CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Manufacturers of marine gas turbine and aircraft jet engine are continuously trying to increase the operating efficiency by increasing the turbine entry temperatures of the jet engine. Turbine components such as blades and discs experience variable loading at the elevated temperatures. The increase in the entry temperature accelerates the process of corrosive attack and causes pitting on the surface of the turbine components, which promote early crack initiation sites and subsequently fatigue life is reduced. Therefore, a special class of materials known as "Superalloys", capable of bearing high temperature, high stress, and oxidizing-corrosive environments; in which nickel is used as the major element of the matrix to improve the high temperature creep resistance at elevated temperature during the service. The broad category of superalloys are: (a) Fe-base alloys containing chromium and nickel, (b) complex Fe-Ni-Cr-Co alloys, carbide strengthened Co-base alloys, (c) solution strengthened Ni-base alloys, and (d) precipitation or dispersion strengthened Ni-base and Ni-Fe base alloys. The superalloys mainly consist of a larger amount of the elements like iron, nickel, cobalt and chromium and smaller amount of tungsten, molybdenum, tantalum, niobium, titanium and aluminium, present in a variety of combinations. Now a days, Ni and Ni-Fe based superalloys are extensively used for turbine component of marine gas turbine and jet engines.

The material application is largely dependent on its mechanical properties which is served by the concentration of different alloying elements. Some elements are

responsible for enhancement of tensile and creep strength, the others play a vital role in improving the oxidation and corrosion resistance. These desired properties may not co-exist together, therefore, now-a-days many techniques like surface modification, surface coating etc., are used to enhance the oxidation and corrosion resistance of these materials.

1.2 DEVELOPMENT OF NICKEL BASE SUPERALLOYS

In the 20th century, the second and third decades were termed as the evolutionary period for the development of superalloys, and before this period steels were used for typical applications. Stainless steels had been developed before 1915 **[Sims et al. (1987)]** and were first termed as 'super-alloys', but later improved Fe-based alloys became 'superalloys'. After the World War-II, the need for the development of new alloys for the exhaust valves and superchargers for aircraft engines was felt, and a new class of material to withstand high temperature, mechanical stressing in corrosive environment was introduced for the aircraft engines. The first Ni-based superalloy was produced during the fourth and fifth decade of the 20th century, and a great extent of improvements took place in material development in the 1970s and 1980s **[Donachie et al. (2002), Durand-Charre (1997)].** The addition of elements for the development of superalloy has progressed over the period to meet the requirement of operating conditions of jet engines. Small additions of Al, Ti and Nb, in the Fe and Ni-based alloys which also contained considerable amount of chromium, evolved the creep resistant phase γ'. Ni and Co replaced Fe to stabilize the stronger face centred cubic structure (FCC), and reduction in the Cr content was made to produce a high strength alloy, but this led to severe degradation of the alloy due to hot corrosion. Therefore, Cr content

was added in controlled fashion to overcome the issues of hot corrosion. Addition of Mo provided solid solution and precipitation strengthening, also many refractory elements like W, Ta and Re were added to provide higher strength. Grain boundary strengthening was controlled by addition of carbon and boron **[Sims et al. (1987)].** Nimonic 80A was developed at the Mond Nickel Company in 1940s in response to the need for a suitable turbine blade material for the first British gas turbine for aircraft propulsion **[Mc Lean (1995)].** The development of single crystal alloys for turbine blades of a jet engine overcome the problem of grain boundary sliding, and also, an increase in the solidus temperature of the alloys was achieved. On the other hand, turbine discs could not be manufactured by single crystal alloys because of their intricate shapes. Over the years, alloy development and improved blade design has increased the maximum operating temperatures **[Durand-Charre (1997)].**

There are many applications of superalloys, like bolts, shafts, cases, vanes thrust reverser, discs, blades, burner cans, after burners in aircraft and industrial gas turbines; in the steam power plants as stock gas re-heater, turbochargers, exhaust valves, hot plungs, pre combustion cups, and valve seat inserts in reciprocating engines; control rod drive mechanisms, valve stems, spring and ducts in nuclear power plants; aerodynamic heat skins and rocket engine parts in space vehicles [**Garimella et al. (1997), Sims et al. (1987), Yang et al. (2002**)]. At present, approximately 90% of the superalloys produced are used as components of gas turbine engines, including marine propulsion, oil and gas pumping, and aerospace. Table 1.1 shows the chemical composition of some common and advanced nickel base superalloys.

Table 1.1: The chemical compositions of few nickel base superalloys (wt.%) **[Furre et al. (1999)]**

Alloy	Cr	Ni	Co	Mo	W	Nb	Ti	Al	Fe	C	B	Others
A286	15	26	-	1.2	-	-	-	0.2	55.2	0.04	0.005	0.3V
AF115	10.7	56	15	2.8	5.9	1.7	3.9	3.8	-	0.05	0.02	0.75Hf,0.05Zr
AF2-1DA	12	59	10	3	6	-	3	4.6	<0.5	0.35	0.015	1.5Ta,0.1Zr
AF2-1DA6	12	59.5	10	2.7	6.5	-	2.8	4.6	<0.5	0.04	0.015	1.5Ta,0.1Zr
Alloy 706	16	41.5	-	-	-	-	1.75	0.2	37.5	0.03	-	2.9(Nb+Ta),0.15Cu
Alloy 718	19	52.5	-	3	-	5.1	0.9	0.5	18.5	0.08	-	0.15Cu
APK12	18	55	15	3	1.2	-	5	2.5	-	0.03	0.035	0.035Zr
Astroloy	15	56.5	15	5.25	-	-	3.5	4.4	<0.3	0.06	0.03	0.06Zr
Discaloy	14	26	-	3	-	-	1.7	0.25	55	0.06	-	
IN100	10	60	15	3	-	-	4.7	5.5	<0.6	0.15	0.015	0.06Zr,1.0V
KM-4	12	56	18	4	-	2	4	4	-	0.03	0.03	0.03Zr
MERL-76	12.4	54.4	18.6	3.3	-	1.4	4.3	5.1	-	0.02	0.03	0.35Hf,0.06Zr
N18	11.5	57	15.7	6.5	-	-	4.35	4.35	-	0.015	0.015	0.45Hf,0.03Zr
PA101	12.5	59	9	2	4	-	4	3.5	-	0.15	0.015	4.0Ta,1.0Hf,0.1Zr
Rene 41	19	55	11	10	-	-	3.1	1.5	<0.3	0.09	0.01	
Rene 88	16	56.4	13.0	4	4	0.7	3.7	2.1	-	0.03	0.015	0.03Zr
Rene 95	14	61	8	3.5	3.5	3.5	2.5	3.5	<0.3	0.16	0.01	0.05Zr
Udimet 500	19	52	19	4	-	-	3	3	<1.0	0.08	0.005	
Udimet 520	19	57	12	6	1	-	3	2	-	0.08	0.005	
Udimet 700	15	55	17	5	-	-	3.5	4	<1.0	0.07	0.02	0.02Zr
Udimet 710	18	55	14.8	3	1.5	-	5	2.5	-	0.07	0.01	
Udimet720	18	55	14.8	3	1.2	-	5	2.5	-	0.03	0.033	0.03Zr
Udimet 720Li	16	57	15.0	3	1.2	-	5	2.5	-	0.02	0.018	0.03Zr
V57	14.8	27	-	1.25	-	-	3	0.25	48.6	0.08	0.01	0.5V

