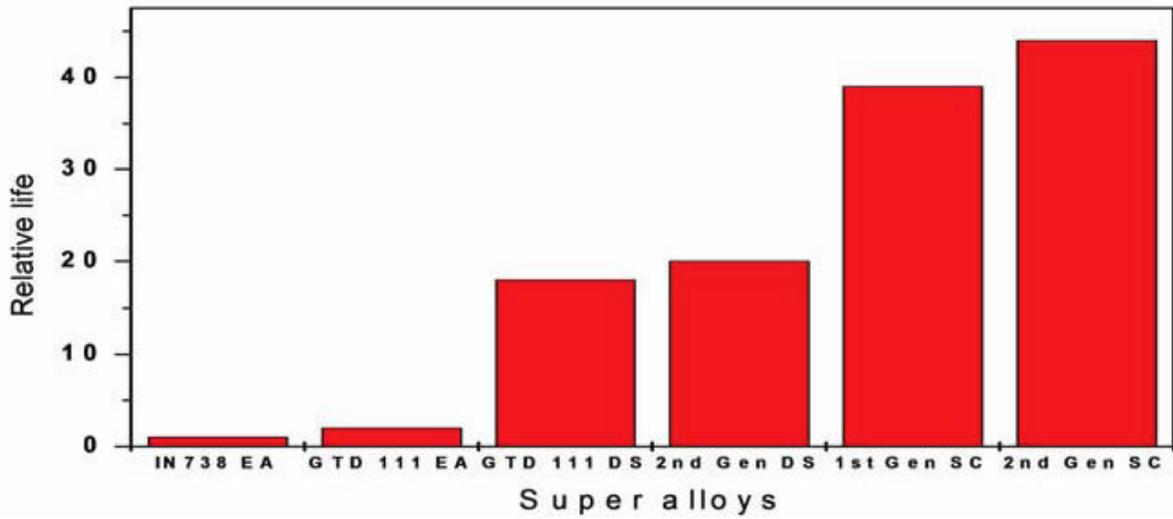


Figure 5. Low cycle fatigue (LCF) of various superalloys

Single crystal superalloys containing rhenium and iridium with low chromium, TMS-75 and TMS-75 + Ir respectively, was observed to exhibit balanced intermediate and high temperature creep, strengths with good hot corrosion resistance based on short term laboratory studies (20 hours only) in 75% Na<sub>2</sub>SO<sub>4</sub> + 25% NaCl (Fig.6) [38]. However, further research is needed on these materials on long term basis with aggressive species like NaCl and V<sub>2</sub>O<sub>5</sub> in order to establish their characteristics.

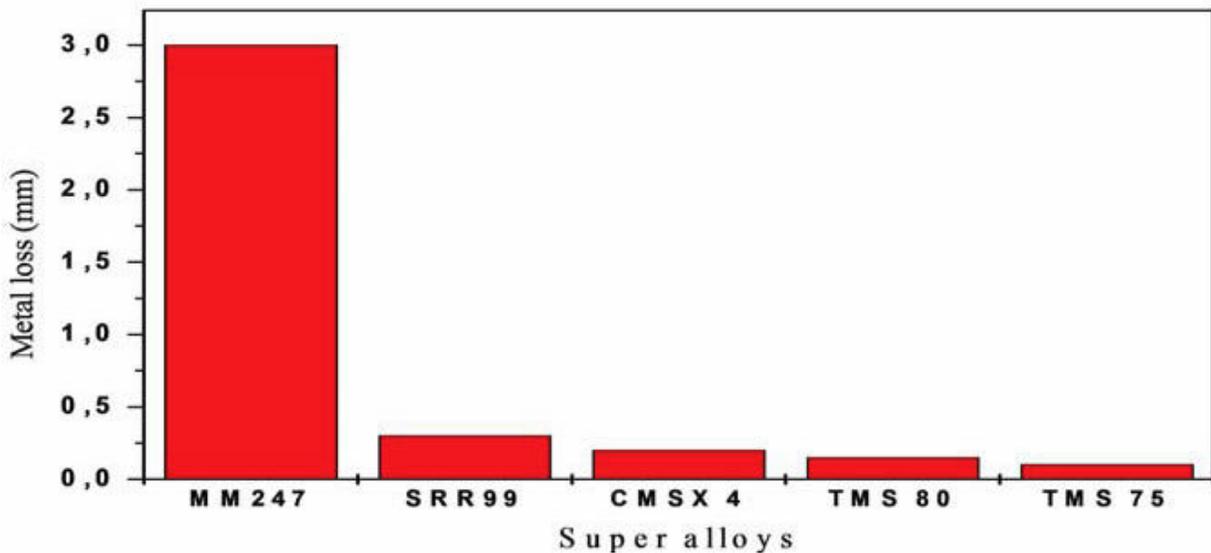
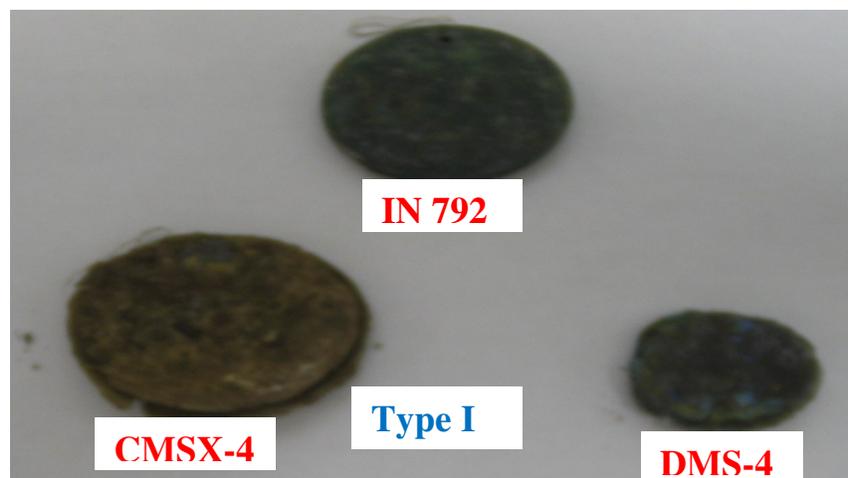


Figure 6. Hot corrosion resistance of different superalloys in 75% Na<sub>2</sub>SO<sub>4</sub> + 25% NaCl at 900° C for 20 hours [38]

Fig.7 shows the hot corrosion behavior of few superalloys like IN 792, CMSX-4 and DMS-4 under type I conditions. The hot corrosion resistance of CM 247 LC and Rene 80 Superalloys

under type II and type I conditions in chloride and vanadium environments are also presented in Fig.7. Appreciable corrosion was observed for all the superalloys. It indicates that hot corrosion plays a significant role in causing faster degradation, thereby reducing the superalloy life considerably. Among the superalloys, CM 247 LC was corroded severely indicating that the superalloy is highly susceptible to hot corrosion. The appreciable corrosion attack of CM 247LC superalloy was clearly evidenced by observing big cracks, broken samples (Fig.7) and large corrosion affected zone (due to appreciable diffusion of corrosive elements present in the environment). Sulphur diffusion and formation of metal sulphides preferentially chromium and nickel sulphides was reported to be the influential factor [6]. When sulphide phases are formed in superalloys, Ni- based alloys are inferior to cobalt and iron based alloys, which are especially effective in destroying the corrosion resistance of alloys [26, 36-42]. In fact, the alloying elements play a significant role and decide the life of superalloys under hot corrosion conditions.



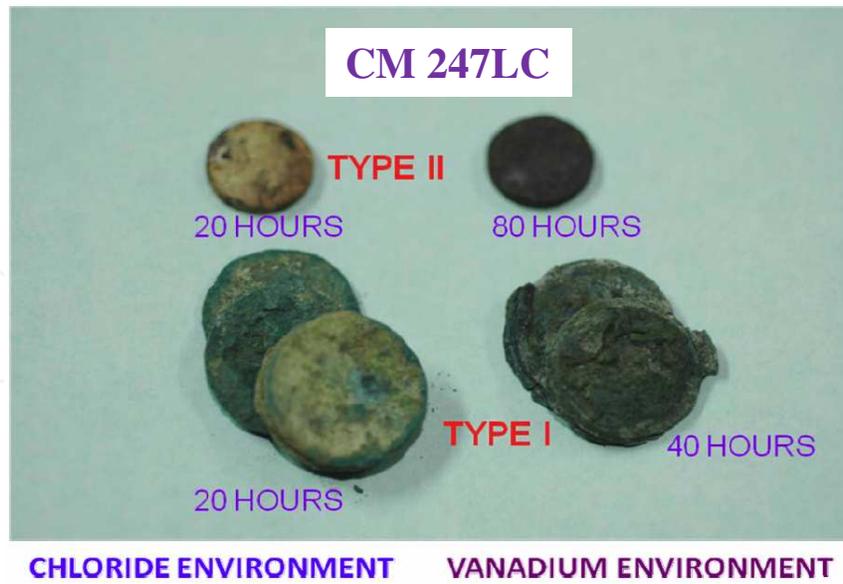


Figure 7. As hot corroded superalloys in various environmental conditions

Alloy	Al	Ti	Cr	Co	Ni	W	Ta	Re	Mo	Hf	Ir	Others
NIMONIC 75	-	0.4	20	-	Bal	-	-	-	-	-	-	Fe, C
NIMONIC-105	4.7	1.3	15	20	Bal	-	-	-	5.0	-	-	C
INCONEL 100	5.5	5.0	10	15	Bal	-	-	-	3.0	-	-	Zr,C,B,V
INCONEL 713	6.0	0.8	12.5	-	Bal	-	1.75	-	4.2	-	-	Zr,C,B,Nb
MAR M200	5.0	2.0	9.0	10	Bal	12.5	-	-	-	-	-	Zr,B,C,Nb,Fe
IN 738	3.4	3.4	16	8.3	Bal	2.6	1.75	-	1.75	-	-	Cb,Fe,C
CMSX-4	5.3	1.0	6.5	10.4	Bal	6.1	4.9	0.8	-	-	-	-
MAR M-247	5.5	1.0	8.0	10.0	Bal	10.0	3.0	-	0.6	1.5	-	B,Zr,C
MAR M-509	-	0.2	23.5	55	10	7	3.5	-	-	-	-	Zr,C
CM 247LC	5.6	0.7	8.1	9.2	Bal	8.5	3.2	-	0.5	1.4	-	B,Zr,C
INCONEL 718	-	-	18	-	Bal	-	-	-	3.0	-	-	Fe,Cb-
CMSX-10	5.7	0.2	2.0	3.0	Bal	5.0	8.0	6.0	0.4	0.03	-	-
TMS-75	6.0	-	3.0	12.0	Bal	6.0	6.0	5.0	2.0	0.1	-	-
TMS-80	5.8	-	2.9	11.6	Bal	5.8	5.8	4.9	1.9	0.1	3.0	-

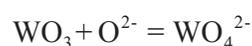
Table 5. Typical superalloys characterised for their hot corrosion resistance [6, 32, 38-44]

Some Ni-based superalloys were designed with the aid of d-electrons concept for industrial turbines. They developed based on the molecular orbital calculations of the electronic struc-

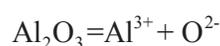
tures of Ni-alloys i.e. based on two electronic parameters such as bond order between an alloying element and nickel atoms  $B_o$ , and d-orbital energy level of alloying element  $M_d$ . Some single crystal superalloys were designed based on this concept. The experimental data on the designed single crystal superalloys was reported to be satisfactory [38-39]. However, the need is essential in order to establish the concept for development of hot corrosion resistant Ni-based superalloys as the superalloys should satisfy both high temperature strength and high temperature corrosion resistance, which is a highly difficult task. It is due to fact that same alloying elements never help to improve both high temperature strength and corrosion resistance simultaneously as mentioned earlier.

