Study of characteristics of plasma nitriding and oxidation of superalloy IN738LC

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STUDY OF CHARACTERISTICS OF PLASMA NITRIDING AND OXIDATION OF SUPERALLOY IN738LC

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirement for the degree of

Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

Mary Shanti Pampana
Bachelor of Technology
Jawaharlal Nehru Technological University, Hyderabad, India 2001
August 2004
Dedication

I praise God for His blessings to be what I am today. This thesis is dedicated to my grandparents, Medisetti SathiRaju, Medisetti Payditalli, parents, Pampana Surya Bhaskar Rao, Pampana Varalakshmi, my major professor, Dr. Aravamudhan Raman, my previous employer Mr. SaiKumar Pampana who always encouraged me to believe in myself, to put continuing effort till the goal is reached, and to other professors and teachers who gave me a good foundation for my graduate studies.
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This research would not have been complete without the help of Dr. E.I. Meletis and Dr. Samuel Ibekwe, who contributed immensely, allowing me to use the very essential equipment available at LSU and Southern University. I am grateful to Dr. Wen Jin Meng for teaching me Material Thermodynamics, Advanced techniques in Material Characterization and TEM. I thank Dr. Xiaogang Xie, High Magnification Imaging and Microanalysis Laboratory, Geology and Geophysics department, for training me to be proficient in SEM image analysis. I am also gratefully indebted to the ME department and to its chairman, Dr. Tryfon T. Charalampopoulos for the special support. I gratefully acknowledge the guidance given by Varshni Singh throughout the nitriding experimentation and analysis. I thank Dr. Jiechao Jiang at the Materials Characterization Facility for providing assistance to carry out XPS study.

I would like to thank Praveen, Aparna, Amol, Rakesh and other friends who gave me lot of moral support, encouragement and advice.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN738LC</td>
<td>A cast Ni-base superalloy strengthened by $\gamma'$ precipitates, containing low carbon; patented trademark of International Nickel Co., USA. See p.14 for its composition.</td>
</tr>
<tr>
<td>L12</td>
<td>FCC superlattice of the Cu$_3$Au type</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Matrix phase in Ni-base superalloy</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>Ni$_3$Al(Ti, Nb) precipitate phase in a Ni-base superalloy with L12 structure</td>
</tr>
<tr>
<td>LSW</td>
<td>Lifshitz – Slyozov and Wagner theory</td>
</tr>
<tr>
<td>AC</td>
<td>Air-cooled</td>
</tr>
<tr>
<td>AAC</td>
<td>Accelerated air or argon-cooled</td>
</tr>
<tr>
<td>WQ</td>
<td>Water quenched</td>
</tr>
<tr>
<td>HIPing</td>
<td>Hot isostatic pressing</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>PO</td>
<td>Preferred orientation (texture)</td>
</tr>
<tr>
<td>IPA</td>
<td>Intensified plasma assisted</td>
</tr>
<tr>
<td>IPAP</td>
<td>Intensified plasma assisted processing</td>
</tr>
<tr>
<td>IPAN</td>
<td>Intensified plasma assisted nitriding</td>
</tr>
</tbody>
</table>
Abstract

IN738LC is a nickel base superalloy, widely used in various applications in turbine engines at high temperatures. Its oxidation and nitriding characteristics were focused in this study.

Oxidation kinetics of IN738LC in dry air was studied at selected temperatures, specially chosen depending on the chemical dynamics of the alloy at such high temperatures during annealing. Isothermal oxidation in dry air was carried out at 1000°C, 1090°C, 1140°C and 1190°C. XRD results indicated an interesting onset of preferred orientation in the γ’ depleted layer in all the samples. The XPS and XRD analyses revealed the main oxide phases present in the oxide layers. Volatilization of Cr₂O₃ was found to be the reason for the weight loss in the superalloy. Al₂O₃ formed a reliable and stable oxide layer above 1100°C. Above 1140°C two different FCC solid solutions were formed and the superalloy oxidized heavily and lost weight.

Intensified plasma-assisted nitriding (IPAN) is one of the most widely used surface nitriding techniques. The surface of the as-received IN738LC was nitrided using this technique. Preferred orientation was observed in the samples nitrided with 0.5, 1.0 and 1.5 mA of current density. The XPS analysis showed the formation of TiN and CrN along with TiO₂. Nano precipitates of TiN were observed on the γ' precipitates. IPAN improved the microhardness value of the superalloy by about 70% and its wear resistance by about 10%.
Chapter 1. Introduction

1.1 High Temperature Materials

Material scientists and design engineers working with heat resistant materials must know the high temperature characteristics, effects of processing and microstructure on high temperature properties, high temperature oxidation and corrosion characterization and application of coatings to prevent the various high temperature corrosion problems. This information enables a property comparison and allows ranking of alloy performance, helping in the selection of the materials and design guidelines for industrial applications. Special topics like creep-rupture data assessment, thermal and thermo mechanical fatigue, elevated-temperature crack growth, creep-fatigue interaction, design for high temperature applications and prevention of excessive oxidation are of great importance in this aspect. Superalloys were developed with a view to improve both reliability and performance in service in gas turbine environments [1].