1.3 ALLOYING ELEMENTS

A comparison capabilities of alloy systems is shown in Fig. 1.1. Nickel base superalloys possesses close packed FCC lattice that has relatively high tensile, creep, rupture, and thermomechanical fatigue properties to homologous temperatures, comparatively higher than that of equivalent body centered cubic (BCC) systems. These alloys possess excellent combination of high strength and oxidation resistance at elevated temperature [**Sims et al. (1987)**]. Precipitation hardening is the main strengthening mechanism of these alloys and is achieved primarily through the addition of Ti, Al and Nb.
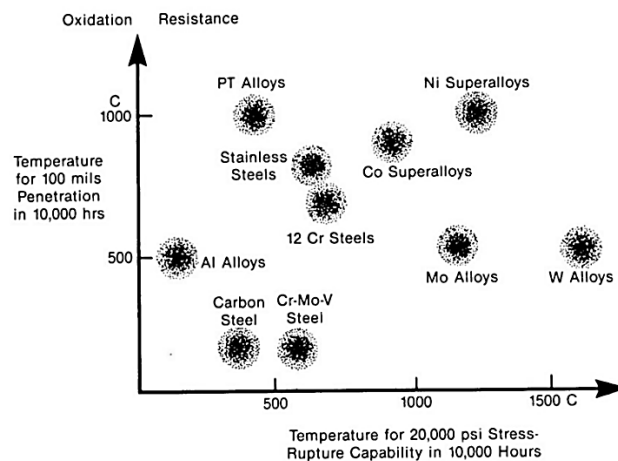
Fig. 1. 1: Comparison of capabilities of different alloy systems **[Sims et al. (1987)].**

The precipitation hardened Ni-Fe base superalloys are primarily strengthened by (i) ordered BCT $(DO_{22})\,\gamma''$ (Ni_3Nb) (e.g, IN718 and IN706), and (ii) ordered FCC $(L1_2)\,\gamma'$ $\{Ni_3(Al,Ti)\}$ (e.g, Nimonic PE16). Chromium (10-25 wt. %) and molybdenum (up to 9 wt. %) are solid solution strengthening elements, typically added to nickel-iron base superalloys. Tungsten imparts superior strength than molybdenum when added in the alloy **[Raynor et al. (1970)],** but due to increased density and high cost it is less popular.

The proximity of lattice parameters of nickel and cobalt is close to each other, and iron in place of cobalt is more effective solid solution strengthener. Cobalt leads to contraction and molybdenum causes expansion of the austenitic lattice of nickel-iron matrix, when these elements are substituted for iron **[Dyson et al. (1970)].** Chromium and molybdenum in nickel-iron superalloys partition preferentially to the matrix, where they cause a number of important changes. The solubility of matrix for the precipitation strengthening elements (Ti, Al, and Nb) reduces, due to their presence. Oxidation and hot corrosion resistance are additionally obtained by chromium in nickel-iron base alloy in aggressive environments at elevated temperatures. The formation of a continuous protective oxide film occurs at approximately 9 wt.% of chromium in the nickel-iron alloys **[Sims et. al (1987)].** Table 1.2 shows the role of alloying elements of Ni-base superalloys.

Table 1. 2: Role of different alloying elements in Ni-base superalloys [**Bradley (1988**)]

Effect	Elements								
	Ni	Cr	Nb	Ta	Mo	Ti	Al	C	Fe
Solid-solution strengthener		✓		✓	✓				✓
Carbide former		✓	✓	✓	✓	✓		✓	
Intermetallic phase former	✓		✓		✓	✓	✓		
Protective oxide former		✓					✓		
TCP/Lave phases		✓			✓	✓			✓

1.4 SUPERALLOY IN718

Before the emergence of superalloy IN718, turbine manufacturers were dependent on precipitation strengthened stainless steel, like A286 and γ′-strengthened Ni-base superalloy, like Rene 41, for high temperature applications. However, mechanical and temperature related issues of stainless steels were faced by GE aircraft engines by the end of 5th decade of the 20th century. Rene 41 faced susceptibility to strain-age cracking during post-weld heat treatment, which required highly costly processing routes to resolve it.

In 1959, superalloy IN718 was developed by the International Nickel Company (INCO) at its research laboratory in Suffern, New York and at its plant in Huntington, West Virginia. Niobium addition helped in the strengthening of the alloy by precipitation of an intermetallic compound (Ni_3Nb) in the nickel matrix during the age hardening treatment. Niobium was found to be unique in view of its ability to avoid strain-age cracking during fabrication of the final components, especially during welding. The outstanding characteristics of the superalloy IN718 are due to its slower response to age hardening. Superalloy IN718 is a precipitation hardenable Ni-Fe base alloy containing significant amounts of chromium, niobium, and molybdenum along with lesser amounts of aluminum and titanium. It is used in temperature range of -253 to 704°C with excellent oxidation resistance up to 982°C. It has high fatigue strength and excellent creep rupture strength up to 704°C, also, it possesses outstanding corrosion resistance along with weldability, including resistance to post weld cracking. It is extensively used in aerospace industry in components of jet engine; nuclear reactors; rocket motors and thrust reversers and space craft. The development of superalloy IN718 significantly improved the ease of manufacturing combined with mechanical properties and replacement of Rene 41 was

recognized early by GE air engine as a revolutionary change for engine designs [**Bassford et al. (1998), Schafrik et al. (2001)**]. About 56% of superalloy IN718 was used in rotating and structural forgings of GE air engines [**Schafrik et al. (2001), Schafrik et al. (2008)**]. Typical composition (Table 1.3), mechanical properties and physical properties of the superalloy IN718 are presented below [**ASM Handbook (1990**)].

Table 1. 3: Typical chemical composition of superalloy IN718 (wt.%).