From the metallurgical point of view, it is known that high temperature strength can be obtained by maintaining certain phases that are responsible for high temperature strength. Since the main motive for metallurgists is to improve the mechanical strength of an alloy at elevated temperatures, the addition of certain alloying elements is essential in order to form  $\gamma'$  and solid solution strengtheners. Among the alloying elements, the significant reduction of chromium content and addition of certain elements like tungsten, molybdenum, vanadium etc. makes the superalloys highly susceptible to hot corrosion [6, 26, 41]. Tungsten (W) and Mo dissolve in  $\gamma$ -phase of the matrix and strengthen the alloy. These elements are particularly effective for improving long-term strength of the alloy. However, excessive addition causes the formation of harmful sigma phase and affects the strength of the alloy. Suitable contents for obtaining good strength are 2 to 15% of W and 6% or less of Mo. The addition of titanium and tantalum produces beneficial effects while small additions of manganese, silicon, boron and zirconium do not significantly influence the hot corrosion resistance of superalloys. Carbon addition is detrimental as the carbide phases provide sites for initiation of hot corrosion [26]. With a large content of chromium and small amount of titanium, hot corrosion resistance of Nimonic-75 is very good [32]. The addition of molybdenum and iron made the Inconel 718 less corrosion resistant [6]. The addition of 9.5% tungsten and minor additions of other elements rendered CM 247LC highly susceptible to hot corrosion [6]. The tungsten present in the alloy forms acidic tungsten oxide ( $WO_3$ ), due to which fluxing of protective oxide scale takes place easily. It is important to mention that this type of acidic fluxing is self-sustaining since  $WO_3$  forms continuously that leads to severe degradation of superalloys. The degradation mechanism comprises two steps as follows:

- a. The tungsten present in the superalloys reacts with the oxide ions present in the environment and forms tungsten ion



- b. As a result, the oxide ion activity of the environment decreases to a level where acidic fluxing reaction with the protective alumina can occur



A similar reaction mechanism occurs if the superalloys contain other refractory elements like vanadium and molybdenum [26, 40].

Cobalt (Co) and chromium (Cr) contents affect the hot corrosion resistance of superalloys. If Co is added excessively, it promotes precipitation of harmful inter-metallic compounds that deteriorates high temperature strength. An appropriate content of Co is 10.5% or less. Cr improves hot corrosion resistance. However, if it is added excessively, it causes precipitation of harmful sigma-phase and coarsening of carbides, thereby deteriorating high temperature strength. An appropriate additive amount of Cr is in a range of 5 to 14%. Aluminium and titanium contribute to improvement of high temperature strength by forming  $\gamma'$ -phase i.e.  $\text{Ni}_3(\text{Al,Ti})$ , which is a strengthening factor of the Ni-based alloys. They improve hot corrosion resistance. Appropriate amounts of Al and Ti are in ranges of 4 to 7% and 0.5 to 5% respectively.

Nb, Ta and Hf dissolve in  $\gamma'$ -phase, which is a strengthening factor and improve high temperature strength of the superalloy. However, if they are added excessively, they segregate at grain boundaries and reduce the strength of the alloy. Appropriate additive contents of Nb, Ta and Hf are, respectively, 3 % or less, 12% or less and 2% or less and preferably 0.2 to 3% of Nb, 3 to 4% of Ta and 0.5 to 1.0% of Hf. Zr and B strengthen grain boundaries and improve high temperature strength of the alloy. Since the addition of these elements are in the low range and there is no much effect on hot corrosion resistance of the superalloys.

The common alloying element for the new generation superalloys is rhenium [41-44]. In rhenium containing superalloys, the Re atoms dissolve preferentially in  $\gamma$  matrix, retards the over-ageing of  $\gamma'$  dispersed phase thereby increase  $\gamma$ - $\gamma'$  misfit. In addition, Re atoms form small domains (clusters) of approximately 1nm diameter, act as barriers to the dislocation movements. The formed clusters improve the creep resistance of the superalloys. Kobayashi et al have reported that Re also helps in improving the hot corrosion resistance though significantly low chromium is present in superalloys [38]. However, the exact mechanism based on which the hot corrosion resistance improved was not reported. It was also reported that rhenium containing superalloys are susceptible to oxidation. It indicates that the oxide scale that forms upon exposure is not protective. It should not form either alumina or chromia scale due to significantly low contents of aluminium and chromium. Extensive studies have been carried out recently with and without Re containing superalloys in order to understand the role of rhenium and confirmed that Re containing superalloys are highly susceptible to high temperature oxidation as well as both types of hot corrosion [41, 45-47].

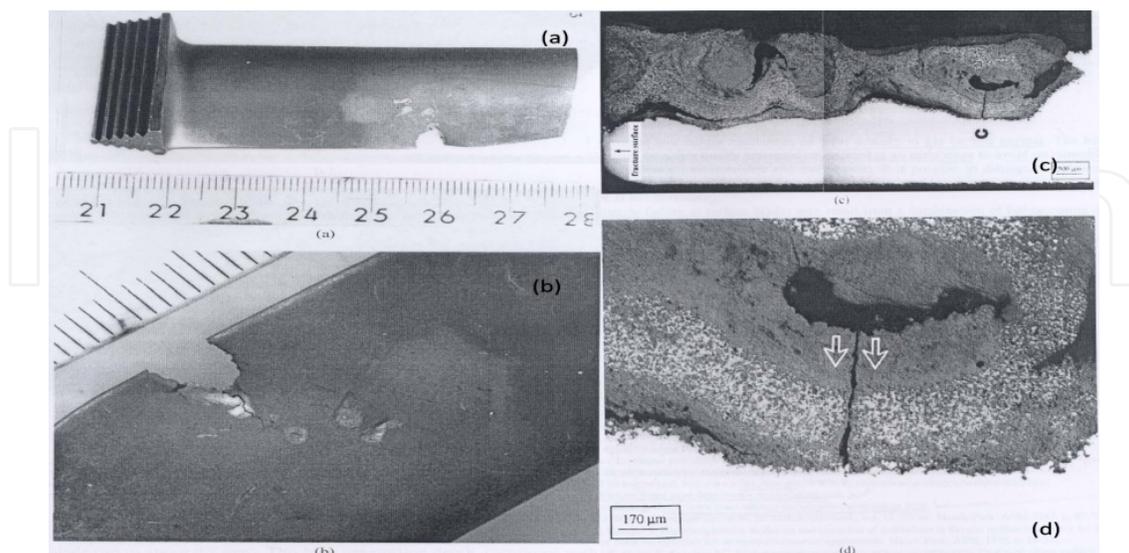
#### 2.4.1. Degradation mechanisms

The mechanisms proposed earlier are sulphides formation and subsequent transformation to corresponding alloy element oxides. Later, it was reported that degradation of superalloy take place due to fluxing processes. Fluxing processes are divided into two types such as acidic and basic fluxing process. The nature of fluxing process depends on the alloying elements and their concentration in the superalloys. It also depends on the environment to which the superalloys are exposed. In the fluxing process, the corresponding oxides dissolve in the components of environment and cause to degrade the superalloys at a much faster rate.

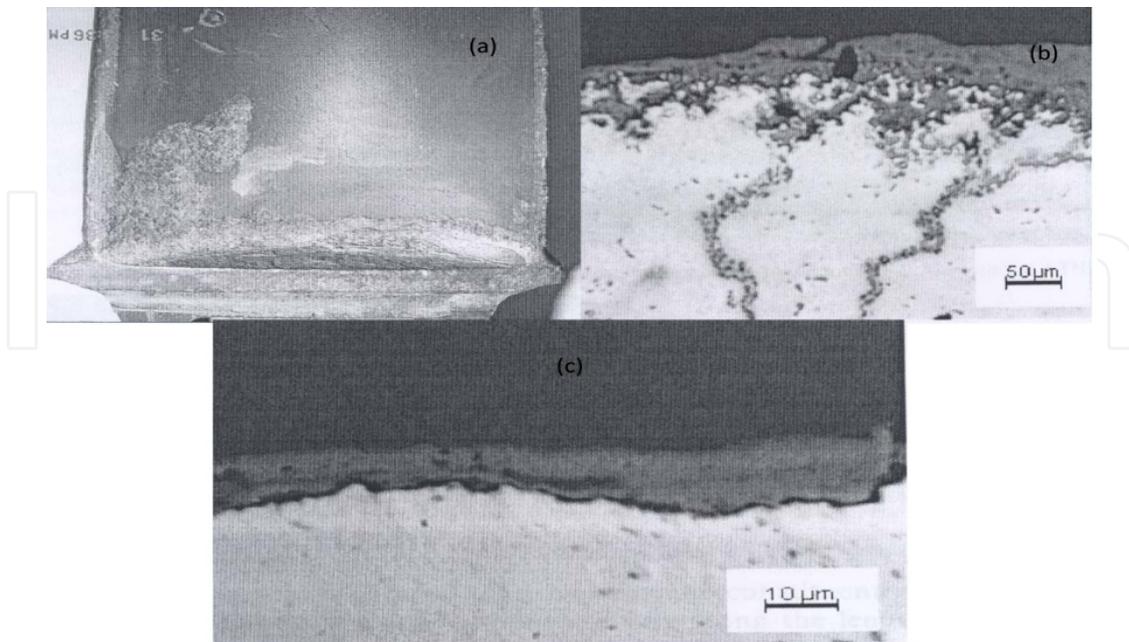
Recently, an electrochemical mechanism was proposed and experimentally proved that all the superalloys, irrespective of their alloying elements and concentration and any type of environments to which they are exposed, degrade due to electrochemical reactions that take place during hot corrosion process. Hence, the electrochemical techniques are more suitable for assessing newly developed superalloys and their ranking [6].

### 3. Coatings

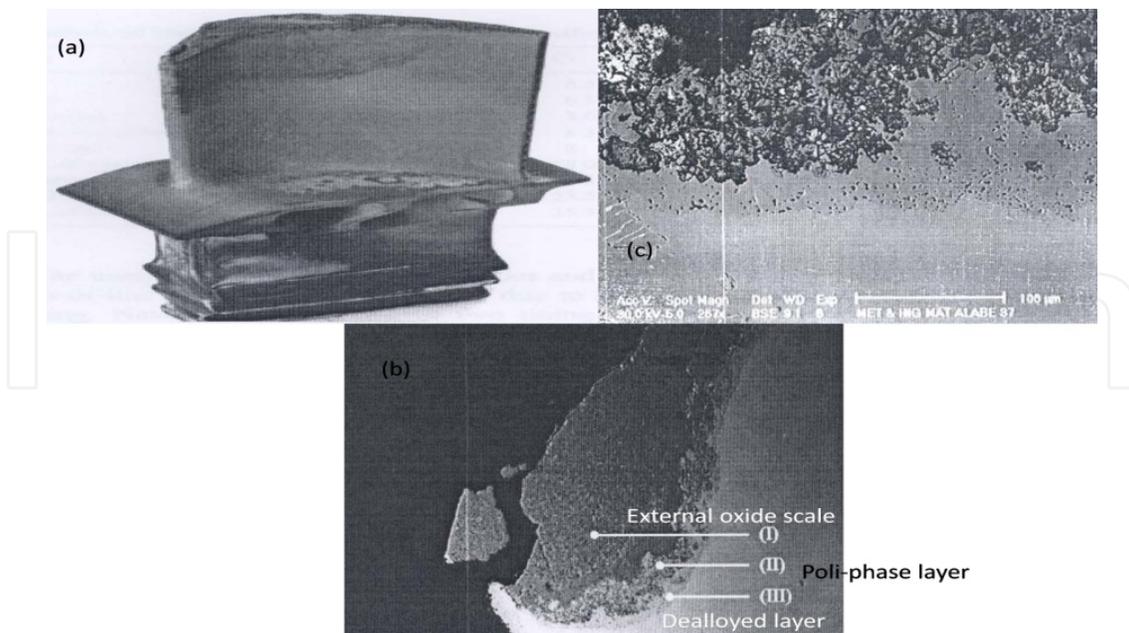
There are a number of cases reported in the literature where the gas turbine blades suffered severe corrosion due to which failures took place [2-5]. Failure investigations confirmed that it was due to hot corrosion, in which extensive penetration of sulphur took place into the material leading to the formation of metal sulphides that in turn led to reduction in mechanical properties of the materials resulting in catastrophic failures (Figs. 8, 9, 10). From literature it is also understood that it is not possible to develop an alloy having both high temperature strength and hot corrosion resistance simultaneously since alloying elements often have opposing effects on the two properties. Particularly, tungsten, molybdenum and vanadium additions to superalloys are helpful in improving the high temperature strength, but their presence make the superalloys highly susceptible to hot corrosion as mentioned above. High performance coatings that can withstand environmental degradation problems such as oxidation and hot corrosion become important. Therefore, it is mandatory to prevent hot corrosion by using appropriate coating technology [41, 46] so as to increase the life of gas turbine components to the designed service life (Fig.11).



**Figure 8.** a) Macroscopic view of damaged blade b) a crack propagating into remainder material c) micrograph showing advanced hot corrosion attack d) secondary crack propagation [3]



**Figure 9.** a) Macroscopic view of hot corrosion affected blade b) grain boundary diffusion and subscale sulphide particles indicating type I hot corrosion c) no grain boundary diffusion and subscale sulphide particles indicating type II hot corrosion [4]



**Figure 10.** a) Macroscopic view of failed blade b) corroded region consisting of three layers c) internal layer of corrosion products [5]

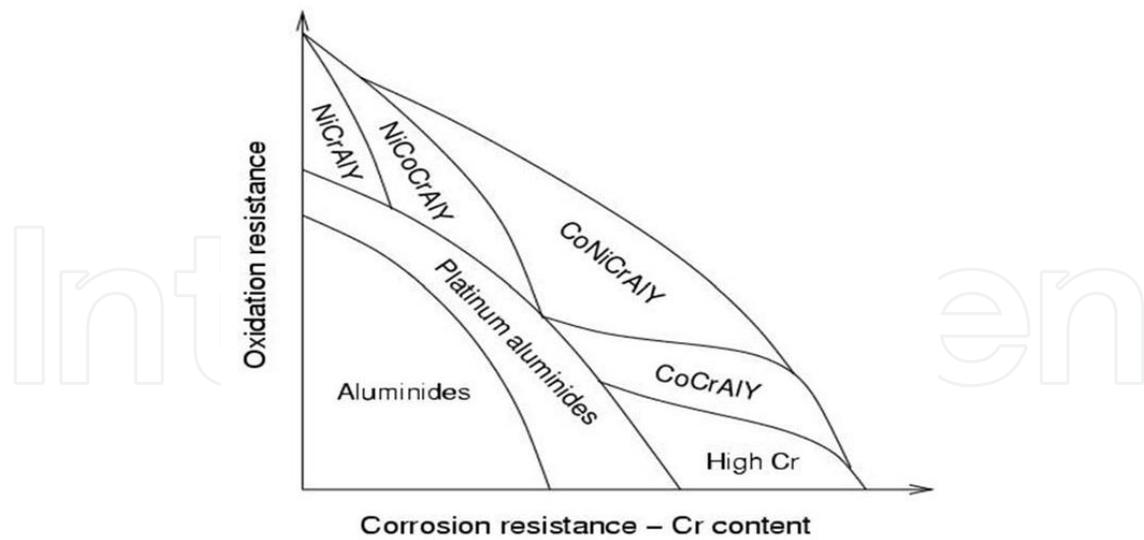


Figure 11. Oxidation and hot corrosion resistance of various coating systems [46]

The blade coatings are usually of either MCrAlY type (where M is Ni or NiCo) or aluminides. These coatings can provide protection against oxidation and hot corrosion and act as bond coatings for zirconia based thermal barrier coating (TBC) systems. In both the cases, slow growth rates and optimum adherence of the alumina scales formed on the coatings during high temperature exposure are of significant for component life. These requirements can be fulfilled only by using coatings with sufficiently high aluminium contents to ensure protective alumina scale formation and re-healing after oxide spallation / reaction with the environment. The life of a coating is mainly limited by aluminium depletion occurring upon aluminium consumption as a result of alumina scale growth and repeated spallation and re-healing of the alumina scale during oxidation process. If a point is reached where the aluminium level in a bond coating falls below the level at which protective alumina scale can not be formed preferentially, faster interaction between the corrosive species present in the environment and the non-protective oxides of other constituents of the bond coating occurs and thereby affects the coating life considerably under hot corrosion conditions. Further, the constituents of ceramic thermal barrier coatings react easily with the corrosive species and shorten the coating life significantly. These aspects are covered in detail in subsequent sections.

Another important aspect is the selection of suitable surface engineering technique by which the coatings are applied since the life of a coating depends not only on coating composition but also on the surface engineering technique employed for coating. Therefore, selection of appropriate surface engineering technique as well as suitable coating composition becomes a challenging task.

### 3.1. Technologies

Surface engineering technique, which modifies properties of the component's surface to enhance their performance should not only be effective but also economical. The following are the most common surface engineering techniques available at present:

- a. Electro-deposition
- b. Diffusion coating processes
- c. Thermal spray techniques
- d. Ion implantation
- e. Hardening & cladding
- f. Selective surface hardening by transformation of phase and
- g. vapour deposition.

Electro-deposition, diffusion and thermal spraying techniques are widely in use to improve the surface of components for hot corrosion resistance. Particularly, thermal spray and vapour deposition techniques are the most efficient techniques for prolonging the life of components significantly.

### 3.2. Thermal spraying processes:

The coatings applied by these processes have the advantage over other techniques i.e. the coating composition can be tailored to suit the specific requirements. Thermal spraying processes can broadly be divided into following techniques:

- i. Flame Spraying
- ii. Arc Spraying
- iii. High Velocity Oxyfuel Spraying
- iv. Detonation Gun
- v. Air Plasma Spraying
- vi. Vacuum Plasma Spraying

#### 3.2.1.1. Flame Spraying

In this process, an oxygen-acetylene mixture is passed through a nozzle and ignited to form a combustion flame. Coating powder or wire is fed into the flame, accelerated and projected onto the substrate to form deposit. The combustion flame temperature is limited to 3000° C and gas particle velocities are relatively low.

#### 3.2.1.2. Arc spraying

This process involves the production of molten particles at the tips of two consumable wires via resistance heating. The material is subsequently atomized and projected onto the substrate by a compressed air jet. The process is limited to the spraying of conductive wires, relatively cheap and can achieve high deposition rates.

### 3.2.1.3. High Velocity Oxy-fuel Spraying (HVOF)

This process involves combustion of a fuel gas with oxygen at high pressure. This creates high velocity flame propelling powdered coating materials onto a substrate. This technique can produce high quality coatings for gas turbine applications.

### 3.2.1.4. Detonation gun spraying

D-Gun and Super D-Gun are developed by Union Carbide, use the energy released by a controlled series of oxygen-acetylene to heat and accelerate the coating powder to high velocities and to propel the powder onto the substrate. The resulting coatings are highly dense and of high quality with a low content of oxide and unprocessed particles.

### 3.2.1.5. Air Plasma Spraying (APS)

In air plasma spraying, a DC arc struck between a central inert cathode and an annular copper anode is used. An inert gas is fed into the arc to form high temperature plasma. Powder is fed into the plasma and is ejected at a high velocity towards the substrate.

### 3.2.1.6. Vacuum Plasma Spraying (VPS)

This process has several advantages over APS. The problems associated with air contamination of the plasma jet gets eliminated, the plasma jet is longer than in air and can achieve 400-600 ms<sup>-1</sup> particle velocities due to which high purity and dense deposits are obtained. A further advantage is coating adhesion. Table VI illustrate the characteristics of various thermal spraying processes [47].

Kuroda et al were developed a novel coating technique namely “warm spray” process recently which incorporates the advantages of both HVOF and cold spray [48]. Further developments may enable them to develop coatings with enhanced hot corrosion resistance.

Process	Gas temperature <sup>o</sup>	Particle Velocity m/s	Adhesion Mpa	Oxide content %	Porosity %	Deposition Rate Kg/Hour	Typical Deposit thickness mm
Flame	3000	40	8	10-15	10-15	2-6	0.1-15
Arc wire	N/A	100	12	10-20	10	12	0.1-50
HVOF	3000	800	>70	1-5	1-2	2-4	0.1-2
Detonati-on gun	4000	800	>70	1-5	1-2	0.5	0.05-0.3
APS	12000	200-400	4 to >70	1-3	1-8	4-9	0.1-1
VPS	12000	400-600	>70	ppm	<0.5	4-9	0.1-1

**Table 6.** A comparison of thermal spraying processes [47]

### 3.3. Electron Beam Physical Vapour Deposition (EB-PVD) processes

The electron beam-PVD process has made the most significant impact over the PVD processes in respect of coating rotating blades. The microstructure of the coating is controlled very closely in this process and coating process is slow compared to conventional PVDs. Thermal barrier oxide coatings obtained with this process has a unique columnar structure with high in-plane compliance, which tends to have higher thermal conductivity and has shown to survive longer thermal cycle life as compared to plasma sprayed TBC. Table VII provides the comparison of different processes and their limitations [47].

Coating type	Advantages	Disadvantages /limitations
Diffusion (e.g. Aluminides)	Simple to produce, proven ability <math><900^{\circ}\text{C}</math>, inexpensive	Thickness limited to 50 $\mu\text{m}$ . Brittle at <math><750^{\circ}\text{C}</math> and degrade by inter-diffusion. Available compositions are limited.
Plasma overlays	High rates of coating and wide range of compositions are available. Thickness not process limited ( 100 $\mu\text{m}$ )	Rough surface and single line of sight coating than EB coatings. Thin multi-layers more difficult than EB. About 15% porosity and degrade by inter-diffusion.
EB-PVD overlays	Good control of microstructure, low contaminant level and control the composition within limits. Layered and graded coatings easily achieved and multi component processing is possible.	Low rates of deposition and expensive process. Degrade by inter-diffusion.
Plasma Spray Thermal Barrier	High rate of coating and wide range of compositions are available. Layered and graded coatings are possible. Porosity is an advantage and not limited by inter-diffusion.	Single line of sight coating and difficult to modify microstructure. High stresses generated in coatings.
EB-PVD Thermal Barrier	Good control of microstructure and low contamination level. Layered and graded coatings are possible and not limited by inter-diffusion.	Low rate of deposition and multiple component processing is possible. Expensive process and generates high stresses but relieved by structure control.

**Table 7.** Comparison of thermal spray and EB-PVD processes [47]

### 3.4. Metallic coatings

The present coatings are broadly divided into two types, diffusion and overlay.

#### 3.4.1. Diffusion coatings

In diffusion coating application process, aluminium is made to react at the surface of substrate, forming a layer of mono-aluminide. For coatings applied over Ni-based superalloys, nickel

aluminide is the resulting species. This type of coatings and surface modification is one of the most widely used for tailoring the surface properties of components. Pack cementation is well-established chemical vapour deposition technique, which has been in use for nearly three decades. It is relatively a simple technique, which consists of immersing the components to be coated in a powder mixture placed in a sealed or semi-sealed retort. The entire apparatus is placed inside a furnace and heated in a protective atmosphere to a high temperature for a sufficient period to form a coating. Most blade and vane coatings were applied by pack cementation since 1970 and subsequently chemical vapour deposition (CVD) process. The surfaces of internal cooling passages are coated more effectively by forced flow gas phase aluminizing and by vacuum pulse aluminizing. From 1970's onwards, developments in the area of diffusion coatings include modification of aluminide coatings with chromium, silicon and platinum. In 1990's aluminide coatings were recognised as useful bond coatings for thermal barrier coatings (TBCs). Advanced systems started using platinum aluminides and MCrAlY coatings [24, 28, 49-50]. The most developed pack cementation processes include aluminizing, chromizing and siliconising. Under this category, two types of processes can be applied; low activity, where the aluminide coating is formed by outward diffusion of nickel from the base metal, or high activity, where the aluminide coating is formed by inward diffusion of aluminium and subsequent heat treatment. High activity process is most suitable for gas turbine applications to combat oxidation but it is susceptible to hot corrosion.