Ni	50-55	Al	0.3-0.8
Cr	17-21	Mn	0.35
Nb+Ta	4.75-5.5	Si	0.35
Mo	2.8-3.3	C	0.08
Ti	0.75-1.15	Fe	Balance

Physical properties:

Density : 8.19 g/cm^3

Melting Point/Range : 1258-1335°C

Specific Heat : 437 J/Kg °C

Average Coefficient of Thermal Expansion : 13.0 µm/m °C

Thermal Conductivity : 11.3 W/m °C

Electrical Resistivity : 1248 microhm-mm

Curie temperature : -112°C

Typical Mechanical Properties at room temperature:

0.2% offset YS	UTS	Elongation in 50 mm	Elastic Modulus	Hardness
1236MPa	1410 MPa	12%	210 GPa	440 HV

1.5 CRYSTAL STRUCTURE AND PHASE STABILITY OF THE SUPERALLOY IN718

The general phases present in the superalloy IN718 are γ'', γ' and δ in an FCC austenitic matrix (γ) along with minor phases like Laves, MC, TiN, etc, also Nb segregation greatly affects the structural properties and phase reaction in the cast alloy IN718 **[Radavich (1989)].**

1.5.1 γ -AUSTENITIC MATRIX

Nickel-iron base superalloys consist of the austenitic face centred cubic (FCC) matrix phase gamma (γ) and a variety of secondary phases. Nickel in the γ phase ranges from 30 to 70%, chromium up to 30%, iron from a relatively small amount to about 35%. Higher iron to nickel ratio causes poor oxidation resistance, but results in lower alloy cost and improved forgeability. In some alloys the γ phase contains small amounts of aluminium, titanium, niobium, molybdenum and tungsten to enhance either strength or corrosion resistance. Since most alloys contain relatively low carbon (<0.10%) and relatively large amount of ferrite stabilizers e.g., chromium and molybdenum, the minimum level of nickel required to maintain an austenitic matrix is about 25%. The addition of austenitic stabilizers, for example cobalt, may lower this requirement.

1.5.2 γ′ PHASE

Most of the precipitation hardenable commercial nickel base and nickel-iron base superalloys (e.g. IN718) are strengthened by precipitates of the γ′ phase ($L1_2$ structure) **[Pineau et.al (2009)]**. The γ′ structure is ordered FCC with nickel atoms occupying the face centers and the solute atoms like Al, Ti or Nb occupying the corners. As reported by a number of researchers the γ′ is coherent with the matrix. In 1970, **Raynor et al.** as well as **Munjal et al. (1975)**, observed that in nickel-base alloys strengthening by precipitation of γ′ is mainly due to order and coherency hardening mechanisms. Strengthening by other mechanisms was considered almost negligible.

1.5.3 γ″ PHASE

The main strengthening phase of the Ni-Fe base superalloys (e.g. IN718) is γ″, which is a metastable phase based on the Ni_3Nb stoichiometry. Significant amount of niobium/tantalum contents are necessary for this phase to form and all the commercial alloys like IN718, 706, 625 contain 2 to 6 wt% niobium **[Singh et al. (1991)].**

The unit cell of the body centred tetragonal DO_{22} structure (γ″) can be considered as composed of stacking of two $L1_2$ unit cells placed one on top of the other in the [001] direction with an antiphase boundary between them. The minority atoms occupy the corners and the body centre of the unit cell. The axial ratio is very close to 2 (c/a~2.05) **[Paulonis et al. (1969), Kirman et al. (1970), Cozar et al. 1973, Oblak et al. (1974)]** and because of this DO_{22} structure is regarded as superstructure forming from disordered FCC lattice, and the lattice misfit between γ and γ″ has been estimated to be 2.86% **[Chaturvedi et al. (1983)].**

Sluggishness of γ ″ age hardening reaction is an important characteristic of the γ ″ strengthened alloys. The sluggishness allows relief of weld residual stresses during ageing treatment, also it contributes to good weldability. In case of superalloy IN718, sluggishness is a function of coherency strain rather than an inherent characteristic of the γ ″ phase.

1.5.4 δ PHASE

The crystal structure of the stable δ-phase is orthorhombic. In the superalloy IN718, forging below δ-solvus ($1000^{o}C$) results in rapid nucleation of δ precipitate not only at grain boundaries but also within the grains. The resultant δ-phase distribution can control and refine grain size, resulting in optimum tensile properties and stress rupture ductility. Long-time service exposure will lead to formation of large amount of δ and cause degradation in properties. Loss of niobium from the matrix and γ ″ coarsening accompanies δ formation. So considering the kinetics of this transformation, exposure to temperature above $650^{o}C$ should be avoided.

1.5.5 MINOR PHASES

The minor phases found in the wrought Ni-Fe base superalloys such as IN718 are Laves, MC, TiN, etc. These phases generally result in an embrittlement of the alloy. During solidification, the Nb along with Mo and Ti segregates heavily to the interdendritic areas where Laves phases form. Segregated superalloy IN718 is generally homogenized to solutionize the Laves phase and diffuse the Nb evenly by high temperature thermal treatments. The primary MC and the TiN phases in the superalloy IN718 are considered to be stable phases and do not change with thermal cycles at lower temperatures.

1.6 MARINE GAS TURBINE ENGINE

Marine gas turbine engines are divided into three parts, namely, compressor, combustor and two turbines **[Zhao et al. (2014)].** The compressor compresses the incoming air to high pressure and directs the high velocity air to the combustion area to burn the fuel and produce high pressure, high velocity gases. These gases impact on turbine to extract energy from the high pressure, high velocity gas flowing from the combustion chamber.

In marine gas turbine, two turbines are used in series. The power for the compressor is taken from the turbine itself. In a series set up, the first gas turbine - also known as the compressor drive, high pressure gas turbine provides the drive for the compressor. The second turbine, also known as the low pressure, free or power turbine, drive the propeller or generator. This splitting of functions, compressor and external load, provides a better torque characteristic such as the one needed for a ship's propeller (Fig. 1.2).
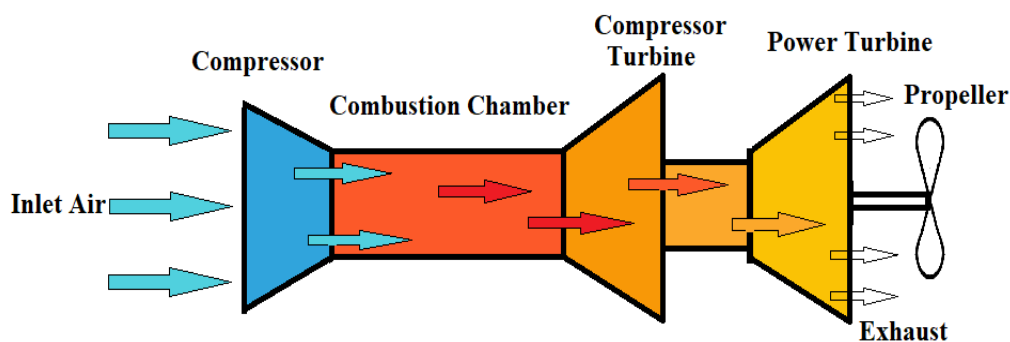
Fig. 1. 2: Schematic representation of marine gas turbine engine.