The most important improvement in the diffusion coatings has been the incorporation of platinum in aluminide coatings. This process involves the deposition of platinum by electrochemical method followed by aluminizing at the suitable temperature for the required period. These coatings became the accepted standard for turbine hot components to combat oxidation as well as hot corrosion. The principal reason for superior performance of these coatings is that the coefficient of thermal expansion of the coating is lower compared to that of underlying superalloy. In addition, platinum enhances the activity of aluminium and allows the formation of continuous alumina scale during high temperature exposure coupled with good adherence, thereby prolonging the life of turbine blades considerably. Failure of coatings under turbine service conditions takes place due to inter-diffusion between the coating and the substrate, with the loss of protective capability. Though diffusion coatings are well bonded to the substrate they have limited compositional flexibility and their usefulness is strongly dependent on substrate chemistry.

#### 3.4.2. *Overlay coatings*

To develop coatings with compositions nominally independent of substrates and with capabilities for tailoring to a wide range of requirements for gas turbine applications, overlay coatings were emerged. Coatings of this type are generally called MCrAlY coatings and essentially comprise a mono-aluminide component contained in a more ductile matrix of a solid solution. The supply of aluminium for formation of protective alumina scale comes largely from the dispersed mono-aluminide phase during the useful life of such coatings. Overlay coatings are typically well bonded and have a wide compositional flexibility. Research and development on this type of coatings has led to a variety of compositions with improved

scale adherence. The function of all coatings is to provide a surface reservoir of critical elements that will form very protective and adherent oxide layers, thus protecting the underlying base materials from oxidation as well as hot corrosion.

Low pressure plasma spraying has been mostly used to apply MCrAlY coatings to critical components such as the high pressure rotor blades because it can produce dense coatings with little oxidation and good adhesion. It has been shown that MCrAlY coatings prepared with air plasma spraying has much inferior oxidation resistance due to severe oxidation during spraying and resultant loss of aluminium during spraying. HVOF sprayed MCrAlY has been increasingly adopted due to its dense and well-controlled oxidation.

### 3.4.3. *Advances in metallic coatings*

The efficiency of a gas turbine engine (aircraft, industrial, marine) is directly proportional to firing or turbine inlet temperature. Increase in temperature is facilitated by improved structural design and airfoil-cooling technology applied to higher strength-at-temperature alloys cast by increasingly complex processes and coated with steadily improved protection systems. First stage turbine blades, the most critical components of gas turbines, made from Ni-based superalloys and augmented by coatings, have been singularly successful materials for the past several years. The turbine airfoils coatings are simple and modified diffusion aluminides, MCrAlY overlay systems and overlay thermal barrier coatings.

The oxidation resistance of alloys and coatings depends upon selective oxidation of elements such as aluminium, chromium or silicon present in the alloy / coating. Oxide scales of  $\text{Al}_2\text{O}_3$  are more effective means for developing oxidation resistance at higher temperatures and  $\text{Cr}_2\text{O}_3$  or  $\text{SiO}_2$  at lower temperatures. However, under hot corrosion conditions, the properties of oxide scales are different. The protective oxide scale should not react with the corrosive environment and at the same time, it should not allow the corrosive species to diffuse into the coating. Therefore, development of a suitable coating is of great interest for such applications. Recent results have demonstrated the necessity of protective coatings with a higher degree of high temperature capability than the existing coating systems in order to prolong the life of superalloy components under hot corrosion conditions [26-30]. Coatings with sufficiently high aluminium contents to ensure protective and chemically inert alumina formation and re-healing after reaction with the corrosive environment can only satisfy these requirements. Literature review reveals that the platinum aluminide coatings perform well under high temperature oxidation and type I hot corrosion conditions, but the performance is poor under type II hot corrosion conditions, although the performance is superior to conventional aluminides. The choice therefore, appears to be MCrAlY based overlay coatings. The chromium rich and /or silicon containing MCrAlY coatings offer improved corrosion resistance at lower temperatures that are encountered in gas turbine engines. However, recent results have shown that Si containing MCrAlY coatings are detrimental to hot corrosion and life reduces significantly at higher temperatures. However, the MCrAlY coatings without Si offer good oxidation and hot corrosion resistance at higher temperatures. As mentioned earlier, the lives of the coatings are mainly limited by aluminium depletion occurring upon aluminium consumption as a result of alumina scale growth and repeated spallation / reaction and re-

healing of the alumina scale during oxidation and type I hot corrosion conditions. Similar is the case with chromia scales under type II hot corrosion conditions.

Stringer has outlined the basic rules for proper selection of a coating for the given application [51]. The hot corrosion resistance of the aluminide coating has improved by the addition of yttrium. Swadzaba et al [52] have shown that regeneration of aluminide coatings on turbine blades, which have worked in highly corrosive environments, is possible to regain their initial properties. The recommended regeneration techniques are pack cementation for vanes and the slurry technique for rotating blades. The degradation of aluminide-coated first-stage blades in the engines of a light military helicopter operated by the Royal Australian Navy (RAN) was reported [53]. The different modes of degradation are foreign object damage, erosion, hot corrosion, coating cracking and coating alloy inter-diffusion. Small concentrations of NaCl, as low as 10 ppm in the gas stream with Na<sub>2</sub>SO<sub>4</sub> cause hot corrosion more severe and attack is greater if NaCl is in solid state.

An overview on protective coatings for gas turbine applications, their role and design was given by Goward [54]. The performance of various pack, gas phase, and noble metal aluminide and overlay coatings applied on F100 first stage turbine blades under simulated service conditions were studied and estimated their relative lives [55]. Ni-Co-Cr-Al-Y overlay coating showed superior performance compared to other coatings in 300 hrs tests. The novel technique namely "Law of mixtures" for evaluation of mechanical properties of aluminide coatings over the temperature range 20-1000<sup>o</sup> C and the ability of the technique to predict the mechanical behaviour was reported [56]. The high temperature corrosion of a commercial aluminide coating on IN-738LC and MAR-M002 at 700 and 830<sup>o</sup> C was found to degrade with different mechanisms at two temperatures. Meethan reviewed various types of protective coatings used in the turbine and combustor sections of gas turbine engines operating in aero environments [57]. He described the factors affecting the coating selection for turbine rotor blade applications and the aluminide coatings continue to provide good and cost effective protection on many turbine blades. The several environmental effects on the mechanical properties of coated superalloys and comparative performance of various coatings are provided [58].

It is widely accepted that multi-layered and graded compositions can offer significant advantages over single layered coatings. A composite coating of aluminide-yttrium exhibits good stability and excellent corrosion resistance in a cyclic high temperature hot corrosion environment [59]. Yttrium addition helps in forming Y<sub>2</sub>O<sub>3</sub> and (Y, Al) O-type compounds in grain boundaries of Al<sub>2</sub>O<sub>3</sub> and NiAl effectively prohibits the fast diffusion of oxidants, thus helps to improve the hot corrosion resistance significantly. Improvement of hot corrosion resistance of the aluminide coating by the addition of yttrium has also been reported in another study. There is a work by a Japanese group showing that elimination of yttrium from MCrAlY has a positive effect on slowing down the TGO growth rate [60].

Platinum aluminide coatings are more resistant to hot corrosion than simple aluminides on land based gas turbines. The role of platinum in improving the hot corrosion resistance of pt-modified aluminide coating through electrochemical method revealed that platinum significantly improves the resistance to basic fluxing by increasing Al<sub>2</sub> O<sub>3</sub> content in the platinum rich surface. Due to this, the difference in breakthrough potential between the two coatings

was found to be 400 mV. The platinum free coating was found to corrode severely while coating with platinum showed slight corrosion after 310 hrs in free corrosion test. However, platinum modified aluminide coatings and simple aluminide coatings are having the same resistance to acidic fluxing.

Significant amount of work was carried out in developing the hot corrosion resistant MCrAlY bond coatings [8, 28, 61-62] and the lifetimes of various coatings including platinum aluminide, tested in number of engines is presented in Table VIII. The lifetime of MCrAlY system has been found to be improved considerably by aluminizing or incorporating platinum into the system. MCrAlY based bond coatings play a significant role in providing rough surface for the application of thermal barrier coatings and to provide protection for the alloy from oxidation and / or hot corrosion. Due to proven performance of these coatings for a variety of superalloys for over two decades in different applications, MCrAlY coatings have been studied extensively [28, 63-65]. It is important to mention that the durability of the MCrAlY coating also depends on the coating technique employed. The life of coating applied by arc ion plating is significantly lower as the attack occurs at the edges due to large variation in thickness i.e. about 6 times less than the coating thickness at the middle. Different degradation mechanisms proposed are oxidation followed by scale cracking and spallation, mixed oxidant attack, erosion and molten salt induced attack.

System	Coating	Relative lifetime
Land based aircraft DS MAR-M200+Hf	Uncoated	<<0.5
	Standard aluminide (PWA 73)	1.0
	Rh-Al (BB)	<1.5
	Gas phase aluminide (PWA 275)	<1.5
	Modified aluminide (PWA 263)	1.5
	Pt-Al (RT 22)	1.5
	NiCoCrAlY overlay (PWA271)	2.75
Marine aircraft MAR-M002	Standard aluminide	1
	Pt-Al	2.5-3
	CoCrAlY	2
Industrial IN 738	Uncoated	1
	PtCrAl	>3
	CoCrAlY (plasma sprayed)	>2
	CoCrAlY (clad) plus Al diffusion coating	>6
	FeCrAlY	2
Marine Rene 80	Standard aluminide	1
	Rh-Al	1-2
	CoCrAlHf	2
	CoCrAlY	1
	CoCrAlHfPt	2.3

**Table 8.** Lifetimes of coatings for aero, industrial and marine gas turbines [8]

The effect of aluminium in forming a thermodynamically and chemically hot corrosion resistant layer and thereby improving the life of the components by reducing mass gain in MCrAlY coatings is very essential. Further, optimum content of aluminium in the coatings is extremely necessary to enhance their lifetime. In fact, it only decides the lifetime of coatings and hence the essentiality of aluminium reservoir in the coatings.

### 3.5. Optimization of aluminium content

Fig.12 illustrates the influence of aluminium on weight loss in the MCrAlY based coating model alloys [30]. It is very clear that aluminium plays a major role in affecting the hot corrosion resistance of MCrAlY alloys though the concentration of other alloying elements remains constant. The weight loss is maximum for the model alloy containing 6% aluminium, decreases with increase in aluminium content to 9% and minimum weight loss is observed for the alloy containing 12% aluminium. The behaviour is same for all the model alloys irrespective of cobalt content i.e. whether the cobalt is 10 % or 20% (Fig.12). Therefore, the minimum amount of aluminium required to be present in the MCrAlY based bond coatings is 9%. It is very important to mention that the optimum content of aluminium required for providing good hot corrosion resistance is 12%, though its effect is marginal when compared with 9% aluminium containing alloys [26-28].

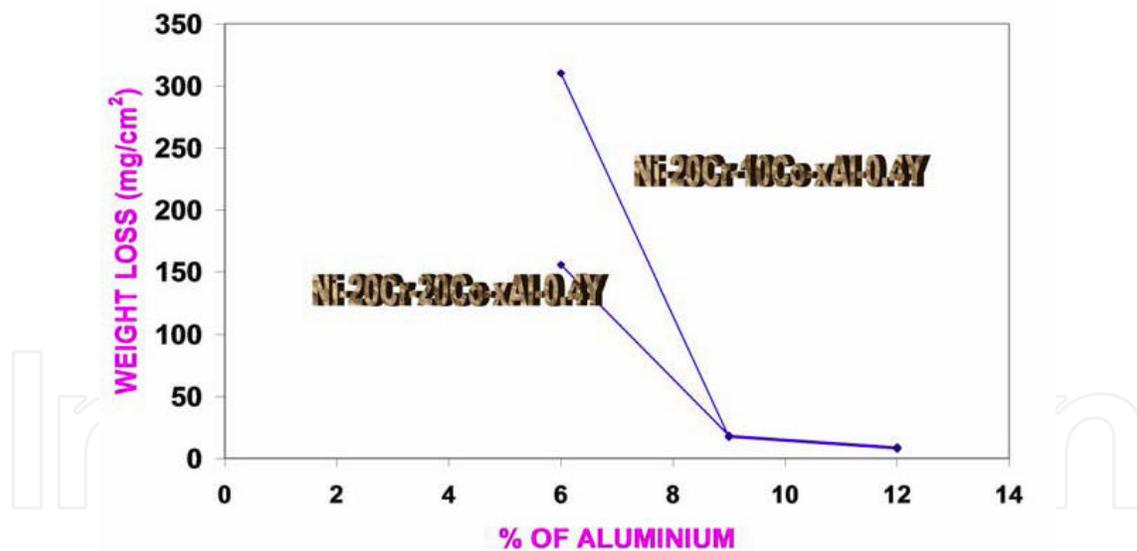


Figure 12. Effect of aluminium on hot corrosion of MCrAlY based coating model alloys [30]

It is also important to mention that the combination of cobalt and aluminium contents is a must to exhibit good hot corrosion resistance. The recent results clearly showed that cobalt plays a significant role in supporting aluminium to form a chemically and thermodynamically stable oxide scale. The optimum amounts of aluminium and cobalt are to be present in the MCrAlY bond coatings. Hence, the combination of cobalt and aluminium in association with chromium, yttrium and nickel provides good hot corrosion resistance [26-29].

### 3.6. Identification of new coating composition

The lives of different typical coatings applied on CM 247 LC alloy exposed at 900<sup>o</sup> C in NaCl and vanadium containing environments showed that the life of coatings varies with the composition and the environment (Table IX) [28]. The NiCoCrAlY coating exhibits maximum life both in sodium chloride as well as in vanadium containing environments. It is interesting to note the effect of absence of cobalt in NiCrAlY and nickel in CoCrAlY coating in reducing the lifetime as maximum lifetime is observed for the NiCoCrAlY coating in both the environments. It is clear that NiCrAlY and CoCrAlY coatings do not improve the lifetime, but the lifetime will be enhanced only if the coating contains Co in NiCrAlY and Ni in CoCrAlY coating. It is also observed that traces of silicon as well as hafnium reduce the coating life drastically (Table IX). It means that hafnium or silicon-containing compounds readily react with the corrosive salts at elevated temperatures and thereby reduce the coating life considerably [26-29]. Therefore, the ideal combination is 22% cobalt and 12% aluminium along with 18% chromium and 0.5% yttrium.

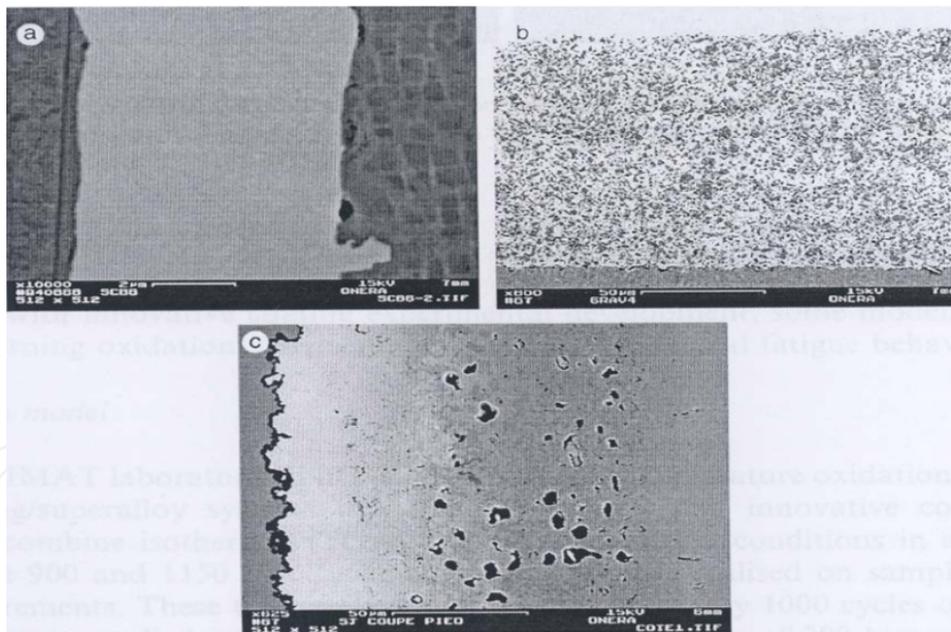
MCrAlY coating	Chloride environment (hrs)	Vanadium environment (hrs)
CM 247 LC alloy	<4	<2
Ni-16Cr-5Al-0.5Y	38	140
Co-30Cr-18Al-0.5Y	152	155
Ni-18Cr-22Co-12Al-0.5Y	>480	>300
Ni-18Cr-22Co-12Al-0.5Y + traces Hf	285	140
Ni-18Cr-22Co-12Al-0.5Y+ traces Si	35	158

**Table 9.** Lifetimes of different MCrAlY type coatings in various environments [28]

To obtain maximum durability of a coating even with low-grade fuels with high pollutant content levels, an innovative coating should contain maximum aluminium reservoir together with high chromium content. Such coatings are usually MCrAlY type. A new MCrAlY coating was innovated by using electro-less technique [66-67]. The aluminium concentration was modified with the use of a modified aluminization and / or by introducing a diffusion barrier and the aluminium was changed by use of platinum aluminide coating. Using platinum aluminide altered chromium solubility [67].

In the new coating, a Ni-W diffusion barrier (5  $\mu$ m thick), which is rich in W up to 50% mass, was introduced to prevent aluminium to diffuse from coating to the substrate. Over this layer 75  $\mu$ m thick MCrAlY coating (NiCrAlYT<sub>a</sub>) was deposited by electro-less route. Subsequently 7  $\mu$ m thick platinum and inward pack aluminizing was done (Fig.13). The hot corrosion tests with sodium sulphate showed improved performance over typical (SC/LPPS) MCrAlY / platinum aluminides and the innovative coating (SC / NiW + NiCrAlYT<sub>a</sub> + Pt + HA) maintained its integrity even after exposure for 1000 hours in pure sodium sulphate environment [67]. In order to prove the performance of a new coating, further experimentation with aggressive species like NaCl and V<sub>2</sub>O<sub>5</sub> is extremely necessary.

Another new coating namely Ir-Ta applied by EB-PVD followed by pack aluminizing was developed for Ni-based superalloys. This coating exhibited good high temperature oxidation and hot corrosion resistance [68-69]. Ir has a high melting temperature (2716K), excellent chemical stability and low oxygen permeability, while Ta also has high melting temperature (3269K), chemical resistance to aggressive propellant gases and low diffusion rates in Ni-based superalloys. During the hot corrosion process, a high melting point compound  $\text{NaTaO}_3$  (2083K) forms ( $\text{Ta}_2\text{O}_5 + \text{Na}_2\text{O} = 2 \text{NaTaO}_3$ ), which is stable. Further, both  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  (2163 K) form on the surface of coating and prevents inward diffusion of sulphur and oxygen and outward diffusion of chromium and nickel from the substrate, thereby eliminating the formation of sulphides which in turn enhances the hot corrosion resistance. The addition of Ir in platinum aluminide is also promising. Deposition of Pt-30at% and Pt-50at% Ir alloys followed by conventional aluminizing demonstrated enhanced oxidation and type I hot corrosion resistance [70-71]. Ir-Ta-Al coating appears to be another effective novel metallic bond coating materials for Ni-based single crystal superalloys. However, the conclusions are based on short-term tests in the presence of pure sodium sulphate. Hence, detailed research is needed in the presence of aggressive species like sodium chloride and vanadium pent oxide to prove its performance.



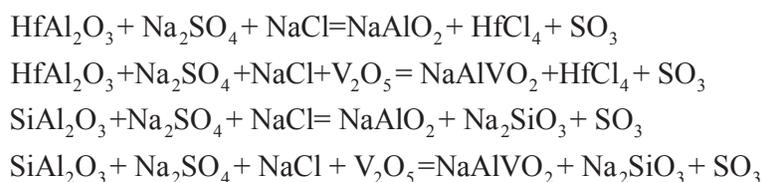
**Figure 13.** New coating deposit details a) 5  $\mu\text{m}$  thick NiW layer b) 75  $\mu\text{m}$  thick composite Ni-CrAlYTa c) 75  $\mu\text{m}$  thick composite Ni-CrAlYTa + 7  $\mu\text{m}$  thick platinum + inward pack aluminization [67]

Kawagishi et al have proposed an equivalent coating system for high temperature corrosion resistance of Ni- based superalloys [72]. This coating composition is designed to be thermodynamically in equilibrium with the substrate so that no inter-diffusion should occur between them. It is also reported that this coating technique helps in repair of turbine blades. Seraffon

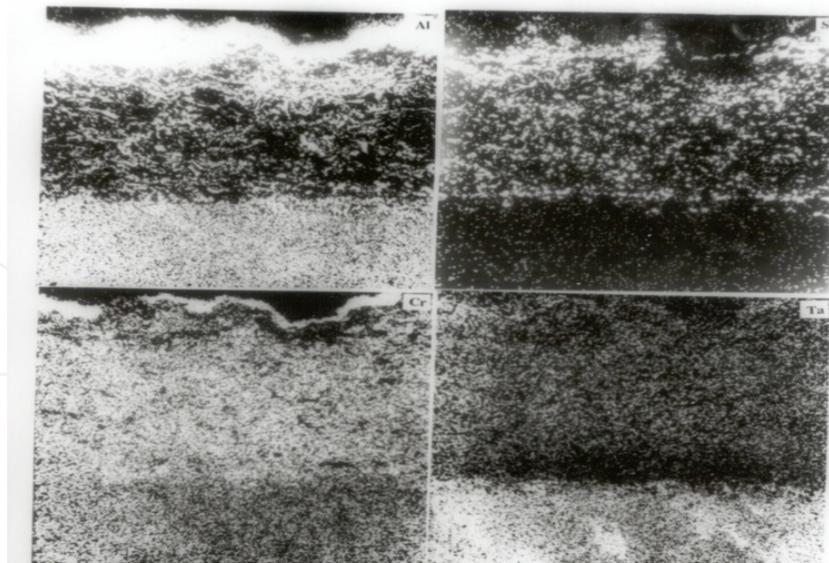
et al have attempted to use combination of physical vapour deposition and magnetron sputtering technique to deposit Ni-Co-Sr-Al coatings of varied compositions and tested for their high temperature oxidation resistance [73]. However, hot corrosion tests have not been studied.

### 3.7. Influence of major and trace elements

As mentioned earlier, the NiCoCrAlY coating exhibits maximum lifetime among the coatings (Table IX) under type I hot corrosion conditions [28]. Neither NiCrAlY nor CoCrAlY coatings prolong the superalloy's life. In fact, CoCrAlY coating contains maximum amounts of chromium (30%) and aluminium (18%), but their positive effect is not observed. Similar is the case with NiCrAlY coating. It is also mentioned that traces of silicon and hafnium make the NiCoCrAlY coating highly susceptible to hot corrosion. Traces of silicon or hafnium modify oxide growth rate, the composition of oxide scale and consequently reduce the coating life significantly. The fluxing of oxide scale also becomes easy when traces of silicon or hafnium are present in the scale. The underlying mechanism is that hafnium and silicon are present in the grain boundaries of alumina scale leach out selectively by readily reacting with chlorine, vanadium, sodium and sulphur present in the environment to form corresponding compounds [28]. This results in dislodging the grains of alumina scale and creates instability of the oxide scale and thereby reducing the life of coatings significantly [28]. Further, the oxides of silicon and hafnium are soluble in molten basic sulphate and the basic fluxing dominates in the high temperature hot corrosion region (850-950<sup>o</sup> C). By observing the maximum life for the NiCoCrAlY coating which does not contain either silicon or hafnium at 900<sup>o</sup> C evidences it. The reaction mechanisms leading to reducing the life of coatings containing silicon or hafnium are given below:



The superior performance was confirmed by observing minimum corrosion affected zone for NiCoCrAlY coatings and more for other coatings [26]. It was further evidenced by observing a uniform, protective and adherent alumina scale on the surface of NiCoCrAlY coating (Fig. 14). The above results clearly confirm that silicon addition is not beneficial for type I hot corrosion resistance rather it helps to combat type II hot corrosion [26]. Luthra et al and Bauer et al were reported that chromium [74] and silicon [75] respectively are particularly beneficial in coatings for protection against type II hot corrosion [76]. Reactive active element research related to oxidation characteristics and relevant mechanisms were the major works in overlay type coatings for the last one-decade [77]. However, the effect of reactive elements on hot corrosion resistance is still not well understood. Therefore, it may not be advisable to use silicon for protection of superalloys against both types of hot corrosion. Rather chromium addition is more appropriate to develop coatings for protection of components against hot corrosion (type I and II) as its presence does not have detrimental effect on type I hot corrosion.