Since, marine gas turbines operate in the environments where ingestion of solid particles of NaCl with air is unavoidable, and this NaCl reacts with S and V which is present invariably in the fuel. This causes high temperature corrosion and oxidation at elevated temperature. Most common cause of failure in marine gas turbine engine are: fatigue and combined effect of hot corrosion & fatigue. Further, the effect of tensile mean stress on high cycle fatigue life of the engine components cannot be ignored. Therefore, several material and surface modification techniques are used to overcome these problems to provide strength, corrosion resistance and thermal stability.

1.7 OXIDATION BEHAVIOUR OF NICKEL-BASE SUPERALLOYS

Li et al. (2003), investigated the oxidation behavior of single crystal Ni-base alloy with prolonged exposure in air at 800 and 900°C. The oxide growth rate was nearly parabolic at both the temperatures. A thin scale of NiO at the outer layer, and Al - rich oxide at the inner layer was found at 800°C. At 800°C, non-uniform oxidation was observed in some areas, and complex phases like $CrTaO_4$, $NiCr_2O_4$, (Ni, Co) Al_2O_4, etc., were observed beneath the NiO outer layer, penetrating into the alloy. On the other hand, the scale formed at 900°C was more uniform consisting of an outer layer of NiO, spinel-rich sublayer, a $CrTaO_4$-rich layer, and an α-Al_2O_3 inner layer. Formation of protective inner layer of Al_2O_3 at 900°C provided better oxidation resistance, than the specimens exposed at 800°C, up to 1925 h. **Chen et al. (1997) carried out** investigation on various commercially available Ni-base superalloys i.e., Astroloy, Waspaloy and Udimet 720, exposed in temperature range from 750 to 1000°C isothermally, and cyclically at 1000°C. A thin and adherent chromia rich scales were formed on the alloys at 750°C after 1000 h, but Waspaloy showed deepest internal oxidation due to oxidation of the grain-

boundary carbides. Chromia rich external scales at higher temperatures up to 1000°C were also observed, but there was much higher internal oxidation. Faceted rutile were formed by oxidation of titanium in the alloys, diffusing through the chromia scale. Alumina formed as discrete internal oxides below the chromia scale, but AstroIoy when oxidized isothermally at 1000°C developed a semi-continuous internal layer of alumina due to its higher Al content. Under cyclic conditions the Astroloy formed a thicker, less protective scale of transition oxides probably due to its lower Cr content. In case of cyclic experiment at 1000°C, the irregular scale-alloy interface for the Udimet 720 and Waspaloy might have been be caused by local oxidation occurring, below the cracks which had been induced by the thermal cycling. Nevertheless, apart from cracks, the external scales of all the three alloys were continuous. The oxidation behavior of a single-crystal Ni-base superalloy DD32 at 900 and 1000°C in air was studied by **Liu et al. (2010).** Two step oxidation kinetics was observed at both the temperatures, the first step was governed by NiO growth; and the second step was controlled by Al_2O_3 growth, until a continuous Al_2O_3 layer formed under the previously grown NiO layer with the passage of time. The scales formed at 900 and 1000°C were complex, and consisted of three layers: an outer columnar NiO layer with a small amount of CoO, an intermediate layer mainly composed of $W_{20}O_{58}$, $CrTaO_4$, a small amount of spinels $NiCr_2O_4$, $NiAl_2O_4$ and $CoAl_2O_4$ probably with other oxides of refractory metals Nb, Mo and Re, and an inner continuous layer of Al_2O_3. **Delaunay et al. (2000)** studied oxidation behavior of the superalloy IN718 at 900°C in air under isothermal conditions. Formation of a layer of a rhombohedral phase $Cr_{2-x}M_xO_3$ resulted due to oxidation, and formation of TiO_2 crystals occurred on the scale surface and was attributed to rapid diffusion of Mn and Ti across this scale. Nb diffuses along the grain boundaries of the alloy and forms $CrNbO_4$ during the initial stage of oxidation. Also, formation of chromium oxide caused depletion of Cr

and formed a depleted zone in the alloy. **Greene et al. (2001)** studied oxidation behavior of the superalloy IN718 in the temperature range from 700 to 1347°C. In the temperature range from 700 to 950°C, after a period of transient oxidation, passivation of samples occurred; in temperature range 900 to 1300°C, the rate of oxidation was limited by diffusion and exhibited a constant parabolic rate dependence; and in the temperature range from 1200 to 1341°C, samples were deformed and damaged by the high rate of oxidation.

An interesting investigation considering the effect of surface roughness on the oxidation behavior of the Ni-Base Superalloy ME3 was carried out by **Evans (2010)**. Isothermal oxidation tests were performed in air for different times to investigate the kinetics of oxide growth. The initial surface roughness was found to affect the oxidation rate; the largest surface roughness caused largest mass gain for 10, 15, 20, and 31 h at 704°C. The mass gain increased with increase in the initial surface roughness for all the times. A Cr-rich oxide was present on the surfaces of all the samples. Larger oxide particles were observed on the sample with the 220 grit surface finish as compared those of 600 and 1200 grit samples.

1.8 HOT CORROSION

In the late 1960s during the Vietnam conflict, military aircrafts operating over the sea suffered severe corrosion, defined as hot corrosion **[Sidhu et al. (2005)].** Hot corrosion is a process of accelerated oxidation occurring mainly due to chemical reactions between a component and molten salt deposits, resulting from the presence of salt contaminants such as Na_2SO_4, NaCl, and V_2O_5. Ni-base and Ni-Fe based superalloys are greatly affected by hot corrosion in marine gas turbine components as well as in the

aircraft engines. Marine gas turbines operate at lower temperature than aero-engines i.e., in the range of 500- 1000°C. To sustain such a high temperature, Cobalt or Nickel-based superalloys have been used for the components of hot section of blades and vanes. Marine gas turbines and aircrafts flying from aircraft carrier operate in the environments where ingestion of solid particles of NaCl with air is unavoidable. The NaCl present in the compressed air reacts with sulfur present in the fuel and form Na_2SO_4, this sodium sulfate gets deposited on the hot sections of the turbine and causes hot corrosion. The process of hot corrosion is categorized as high-temperature hot corrosion (HTHC, 750-950°C), and low-temperature hot corrosion (LTHC, 550-750°C).