**Figure 14.** EPMA data showing the formation of continuous and protective alumina scale on coating surface [28]

### 3.8. Degradation mechanisms

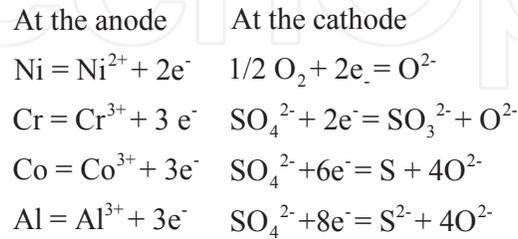
Inter-diffusion of aluminides with the base alloys resulting decrease in life is the dominating degradation mechanism in diffusion aluminide coatings. Lower sulphur contents of diffusion coatings improves alumina scale adherence and the adherence of alumina scale is very good with platinum aluminide coatings. Though platinum improves the adherence and improves the life of coating, the degradation is same at the end. Clear understanding on the effects of platinum and various forms of active metals and their oxides will help to improve the use of aluminide coatings as well as bond coatings for thermal barrier coatings.

During service, coatings degrade at two fronts: the coating / gas path interface and the coating / substrate interface. Deterioration of the coating surface at the coating / gas path interface is a consequence of environmental degradation mechanisms. Solid-state diffusion at the coating / substrate interface occurs at high temperatures, causing compositional changes at this internal interface that can compromise substrate properties and deplete the coating of critical species. In the worst case, inter-diffusion leading to the precipitation of brittle phases can cause severe loss of fatigue resistance. The following section describes a novel mechanism namely an electrochemical phenomenon that explains MCrAlY based bond coating degradation process in detail.

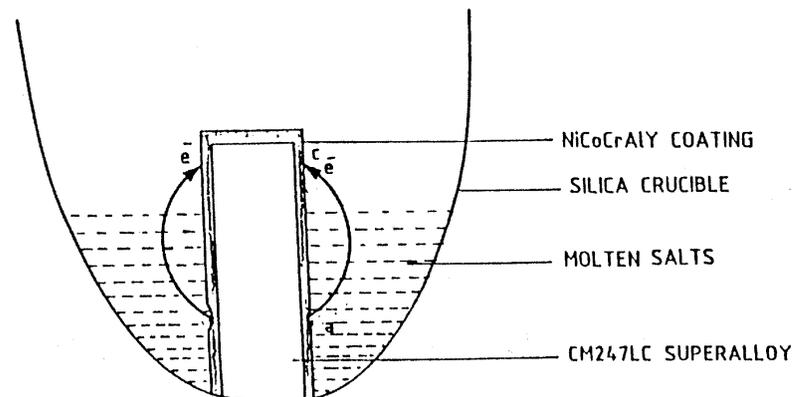
If NiCoCrAlY coating is considered, hot corrosion takes place by oxidation of nickel, cobalt, chromium and aluminium at the anodic site (forms  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  ions) while at the cathodic site,  $\text{SO}_4^{2-}$  is reduced to  $\text{SO}_3^{2-}$  or S or  $\text{S}^{2-}$ . Since the metal ions i.e.  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  are unstable at the elevated temperature and therefore reacts with the sulphur ions to form metal sulphides. The metal sulphides can easily undergo oxidation at high temperatures and form metal oxides by releasing free sulphur ( $\text{MS} + 1/2 \text{O}_2 = \text{MO} + \text{S}$ ). As a result, sulphur concentration increases at the surface of the coating and enhances sulphur diffusion into the

coating and forms sulphides inside the coating. The practical observation of sulphides in hot corroded components clearly indicates that electrochemical reactions take place during the hot corrosion process [26, 28]. Similar reactions take place in vanadium environments except the formation of oxides at cathodic sites. Fig.15 illustrates an electrochemical model showing the NiCoCrAlY degradation is electrochemical in nature.

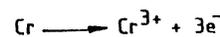
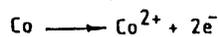
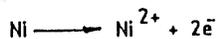
Therefore, the hot corrosion of NiCoCrAlY coating can be considered electrochemical in nature and the relevant electrochemical reactions are shown below:



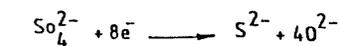
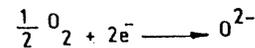
Similar mechanism is applicable to MCrAlY coatings family.



#### AT THE ANODE



#### AT THE CATHODE



**Figure 15.** An electrochemical model showing degradation of MCrAlY type coatings is an electrochemical phenomenon [26]

The motivation behind suggesting an electrochemical model is to show that degradation of materials (alloys or coatings) in molten salts is electrochemical in nature and thereby to develop a rapid hot corrosion test, which will be extremely useful to select the most potential candidate materials. The normal weight gain method requires hundreds of hours to test one material

whereas the electrochemical method needs hardly 4 to 5 hours. It is a major advantage of electrochemical techniques over conventional weight change methods. Electrochemical monitoring of corrosion by linear polarization, coulometric and A.C. impedance techniques have been established and widely used in aqueous solutions. On the contrary, the evaluation of corrosion resistances of various metals and alloys in molten salts are usually conducted by weight loss methods. Since the degradation of superalloys [6] and MCrAlY coatings [26,28] is shown as an electrochemical process, same as in aqueous solution, the electrochemical techniques should be quite helpful not only in evaluating coatings for hot corrosion resistance, understanding their hot corrosion mechanisms but also for developing hot corrosion resistant coatings for the superalloys [6,28].

### 3.9. Ceramic coatings

Thermal barrier coatings (TBCs) are finding increased application on overall component design. Over the past 25 years, cooling technology has contributed roughly 370<sup>o</sup> C (700 F) (from solid blades to advanced film cooling) in turbine temperature capability; further advances may be achieved with even more sophisticated cooling schemes. Superalloy material and processing advances (from equiaxed crystalline structure to third generation single crystal) have added approximately 120<sup>o</sup> C (250 F). However, superalloys now operate in some applications at 90% of their melting point. TBCs have the potential to reduce the substrate temperatures further with improved current production methods.

Application of zirconia thermal barrier coatings over diffusion aluminide and / or MCrAlY bond coatings is known to increase the life of components further. The function of the ceramic topcoat is to insulate the metallic substrate from high surface temperature, thereby lower the components temperature and reduce the oxidation and hot corrosion of bond coatings. The ceramic coating can lower the temperature of a cooled blade by up to 170<sup>o</sup> C (306<sup>o</sup> F), while simultaneously reducing cyclic thermal strains and has gained prominence in coating technology. ZrO<sub>2</sub> stabilized or partially stabilized by the addition of MgO, CaO, Y<sub>2</sub>O<sub>3</sub> is found to exhibit good performance because of its high coefficient of thermal expansion and very low thermal conductivity. It has been demonstrated that columnar structures applied by EB-PVD (Fig.16) has a significant improvement in life over plasma sprayed coatings [46]. The early work used EB-PVD ceramic coatings on NiCoCrAlY bond coating applied by low-pressure plasma. The latest trend is to use platinum aluminide as bond coatings. EB-PVD is often favoured over plasma deposition for TBCs on turbine airfoils since it provides a smooth surface of better aerodynamic quality with less interference to cooling holes [47]. However, the widely used plasma spray process has benefits, including a lower application cost, an ability to coat a greater diversity of components with a wider composition range and a large installed equipment base. The established ceramic topcoat for effective prevention of high temperature corrosion is the use of ZrO<sub>2</sub> partially stabilized with 8 wt% Y<sub>2</sub>O<sub>3</sub>. This coating exhibits satisfactory performance for aero gas turbines and primary degradation mechanism is due to bond coating oxidation. An encouraging trend was observed by chemical vapour deposition of Al<sub>2</sub>O<sub>3</sub> over NiCoCrAlY bond coating surface prior to overlaying a ZrO<sub>2</sub>-8Y<sub>2</sub>O<sub>3</sub> topcoat to the cyclic life of partially stabilized zirconia by suppressing the bond coating oxidation effectively.

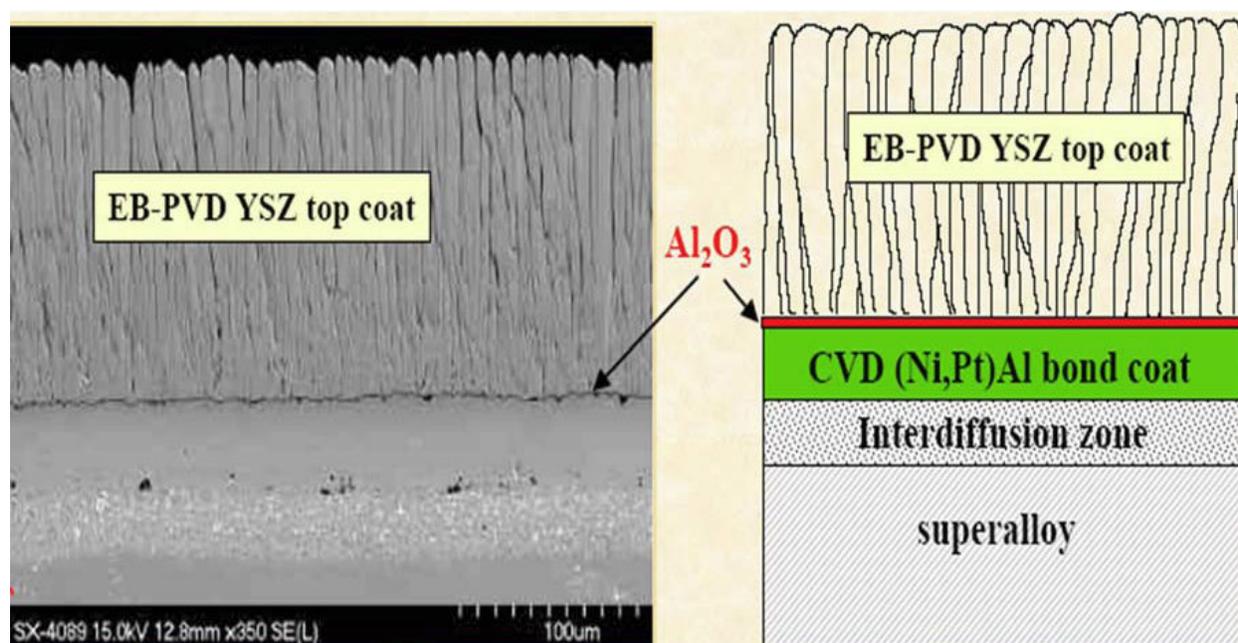


Figure 16. TBC structure deposited by EB-PVD over (Ni/Pt) Al bond coating [47]

However, it is not useful to marine gas turbines or industrial gas turbines because yttria ( $Y_2O_3$ ), which is the stabilizer for zirconia reacts with vanadium present in many industrial quality fuels or  $NaVO_3$  and forms  $YVO_4$  [31]. Vanadium depletes the  $Y_2O_3$  stabilizer from  $ZrO_2$  matrix and thus destabilization of zirconia (i.e. transformation of zirconia from tetragonal and/or cubic to monoclinic phase upon cooling, which is accompanied by a large volume change) takes place. Destabilization of zirconia eventually causes delamination and spalling of the ceramic coating. In addition, molten salt can penetrate into the YSZ through pores and cracks (present in YSZ) and react with the metallic bond coatings. As a result, various corrosion products are generated, leading to crack formation and propagation within the oxide scale. In order to combat this problem, the pores and cracks should be sealed either by using lasers or application of an additional protective layer. Silicates like mullite ( $3Al_2O_3 \cdot 2SiO_2$ ) or cordierite ( $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ ), CAS ( $CaO \cdot Al_2O_3 \cdot 5SiO_2$ ), BAS ( $BaO \cdot Al_2O_3 \cdot 2SiO_2$ ) and calcium silicate ( $1.8CaO \cdot SiO_2$ ) applied over ceramic TBC helps in improving the hot corrosion resistance due to formation of high melting point sodium-alumino-silicates ( $>1573K$ ) [78-85]. The rate of destabilisation of zirconia was restrained by the presence of additional over layers. However, as the pores can be present in over layered coatings, the molten salt can easily penetrate and interact with zirconia to form  $YVO_4$  but the time required to reach the ceramic layer is higher. This aspect led to identifying  $CeO_2$ , an effective alternative to  $Y_2O_3$  for marine and industrial gas turbine applications. Alternative stabilizers to zirconia are needed to further prolong the life of TBC coatings.