1.8.1 HIGH TEMPERATURE HOT CORROSION (HTHC)

High temperature hot corrosion (HTHC) occurs in the temperature range of about 750-950°C and sodium sulphate remains in molten state. Other contaminants present in the fuel or in the air, like phosphorous, lead, vanadium, phosphorus, and chlorides react with sodium sulphate to form eutectic compounds, thus intensifying the corrosion attack. Hot corrosion by potassium sulphate shows similar behaviour like sodium sulphate in terms of corrosion attack [Eliaz et al. (2002)]. Sulfur is liberated from sodium sulphate which diffuses inward, then reacts with elements of base material to form their sulfides [Koul et al. (1993)]. Intense spalling, sputtering and enormous weight gain during HTHC in aggressive environments was observed by several investigators [Saigusa et al, (1982), Jian et al. (2000), Prakash et al. (2005), Sidhu et al. (2006), Sidhu et al. 2007, Cho et al. (2007), Kamal et al. (2008), Sreedhar et al. (2009), Sreedhar et al. (2010), Kamal et al. (2010)].

1.8.2 LOW TEMPERATURE HOT CORROSION (LTHC)

Low temperature hot corrosion (LTHC) occurs much below the melting point of pure sodium sulphate, i.e. in the temperature range of about 550-750°C. The eutectic Na_2SO_4-MSO_4 (M = Ni, Co and Fe) undergoes to molten state [Eliaz et al. (2002), Xueming et al. (2008), Mahobia et al. (2013), Mannava et al. (2016)]. This type of corrosion is exceptionally noticed in aero engines due to the higher operating temperature of the turbine blades [Koul et al. (1994)], occurs mainly in the marine and land base industrial gas turbines. Several corrosion mechanisms have been suggested and the salt fluxing mechanism is most extensively accepted. Depending on the salt composition, oxides dissolve in Na_2SO_4 by basic fluxing through anions or by acid fluxing through cations [Rapp (2002), Meier (1989)].

1.8.3 HOT CORROSION OF NICKEL-BASED SUPERALLOYS

Li et al. (2006), studied hot corrosion behavior of a single crystal Ni-base superalloy coated with Na_2SO_4 and 75% Na_2SO_4 + 25% NaCl mixture exposed at 900°C. The corrosion products formed were laminar structured, porous and easily spalled and non-protective scales were formed. The oxidation of sulfides released sulfur, which again diffused inward into the SC superalloy to cause further attack. The repetition of oxidation and sulfidation in turns led to penetration of the sulfides deep into the base alloy. The accelerated corrosion of the SC superalloy coated with salt mixture was attributed to formation of Cl_2, which reacted cyclically with oxides as well as Ni, Al and other elements in the superalloy and formed volatile chlorides. **Zheng et al. (2011),** investigated hot corrosion behavior of the powder metallurgy (PM) Rene 95 Ni-based superalloy in molten 25%NaCl + 75%Na_2SO_4 salts at 650, 700 and 750°C, by weight loss measurements. The hot corrosion kinetics followed square power law at 650°C and

linear power law at 700 and 750°C. The corrosion layers on the surface of PM Rene 95 superalloy mainly consisted of Cr_2O_3, NiO, and Ni_3S_2 at the each temperature. Also, $NiCr_2O_4$ at 700°C and NaCl at 750°C were observed respectively. The cross-section and corresponding elemental mapping represented the corrosion layer near scale/alloy interface which mainly consisted of oxides at 650°C, but oxides and sulfides were observed at 700 and 750°C. These results confirmed the combined mode of attack, i.e., oxidation and sulfidation, for hot corrosion. **Seybolt (1968),** studied the effect of Na_2SO_4-induced hot corrosion of Ni–Cr alloys and suggested that sulphide formation is a prerequisite for the occurrence of hot corrosion. **Bornstein et al. (1971, 1973)** proposed a mechanism based on the dissolution of the protective oxide scale in the fused salt, i.e., basic fluxing. On the otherhand, **Goebel et al. (1970) and Goebel et al. (1973)** suggested that there is also occurrence of acidic fluxing with the re-formation of oxides leading to oxidation by Na_2SO_4 of the alloys containing strong acidic components, such as V or Mo.

Balasone (1985) studied hot corrosion behavior of nickel based superalloys Rene 77 and Rene 88 in 100% Na_2SO_4, and 90% Na_2SO_4 +10% NaCl salt mixture at 900°C up to 72 h. Rene 80 showed better hot corrosion resistance than Rene 77 due to adherent oxide layer, rich in Cr and Ti, formed on the surface of the Rene 80. **Deb et al. (1996)** studied the effect of oxidation and hot corrosion in Na_2SO_4, NaCl-Na_2SO_4, Na_2SO_4-$NaVO_3$-NaCl environments on cast nickel base superalloy, at the temperatures of 900, 925, 950 and 975°C, up to 100 h. Oxide formation on the coated and uncoated samples, followed parabolic kinetics and sulfates caused internal sulfidation of the alloy beneath the external oxide layer. Formation of voids and pits took place due to formation of volatile species of chlorides, which provided an easy path for the flow of corrosive species. The presence of vanadate with sulfate and chlorides, provided additional fluxing action which damaged the integrity of alloy and caused reduction in its mechanical

properties. **Gurrappa (1999)** performed hot corrosion tests on the CM247LC alloy, in Na_2SO_4, and also inNaCl-Na_2SO_4 environments, at various temperatures and found that a chloride containing melt was more corrosive than the pure Na_2SO_4. **Zhao et al. (2004),** investigated hot corrosion behavior of IN740, with and without Na_2SO_4 deposit, over the temperature range from 850 to 1000°C. Oxides of Cr, Ti, Al were formed along with the formation of internal oxides and sulfides, at all the temperatures. Degradation in corrosion resistance of this alloy was due to the dissolution of Cr_2O_3, induced by basic fluxing in the molten Na_2SO_4. **Sidhu et al. (2006)** evaluated high temperature oxidation and hot corrosion behavior of Superni 75 and Superfer 800H in the Na_2SO_4-NaCl environment at 800°C under cyclic test conditions. Formation of scale, rich in Cr_2O_3, NiO and spinel $NiCr_2O_4$ provided hot corrosion resistance to the Superni 75, on the other hand, formation of non-protective oxide of iron, and sulfides of iron and nickel led to relatively less hot corrosion resistance of the Superfer 800H. **Khorsand et al. (2018),** conducted high temperature corrosion tests on the IN625 Ni-based superalloy in molten nitrate salt of 40 KNO_3–60 $NaNO_3$ (wt.%) at 500 and 600°C. The corrosion tests were performed using open-circuit potential, potentiodynamic polarization, electrochemical impedance spectroscopy and gravimetry to evaluate the degradation of the alloy. The oxidation rate and mass gain increased with the increase in temperature and followed parabolic rate law of oxidation. During the electrochemical corrosion test, formation of a non-protective oxide layer which led to dissolution of nickel was the main reason for the less corrosion resistance of the alloy at 500 and 600°C. Sodium nitrite was found to be pitting inhibitor and was confirmed by cyclic polarization tests, which showed a positive hysteresis confirming the nucleation and growth of stable pits on the surface of the superalloy IN 625.

Superalloy IN718 is known for its excellent high strength and oxidation resistance at elevated temperatures but suffers from salt induced corrosion of its components in marine gas turbine engine. **Paton et al. (1973)** also studied the effect of NaCl induced corrosion on the superalloy IN718 at 704°C and found that degradation of the alloy depended upon the oxygen partial pressure. **Mansfeld et al. (1973)** studied corrosion behaviour of the superalloy IN718 in NaCl and KCl environment at 820°C. At this temperature, NaCl in molten state gets diffused in the substrate, and causes degradation of the alloy. **Gurruppa et al. (2003)** investigated the effect of Na_2SO_4-NaCl environment at 900°C, and found that molybdenum and iron in the superalloy IN718 are more prone to hot corrosion. **Prakash et al. (2005), Sidhu et al., (2006), Sidhu et al. (2007), Kamal et al. (2008), Kamal et al. (2010),** studied the effect of hot corrosion on the superalloy IN718 in Na_2SO_4-V_2O_5 environment at 900°C. Intense spallation with weight gain was found to take place due to presence of Mo, which induced rapid fluxing of the oxide scale and led to hot corrosion. Diffusion coating was found to improve the hot corrosion resistance. **Trinstancho et al. (2011)** conducted electrochemical hot corrosion tests on the superalloy IN718 in the Na_2SO_4, $80V_2O_5 + 20Na_2SO_4$, and $NaVO_3$ environments and found an increase in corrosion rate with the addition of V_2O_5 and $NaVO_3$ in Na_2SO_4 and with increase in the temperature. **Mahobia et al. (2013),** investigated the effect of variation in the amount of coating, in different salt mixtures (100wt.% NaCl, 75 wt.% $Na_2SO_4 + 25$ wt.% NaCl, and 90 wt.% $Na_2SO_4 + 5$ wt.% NaCl $+ 5$ wt.% V_2O_5) on hot corrosion behavior of the superalloy IN718 at 550° and 650°C under cyclic heating and cooling for 100 h. The samples coated with 100% NaCl showed maximum damaging effect due to oxy-chlorination reaction at both the temperatures. On the other hand, the salt mixture of NaCl and Na_2SO_4 had no effect at 550°C, however; it was detrimental at higher temperature of 650°C. Coatings of the salt mixture of Na_2SO_4, NaCl and V_2O_5 caused slow oxidation at

both the temperatures. Increase in the amount of salt coating led to high corrosion kinetics for all the types of coating. **Mannava et al. (2016),** also studied hot corrosion behavior of the superalloy IN718, in Na_2SO_4-NaCl and Na_2SO_4-$NaVO_3$-NaCl environments, exposed at 650°C. $NaVO_3$ was found to accelerate the oxidation behavior. Also, in the case of isothermal studies formation of $NaVO_3$ took place by the reaction of V_2O_5 and Na_2SO_4, and formation of chromium sulphides and chromium vandate led to depletion of Cr from the substrate. Hot corrosion followed basic fluxing mechanism. **Koech et al. (2018),** investigated corrosion behaviour of hot-dip aluminized-coated and uncoated superalloy IN718, exposed at 750°C for 10 h, in air and NaCl salt environment. Cr_2O_3 was formed on the surface of uncoated material, oxidized in air. However, porous scale of Fe_2O_3 was formed on the top of the Cr_2O_3 oxide on the surface of the uncoated sample exposed in NaCl environment with heavy scale spallation and corrosion. The hot-dip coating on the superalloy IN718 showed enhanced oxidation resistance. Scale spallation with formation of voids in the aluminium layer increased with thermal cycle. The coating also improved corrosion resistance of the substrate, exposed in the NaCl environment. However, degradation of the aluminized layer by formation of cracks and voids led to diffusion of NaCl in the substrate, causing extensive corrosion. The presence of voids in the coating was due to outward diffusion of aluminium to form oxide scale, inward diffusion to form NiAl layer, and oxychlorination process.

1.8.4 EFFECT OF OXIDATION AND HOT CORROSION ON MECHANICAL PROPERTIES OF NICKEL BASED SUPERALLOYS

Duquette et al. (1972) investigated the effect of air and vacuum on fatigue behavior of single crystal of the nickel-base superalloy MAR-M200. The fatigue life was found to be higher in the air than in vacuum. Fatigue cracking was internally initiated in the air,

whereas cracking was initiated in vacuum at the specimen surface. **Floreen et al. (1979)** studied about the fatigue crack growth rate of the superalloy IN718 at 650°C in different gaseous environments. Presence of oxygen or sulfur in the gaseous environment was found to cause a significant increase in the rate of fatigue crack growth. **Nazmy (1982)** exposed IN738 to synthetic ash and SO_2/SO_3 containing air, at 850°C for 1000 h, and its LCF life was found to be less than that of the standard unexposed specimen. The decrease in the LCF life of the exposed specimens was attributed to the effect of sulfidation on the process of crack initiation. LCF behavior of the as heat treated IN-738LC in the air, and in the corrosive environment of $25NaCl + 75Na_2SO_4$ (wt.%) at 900°C was studied by **Jianting et al. (1983)** and fatigue life was found to be reduced in the corrosive environment. **Ghonem et al. (1982)** studied the fatigue crack growth behavior of the superalloy IN718 at 650°C, subjecting to a loading frequency lower than the transitional frequency of this alloy, and found it to be fully environment dependent. **Bagui et al. (2013)** investigated the effect of $Na_2SO_4 + NaCl$ salt mixture on creep rupture properties of the Nimonic-263 alloy at 800 and 850°C, the rupture life was found not much affected by the corrosive action of the salt mixture for the short duration tests at both the temperatures. However, degradation of creep rupture properties was observed during the long term creep tests. Low cycle fatigue behavior of the nickel base superalloys was studied by **Gordan et al. (2009), Sahu et al. (2013), Mahobia et al. (2013), Li et al. (2016)** at elevated temperatures in different salty environments, and fatigue life was found to be drastically reduced. Recently, **Brooking et al. (2018)** studied the combined influence of hot corrosion and stress on single crystal CMSX-4 alloy, under both fatigue and static stress loading conditions and observed cracking under both the loading conditions in the corrosive environment. **Smialek et al. (2018)** studied the effect of corrosion resistant coating of Cr_2AlC on thermal mechanical fatigue of low solvus high