Knowledge that active elements in Ni-based superalloys and / or platinum modifications caused improved scale adherence in diffusion aluminide coatings might have led to the use of these coatings as bond coatings. The large beneficial effects possible in gas turbine efficiency by the use TBCs have sparked a resurgence in research on all aspects of scale adherence and

failure mechanisms involved in loss of ceramic layers or reactions with hot corrosive salts. It was expected that future research will yield incremental improvements in scale adherence towards the goal of perfection required to attain prime reliant status necessary to take full advantage of saved cooling air. Research in this direction led to the application of TBCs directly on an advanced yttrium containing superalloy without the need for a bond coating [86-87].

In practice, the inlet gas temperature in the state-of-the-art gas turbines has already reached 1773 K, which exceeds the melting points of Ni-based superalloys used for gas turbine blades and vanes. Therefore, the necessity of improving the performance of TBC is highly essential. In addition, the coating degradation takes places due to erosion as well. Therefore, it is essential to apply multilayered coatings in a perfectly ordered manner to protect the components from all attacks / damages. It is worthwhile to concentrate on the development of appropriate coating system (multilayered) including thickness for different types of gas turbine engines. Optimization of coating process taking all the experimental parameters into account is another area of critical importance.

### **3.10. Life prediction modelling**

Because of the dependence of blade integrity on TBCs, considerable efforts are necessary to develop life prediction models to aid the gas turbine design. It is important to validate the developed model with experimental data obtained both in the laboratory as well as in the field. Development of a suitable laboratory test for predicting the life of developed materials / coatings accurately in service is an important task for the Corrosion Engineers. Recently, Rensch and Schutze [88-89] have developed a prototype software to predict the lifetimes of yttria stabilized zirconia (YSZ) top coating as a function of a bond coating temperature for a given input of hot dwell time and temperature gradient and the results have been validated with laboratory data. Attempts were made to find a solution for the transient temperature transfer problem in bare and thermal barrier coated alloys with the computational fluid dynamics (CFD) part of analysis by application of ANSYS Fluent code receiving the temperature field of combustion gas, whereas computational structural mechanics (CMS) part concerning the temperature distribution inside the turbine blade was done by ABAQUS [90-94]. Degradation modelling is most important to coating design and development. Process modelling is most important to coating manufacture. Coating life and inherent substrate environmental resistance are key determinants in setting the intervals for engine inspection and overhaul. Only few models exist in the public domain that addresses any of these needs.

It is pertinent to note that predicting the lifetimes of same YSZ top coating under hot corrosion conditions has not been attempted yet. In fact, it is a complex and challenging aspect as software development involves taking into account various reaction mechanisms that takes place under a variety of service conditions [95]. Serious attempts are needed to develop such software, which will have tremendous improvement in enhancing the efficiency of various advanced gas turbine engines. As mentioned above, the results have to be validated with both laboratory and field data and achieve an excellent agreement.

### 3.11. Reliability

Reliability is a critical design factor that is needed for further development if TBCs are to be fully exploited to increase turbine efficiency [96-97]. TBCs fail as a result of erosion, impact damage, and interfacial oxidation of the bond coating or thermo-mechanical strain at the ceramic / metal interface. These factors and process variability, more than any other design factor, has slowed the introduction of these coatings for turbines. Improved understanding of interfacial behaviour is required to control coating properties and to predict performance. A more compatible and high temperature corrosion resistant bond between the TBC and either the metallic substrate or the bond coating requires continued long-term emphasis [98]. The processes by which TBCs are currently applied, namely air plasma spray and EB-PVD will likely continue to be the major manufacturing methods.

Engineers currently rely heavily on visual inspection to assess the condition of coated structures [97]. As a result, in-service condition monitoring and repair decisions focus on deterioration at the coating / gas path interface. Improved non-destructive evaluation methods would provide information on when the coating has to be removed and on the extent of base metal attack. An important need for repair of industrial gas turbine components is industry wide repair specifications and regulations of the quality of repairs. The most effective method to achieve a consensus of all interested parties remains unclear. Methods to make local repairs of coatings are needed both during manufacture and operation. Also required are standard, industry-accepted methods to determine the durability and properties of refurbished coatings.

Aircraft engine repair needs are parallel to those for the industrial turbines, with the further complexity that these coating structure systems include more advanced designs and materials that tend to limit repair options. Incorporation of better models and data from condition-monitoring sensors will improve repair / replacement decisions. Still unclear is the extent to which many of the advanced coatings, such as TBCs, lend themselves to repair. Although some TBC overhaul is currently done, the extent to which TBC coated components can be repaired and re-used has never been fully determined.

Exploiting existing and advanced non-destructive evaluation (NDE) methods can aid significantly in developing and qualifying coating systems, improving process control during coating operations and characterising the integrity of coated structure during turbine engine manufacture, in-service condition monitoring and repair and overhaul operations [98-101]. Since each of these applications has specialised requirements, no single NDE technique will likely to serve all purposes. Development of programs for advanced NDE methods should focus on supporting these key areas with the goal of bringing the new methods into practice. The highest priority for further NDE development should be for those non-contacting methods that can examine the interior structure of the coating system, such as the coating / substrate interface and base metal. For aircraft engines in particular, the development of advanced NDE techniques and cost effective models will be essential for the assessment of components that are expected to be multi-wall or thin-wall structures with multilayered coatings used as an integral part of the component design and manufacture.

Future generations of higher-performance aerospace turbine structures will require newer materials, because in service superalloys are approaching the upper limit of their inherent temperature capability as mentioned earlier. Potential candidate materials to replace superalloys are inter-metallic compounds, monolithic and composite ceramics and refractory alloys. In addition, advanced cooling concepts will result in processing modifications and more complex cooling paths to meet the demands of advanced component designs. Most advanced materials and design modifications may result in component structures with inherently less resistance to aggressive environmental attack than current superalloys.

An important element that must be considered in innovative coating systems is the stability of structural components in the high temperature environment of an operating engine. The stability includes the long-term ability of the material to maintain its initial mechanical properties, chemical and micro-structural morphology. Research is needed on continuously graded coatings. Graded coatings like functionally graded materials (FGM) and nanostructures, offer potential advances in coating performance. The need also exists for ceramic coatings that can withstand higher temperatures. Graded coatings may demand alternative materials as well as alternative applications processes. Most significant in this area would be critical assessment of the use of FGMs as coatings and definition of the influence of multilayer and nanostructure morphology on resulting properties. However, the inherent in-homogeneity in the microscopic scale of these materials raises questions of high temperature stability that must be answered to establish the viability of these approaches. Advanced substrates like composites, ceramics and inter-metallic compounds will possess coating ability characteristics (e.g., diffusion rates and surface chemistry) very different from current superalloys. Novel concepts may be needed for coatings and surface treatments to protect these substrates. In essence, advanced processes and intelligent coatings are needed to manufacture future gas turbine engines for exhibiting ever greater efficiency.

#### **4. Correlation between laboratory and service experience**

Performance evaluation of materials / coatings in actual gas turbine engines is hardly practicable. Therefore, several simple methods were developed to assess the hot corrosion resistance of possible materials for blades and vanes. A satisfactory test should yield a prediction of service performance, with an estimation of component lifetime as a desirable objective. Attempts were made earlier to compare the results of laboratory corrosion tests with service experience. It is important to note that the corrosion of gas turbine components is greatly influenced by fuel and air quality. Generally, highly rated engines use relatively pure fuels and the air purity is also good unless move in marine environments.

In general, a more complete gas turbine engine environment can be simulated in burner rigs and the ranking of materials / coatings are in good agreement with the engine experience. The crucible test results are in agreement with burner rig test results in ranking the alloys. On the basis of corrosion products identification, it is concluded that burner rig test give the most realistic reproduction of corrosion mechanisms found in service, although furnace test as well

as crucible tests could give satisfactory results. The burner rig and electrochemical tests produce similar corrosion morphology and corrosion rates are in good agreement with each other [22]. The performance of materials tested in electrochemical tests behaved in a similar manner in actual engines.

General Electric developed an advanced burner rig test cycle for studying the combined effects of oxidation and hot corrosion on gas turbine materials [22]. This test combines the cyclic elements of an aircraft engine operation cycle with the fundamental elements of the standard oxidation and hot corrosion tests. A dilute sea salt solution is atomized inducted into one atmosphere burner rig to simulate hot corrosion conditions present at coastal airports. Specimens are romped to oxidizing conditions similar to those present during take off and climb. The thermal gradients present along the length of the test specimens simulate those present on actual aircraft engine hardware and produce areas of oxidation, hot corrosion and combined hot corrosion / oxidation attack. This burner rig test was reported to be successful in reproducing the accelerated combined hot corrosion / oxidation attack observed in factory engine testing. The ranking of substrate / coating obtained with this method vary greatly from those obtained with conventional test methods. This is due to the fact that the ranking recorded in advanced burner rig test is a function of location on the pin and distinctly different rankings can occur in each attacked region.

The advanced burner rig test was used to test tube specimens that can be internally cooled during exposure to the combustion system. Several thermal gradients can be established across specimen walls like actual turbine hard ware by using this method. With the advanced burner rig test, it is possible to compare life times of TBC coatings with the function of thickness [22]. Nevertheless, significant surprises in terms of actual versus predicted coating performance continue to occur in the field. As a result, new laboratory tests or improved existing procedures are needed in real world applications.

## 5. Smart coatings

### 5.1. Concepts

A primary requirement for a coating to use in high temperature applications is slow growth rates and optimum adherence of the protective scales that forming on the metallic coatings during high temperature exposure. As the gas turbine engines experience both types of hot corrosion as well as oxidation and hence the need to develop smart coatings to effectively combat high temperature corrosion problems for obtaining maximum efficiency.

If a single coating can operate successfully over a range of temperatures with different forms of corrosion attack like type I and II hot corrosion and high temperature oxidation, the coating essentially respond to local temperature in such a way that it will form either alumina or chromia protective scale as appropriate. High purity alumina scales offer best protection against high temperature oxidation and type I hot corrosion and chromia scales against type II hot corrosion. Ideally a single coating should satisfy both the requirements. It is possible for

a coating only if it contains chromium and aluminium rich graded coatings (Fig.17). The base coating should be a standard MCrAlY coating enriched with aluminum at its outer surface and a chromium rich layer at its inner surface. Under high temperature oxidation and type I hot corrosion conditions, the outer layer of the coating forms alumina scale, which provides protection and it, offers less protection under low temperature conditions. Under type II hot corrosion conditions, chromium rich layer forms chromia scale at a faster rate and provides protection. Thus, the smart coating can provide optimum protection by responding suitably to the temperatures that are encountered under actual service conditions of gas turbine engines. This optimum protection is possible because of the formation of the most suitable protective oxide scale in each temperature range of operation envisaged. In this sense, the coating responds to its environment in a pseudo-intelligent manner and hence the name **SMART COATING** [102-103]. The smart coating permits operation of gas turbine engines over a wide range of temperatures successfully for more than the designed life and helps in enhancing the efficiency significantly by effectively preventing oxidation, type I and type II hot corrosion. Such coatings were developed by the principle author and recommended to use for marine, industrial and aero gas turbines (Fig.18) [102, 104-105].