refractory disk alloy at 760°C. The protective coating served as a barrier to formation of pits due to hot corrosion. **Li et al. (2018)** investigated the influence of low-temperature hot corrosion in Na_2SO_4–NaCl salt environment, on LCF behavior of the powder metallurgy Ni-based superalloy FGH96 at 700°C. The LCF life of the salt-coated samples was reduced due to hot corrosion which led to early crack initiation resulting from the deterioration of the surface due to corrosion pits and accelerated fatigue crack propagation because of weakening of grain boundaries. **Kumar et al. (2018)** conducted a case study in which an aircraft crashed shortly after the take-off. Engine failure was identified as a cause of crash in the initial investigation, engine teardown revealed that several turbine blades on the second-stage power turbine (PT) had failed due to fatigue in the airfoil. However, subsequent failure analysis revealed that the fatigue failure was due to the presence of liquid lead on the airfoil at the operating temperature which reacted with the nickel-base superalloy and caused the fatigue crack initiation. Lead was used in the manufacturing process for fixture support during machining of the blades. The general operating temperature in the second-stage turbine was reported as 315 – 370°C, while the melting point of lead is 327°C. During the engine operation, molten lead penetrated in the surface of the alloy and generated fatigue crack initiation sites on the high-pressure side of the blade airfoils and caused high cycle fatigue failure.

Yoshiba et al. (1988) found that there was considerable stress concentration at the bottom of the corrosion pits to cause early initiation of fatigue cracks. High temperature corrosion fatigue behavior of the superalloys IN751, IN718 and Fe-42Ni-15Cr-3Mo was studied at 800°C in 90 wt.% Na_2SO_4 + 10 wt.% NaCl salt environment at 1500 rpm. The hot corrosive environment was found to cause drastic reduction in fatigue strength. **Prakash et al. (2014)** also studied the high cycle fatigue behavior of the superalloy IN718

in the 75 wt.% Na_2SO_4 + 25 wt.% NaCl atmosphere at 550 and 625ºC at a low frequency of 2 Hz. Pit formation on the smooth specimen at 550ºC in the corrosive environment caused reduction in the number of cycles for fatigue crack initiation. At 625ºC, crack growth was along the grain boundaries, thus the attack was more severe than that at 550ºC.

1.9 NEED FOR HOT CORROSION RESISTANCE

The need for the development of substrate alloys to achieve high strength, corrosion resistance and creep resistance at elevated temperature does not go hand in hand with these objectives. For example, an increase in the Al and Cr content leads to improved oxidation and corrosion resistance, but after a certain level, these elements reduce creep strength of the resulting alloys. To achieve both strength and resistance to the environmental degradation, the two functions are separated. The load capability is provided by the substrate alloy, whereas oxidation and corrosion resistance is achieved by the application of thin coatings with adequate Al and Cr and with some surface modification techniques.

Various types of coatings such as diffusion coating, overlay coating and thermal barrier coating are used for improving oxidation and high temperature corrosion resistance of turbine blades. Diffusion coating is a type of surface enrichment process which consists of a substrate alloy surface layer enriched with oxide scale formers Al, Cr, Si, or their combination to a depth of 10 to 100 µm. High temperature coatings based on intermetallic compounds such as aluminides are extensively used to protect gas turbine hot section components from attack in aggressive environments **[Houngninou (2004)].** Overlay coating consist of MCrAlX where M (nickel and/or cobalt and/or iron) and X is one or more reactive elements such as yttrium, hafnium, etc. At high temperature

these coatings initially form chromic oxide and then aluminum oxide **[Warnes (2003)]**. There are also some other methods like cold spray, plasma spray, electro-spark deposition, physical vapor deposition, low pressure plasma spray, high velocity oxygen fuel (HVOF) etc., used for deposition of overlay coatings. Another type of protective coating is thermal barrier coating (ceramic coating), a combination of multiple layers of coatings with each layer having specific function. The topmost layer consists of a ceramic mainly ZrO_2, which provides thermal insulation, the ceramic insulating layer is deposited on the substrate alloy with an intervening oxidation resistant metallic layer called the bond coat. TBCs are most superior coating than the overlay coating followed by diffusion coatings, and are used in rotating parts of aero-engine such as, turbine blades, nozzle guides and combustor section **[Bose (2007)]**.

Apart from protective coating, researchers are also focussing to enhance the oxidation, corrosion resistance and fatigue strength by various surface modification techniques. Multi-pass friction stir process, laser shock peening, shot peening, ultrasonic shot peening, high energy shot peening, etc., are used to enhance the properties of structural components. High temperature oxidation-corrosion resistance and fatigue life of the structural components are improved by these techniques [**Li et al. (2013)Ren et al. (2014), Shadangi et al. (2015), Montross et al. (2002), Clauer (1991), Peyre et al. (1998), Clauer et al. (1983), Fournier (1989), Chao et al. (2012), Umemoto et al. (2005), Tan et al. (2008), Kumar et al. (2016)**].

Ultrasonic shot peening are nowadays used for improving mechanical properties of metals and alloys without changing their chemical compositions [**Sanda et al. (2011), Kumar et al. (2014)**]. The compressive residual stresses induced on the surface and surface grain refinement retard the process of corrosion. In this process, the surface of

workpiece is subjected to impact of small shots, at ultrasonic frequency which causes severe plastic deformation at room temperature. Fig. 1.3 shows schematic representation of USP process. Hot corrosion resistance is improved by USP **[Kumar et al. (2016)]** and also improvement in the fatigue life is reported **[Pandey et al. (2015), Pandey et al. (2017) and Kumar et al. (2017)].**
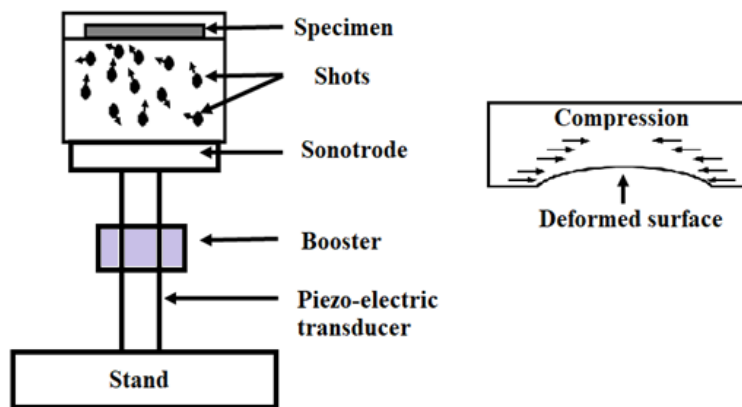

Fig. 1. 3: Principle of ultrasonic shot peening.

1.10 ROLE OF STRESS RATIO AND MEAN STRESS ON HIGH CYCLE FATIGUE BEHAVIOUR

In the recent past, gas turbine engine failures due to low cycle fatigue was main concern of engineers and designers. But, now a days a sharp reduction in LCF failure is observed due to focused development in damage tolerant methodology and a majority of failures are associated with HCF. Components of turbine engine encounter variable loading which causes initiation and propagation of fatigue cracks, leading to catastrophic failure. High cycle fatigue resistance of compressor airfoils and fan is needed, in the brief sweeps along resonant modes through the throttle transients. An airfoil experiences an increase in stress amplitude with continuous change in the stress ratio, also high tensile mean stresses are involved in many other parts like turbine blades, wings of airplane, and

bolts. The deleterious effect of mean stress on endurance limit at low stress ratios (R ≤ 0.5) is known, however, there is limited literature available on the effect of higher stress ratio. Several investigations have been reported on the effect of high stress ratio for notched specimens **[Ritchie et al. (1999), Prakash et al. (2009)]**, and limited studies are reported on the high stress ratio for un-notched specimens. Gas turbine engines experience short bursts at high mean stress at frequencies more than 1 kHz. Influence of positive mean stress on HCF life is focused on several methodologies over the years. Variation of mean stress with stress amplitude commonly known as Haigh diagram is one of the most accepted way for constant fatigue life. This diagram is extensively used to find out the stress amplitude with respect to the mean stress. Mostly the studies on HCF have been carried out on symmetric loading and data are extrapolated to high stress ratio. Therefore, it is very important to determine the limit for safe life of components and develop a system to forecast in real time, by understanding the contribution of stress ratio on fatigue life **[Morrissey et al. (1999), Caton et al. (2012), Karadag (2003)].**

Kunz et al. (2006) described the role of positive mean stress on IN713LC, exposed at 800°C, and observed that small cyclic component of stress amplitude superimposed on the mean stress is safe and does not reduce fatigue life. The time to fracture even increased with increasing amplitudes. The reverse of this trend was observed from the change of damage mode from ductile to fatigue that occurred with increasing HCF amplitude. Most of the HCF tests have been performed on steel, titanium, polycrystalline copper, aluminum and their alloys at low stress ratios and frequencies **[Ritchie et al. (1999)**, **Caton et al. (2012), Karadag (2003), Kovacs et al. (2013), Lucas et al. (1989)].**

1.11 SCOPE OF THE PRESENT WORK

Now a days, gas turbine is one of the most important unit for deriving power in variety of applications like military aircrafts, land base power plants, jet and marine propulsion systems. Presence of contaminants in the fuel and salt particulates in the ingested air leads to deposition of a highly damaging compound of sodium sulfate on the surface of turbine engine components, leading to accelerated oxidation or hot corrosion. This causes roughening of surface which leads to severe damage of the component and results in premature failure of the turbine component. These component suffers combined hot corrosion and high cycle fatigue in actual service environment. Corrosive environment can lower the endurance strength of the alloys, thereby reducing the fatigue life. Currently, researchers are only focusing on two parameters, temperature and salt environment for hot corrosion, and there is no systematic study related to effect of surface roughness on hot corrosion behavior of any superalloy. Hence, it is very important to carry out hot corrosion studies considering the effect of surface roughness. Very limited literature are available on high cycle fatigue life estimation based on actual operating conditions. Therefore, it is important to study the high cycle fatigue behavior in air and salt environment to assess the effect of hot corrosion on fatigue life. Apart from the combined effect of the hot corrosion and high cycle fatigue, under symmetric loading, many components such as bolts, gas turbine blades and airplane wings experience high tensile mean stresses. The effect of mean stress on fatigue life of metals is well known for lower stress ratios, but there is less information available in the literature for the high stress ratio. Therefore, it is also significant to carry out systematic investigation on the effect of high stress ratio and mean stress on high cycle fatigue behavior.

It is worth mentioning that the actual operating temperature of the superalloy IN718 in gas turbine engine is up to 650ºC, however, the temperature inside the gas turbine chamber may shoot 650ºC, and therefore, the temperatures for the present investigation are chosen 600 and 700 ° C (±50 ° C of actual operating temperature). The scope of the present investigation includes systematic investigation on the effect of surface roughness on hot corrosion behavior of the bare nickel based superalloy IN718 with three different salt coatings : 100wt.% NaCl (S1), 60wt.% Na_2SO_4 + 40wt.% V_2O_5 (2SM) and 75wt.% Na_2SO_4 +15wt.% NaCl + 10wt.% V_2O_5 (3SM), at two intermediate temperatures of 600 and 700°C for a period up to 100 h. Surface nanostructuring is considered to be helpful in reducing the corrosive attack, therefore, an attempt is made to study the effect of surface nanostructuring by ultrasonic shot peening (USP) on hot corrosion resistance of the superalloy IN718 in the above mentioned test environments. The role of pre-hot corrosion, high stress ratios (R = -1, 0.5 and 0.7) and mean stress on high cycle fatigue behavior of the superalloy IN 718 is studied at 600ºC.

1.12 OBJECTIVES OF THE PRESENT INVESTIGATION

The objectives of the present investigation are to study the effect of the following:

- Surface roughness and ultrasonic shot peening on hot corrosion behavior of the superalloy IN718 at 600 and 700°C for a period up to 100 h.

- Pre-hot corrosion by three salt mixture (75 wt.% Na_2SO_4 + 15 wt.% NaCl + 10 wt.% V_2O_5) on high cycle fatigue behavior of the superalloy IN718 at 600°C.

- Stress ratio and mean stress on high cycle fatigue behavior of the superalloy IN718 at 600°C.