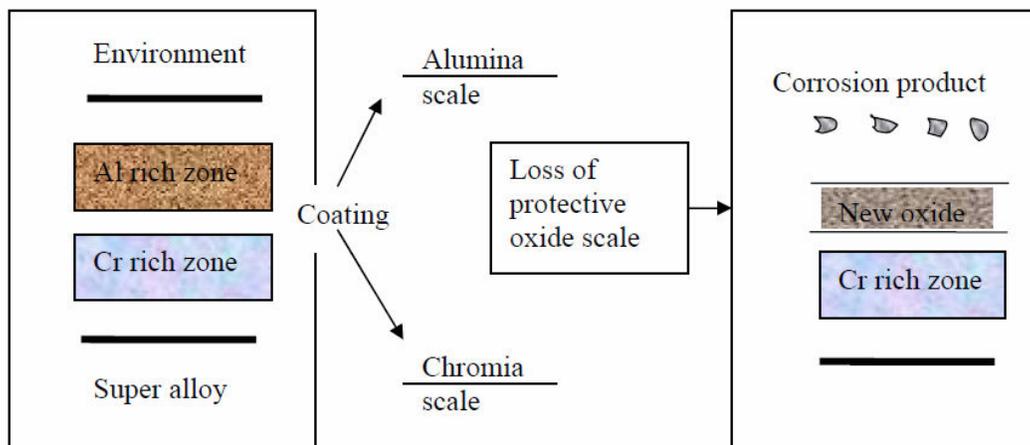


Figure 17. Schematic representation of response of a smart coating [102, 103]

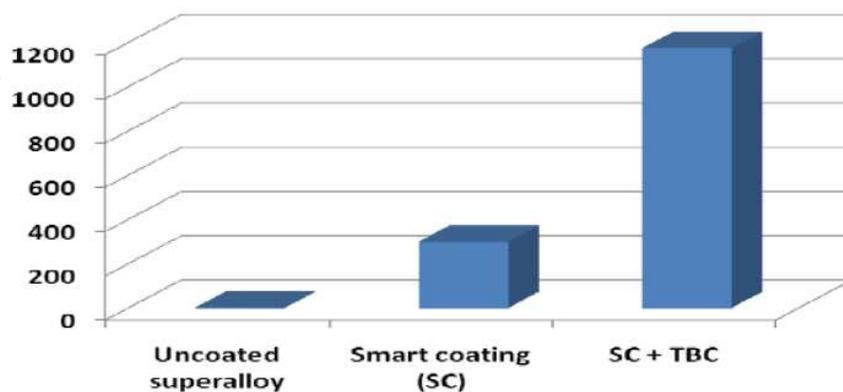


Figure 18. The performance of a Smart Coating (SC) [102]

## 5.2. Preparation

Preparation of smart coatings is really a challenging task. Therefore, selection of suitable surface engineering techniques to produce a quality coating is extremely essential. Here, selection of a single technique may not be of any help, but a combination of techniques is quite useful [102]. Further, the order of usage of selected techniques is also important as the microstructures of coatings vary and play a significant role in enhancing the life of components. The selection of technique for coating preparation should be based on the parameters that are controllable to get required microstructure. As mentioned earlier, the smart coating is a graded coating consisting of different zones (Fig.19) [102]. Each zone has its specific microstructure with definite composition and extends the life of gas turbine engine components significantly. Extensive research is needed both at the laboratory and field in order to establish the appropriate coating compositions, thickness, microstructures, coating techniques and superior performance of new smart coatings over conventional coatings.

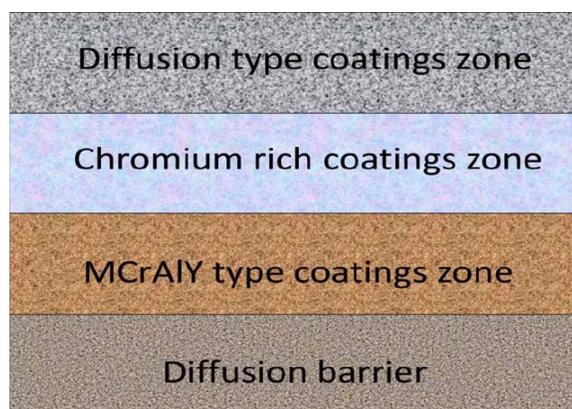


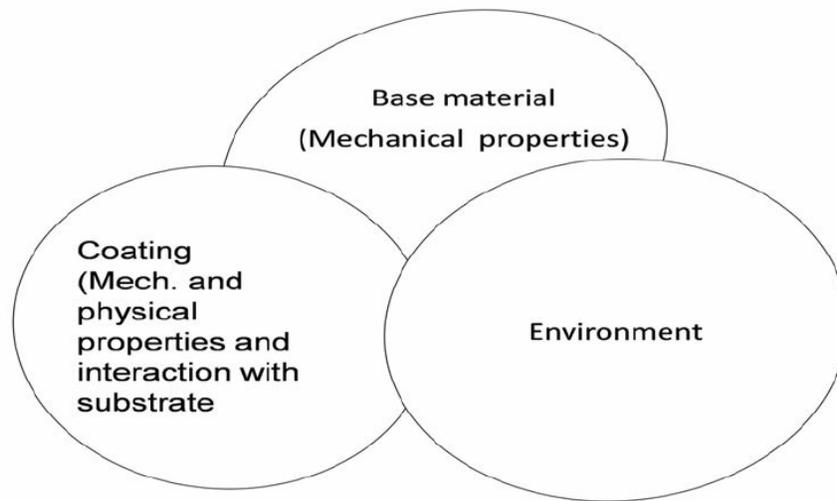
Figure 19. A schematic representation of microstructure of a smart coating [102]

## 6. Mechanical properties of coated superalloys

The mechanical properties of superalloys (especially cast alloys, which have their optimum mechanical properties in the as-cast condition) may deteriorate during the coating process (e.g. on thermal cycling during coating, during post-coating heat treatment, or by coating surface effects). The degradation of mechanical properties of the base material may lead to an increase in creep rate, thereby the elongation that can be tolerated before the coating starts to crack will be reached in a shorter time. In a corrosive environment, stresses are enhanced due to corrosion of coating and result in a measurable reduction of the cross section or by selective corrosion attack after a crack is initiated in the coating and propagates rapidly along grain boundaries or by both general and selective attack.

With the solid blades that used to be installed in turbines, the interaction between coating and base material was not significant because the potential influence on the load-bearing cross-

section was very less. However, today's channelled, cooled blades have thin walls and a substrate-coating interaction over a depth of only few tenths of a millimetre can have a significant effect. Such interactions have been investigated in detail and reported [106]. It is important to mention that the coating-substrate interaction complicates the task of determining the various factors that are involved. The effectiveness of a protective coating for a particular material under service conditions can therefore be assessed only by techniques in which all the parameters like substrate, coating and environment as shown in Fig.20 are taken into account [40].



**Figure 20.** Factors affecting the coated superalloy components [108]

Swindells [107] and Cooper and Strang [108] have shown that one of the major problems faced by all coating systems is their mechanical properties. To achieve a good coating without discontinuity at the interface some inter-diffusion is required, but, if this diffusion occurs to any significant level during operation, the coating will slowly be degraded. The work on diffusion mechanisms is important in determining the long-term stability of the coatings. However, it has particular significance when discussing the mechanical properties of coated components, reviewed by Strang [109] and Czech et al [110].

The major problem is how to compare the properties of a coated component with an uncoated component. When such comparisons are made, it is of great importance how the cross section is measured, whether comparisons are made on the dimensions of the section before coating or whether the total thickness of base metal and coating are compared with a similar thickness of uncoated metal. This choice dominates the results in thin-section components, particularly when the coating has very different mechanical properties from the underlying metal. It affects the results obtained in creep, fatigue and thermal fatigue tests. However, the problem of the effect of coating properties on the mechanical integrity of the component is only of interest in some cases. For instance, as pointed by Goward [111] if failure is by thermal fatigue as in aircraft turbines, then the surface coating effects on mechanical stability are important; if failure is by hot corrosion, as in industrial and marine turbines, then the effect on mechanical properties is generally of a second order compared to the protection afforded by the coating.

## 7. Summary and future research trends

### 7.1. Summary

High temperature corrosion i.e. oxidation, type I and II hot corrosion are the degradation modes for the gas turbines. Hot corrosion is a major problem for the gas turbines engines due to which failures take place during service. Though advanced superalloys comprising new alloying elements such as rhenium, ruthenium and iridium (4<sup>th</sup> and 5<sup>th</sup> generation) that have been developed recently, exhibit considerably improved high temperature strength properties, their hot corrosion resistance is found to be very poor. Therefore, there is a need to apply appropriate hot corrosion resistant coatings on the superalloys as the gas turbine engine components should exhibit both high temperature strength as well as hot corrosion resistance. Considerable amount of research has been carried out in the coatings area. As a result, new compositions, graded coatings have been emerged and efforts have also been made to predict their lives. However, no work was reported to predict the lives of coatings under hot corrosion conditions. Recently, smart coatings with varied techniques and compositions have been reported, which provides total protection to the superalloy components against high temperature oxidation, type I and II hot corrosion with their intelligent behaviour which in turn enhances the efficiency of gas turbines by eliminating failures during service. Therefore, it is recommended to apply smart coatings for the advanced superalloys as bond coatings used in all types of modern gas turbines i.e. aero, industrial, marine in order to obtain ever greater efficiency, which is essential in the present world.

### 7.2. Future research trends

No established ISO standard procedure is available till now for evaluation of materials and coatings for their hot corrosion resistance and hence the need to establish such standards in near future. In fact, the immediate concentration should be focused on this issue. Development of new alloys with a combination of experimentation, modelling and black art is necessary as further improvements in Ni-based superalloys are less possible because the superalloys now operate at about 90% of their melting temperature. The future generation of high performance aerospace structures or potential candidate materials to replace superalloys are inter-metallic compounds, monolithic and composite ceramics, refractory alloys and research is needed in this direction. The developmental work should take place concurrently with coating system. Improved understanding of interfacial behaviour of TBCs and a more compatible hot corrosion / oxidation resistant bond coatings either by modification of chemistry or more stringent control of undesirable elements to control coating properties and to predict their performance is highly essential. Hence, the development of constructive life prediction modelling under simulated gas turbine engine conditions is necessary. Improved on-line control to ensure reproducible coated structures and within the service limits is also needed as increased improvements to current coating technologies are unlikely to meet the goals of future generation high performance turbine engines. Then, development of Smart Coatings to combat type I & type II hot corrosion and high temperature oxidation for gas turbines is a challenging task to the Corrosion Engineer and developmental work in this area has led to some smart

coatings. Further research is highly essential for their understanding and to develop alternative smart coatings. Extensive research is needed both at the laboratory level and field to optimize coating composition, thickness, microstructure, identification of appropriate surface engineering techniques, and their priority of use and to prove their performance for manufacture of advanced gas turbine engines for exhibiting ever-greater efficiency.

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## Author details

I. Gurrappa<sup>1\*</sup>, I.V.S. Yashwanth<sup>2</sup>, I. Mounika<sup>1</sup>, H. Murakami<sup>3</sup> and S. Kuroda<sup>3</sup>

\*Address all correspondence to: [igp1@rediffmail.com](mailto:igp1@rediffmail.com)

1 Defence Metallurgical Research Laboratory, Kanchanbagh PO, Hyderabad, India

2 University of Louisiana, Lafayette, LA, USA

3 National Institute for Materials Science, Sengen, Tsukuba City, Ibaraki, Japan

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