Superalloys find extensive application in aerospace industries, nuclear reactors, chemical, petrochemical, power generation plants, environmental protection systems, cryogenic applications and furnaces, where extreme temperatures, mechanical stresses and corrosive environments are encountered [2]. They are classified as nickel based, cobalt-based and iron based superalloys.

The turbine system that functions at high temperatures consists of many expensive components, which must all work together without failure. Each of the components must be monitored and controlled and taken care of to avoid serious damages. The components in the path of the hot gas stream must have excellent resistance to oxidation and hot corrosion in order to sustain the cyclic loading [3]. Blades and vanes are the most important components in a combustion turbine [4]. Often people
try to increase the efficiency of the turbine by increasing the rotor inlet temperature. So, effective cooling of the system must be ensured for safe operation over a long period of time.

Apart from the required cooling of the system, the rotating blades must also have better oxidation and corrosion resistance, high thermal fatigue resistance at both low and high cycles, excellent microstructural stability [5] and high creep resistance.

1.2 Ni–Based Superalloys

Nickel-based alloys are the ones widely used for high temperature applications. Over 50% of the advanced aircraft engines use superalloys. The physical metallurgy of the superalloy is complex, subtle and sophisticated; yet the relationship of properties to microstructures in these alloys is certainly the best known for all materials used in the temperature range of 650-1050°C [9].

The superalloys consist of solid solution formers, precipitate formers and carbide formers. The first class consists of elements that form the FCC austenitic γ matrix. These are from groups V, VI and VII and include nickel, cobalt, iron, niobium, tantalum, chromium, molybdenum and tungsten. The second class of elements form the γ' (Ni3X) precipitates. These elements are from groups III, IV and V and include Al, Ti, Nb, Ta and Hf.

Boron and C make up a third class of elements that tend to segregate to grain boundaries. These elements are from groups II, III, and IV and form compounds that usually precipitate out of the matrix at high temperatures. Al is noted as a precipitation strengthener and a potent solid solution strengthener. W, Mo and Cr also contribute strongly as solid solution strengtheners, whereas Ti and Co are weak solid solution strengtheners. The slow-diffusing elements Mo and W would be expected to be the most
potent hardeners. An additional beneficial effect on diffusion has been shown in a Ni-22%Cr-2.8% Ti-3.1%Al alloy; the presence of Mo and W lowered the diffusivity of Ti and Cr at 900°C [6]. Nickel-based superalloy basically consists of γ′ precipitates in γ solid solution matrix, the former ranging in amount from ~ 30 to 75% by volume in different alloys.

1.3 Strengthening of Superalloy

Many Inconel alloys are cast alloys having good oxidation and creep resistance. The strength of these superalloys arises from a combination of hardening mechanisms, including contributions from solid solution elements, grain boundaries and precipitates. In addition thermo mechanical processing is sometimes used to provide strengthening through increased dislocation density and the development of a dislocation substructure. That the modulus difference between the solute and solvent may give rise to strengthening is based on the argument that extra work is needed to force dislocations through hard regions in the matrix or precipitates. Borides and carbides only provide little additional strengthening at low temperatures due to their small volume fractions, although they may have significant effects on creep rate, rupture life, and rupture strain through their influence on grain boundary properties.

1.4 Phases in the Superalloy

Superalloys are dynamic systems at high temperatures. The phases present are reacting and interacting continuously. The very complex high temperature solid-state reactions prevent defining chemical equations of state to categorize the systems.

- **Gamma Phase (γ):** The continuous matrix is an FCC nickel base austenitic phase called gamma phase, that usually contains a high percentage of solid solution formers such as Co, Cr, Mo and W.
• **γ’-Ni₃X Phase**: Al and Ti are added in small amounts and mutual proportions to precipitate high volume fraction of FCC γ', which invariably precipitates, remaining coherent with the austenitic γ matrix. Ni₃Al is a superlattice possessing the Cu₃Au-L₁₂ type structure [7] and it exhibits long-range order to near its melting point of 1385ºC. Ni base alloys are vastly strengthened by γ' precipitate. For the stronger alloys, heat treatments and service exposure generate a film of γ' along the grain boundaries which improves rupture properties.

**Carbide Phase**: Carbon added at levels of about 0.055-0.2% combines with reactive and refractory elements such as Ti, Ta and Hf to form MC carbides. During heat treatment and service these begin to decompose into lower carbides such as M₂₃C₆ and M₆C, which segregate at the grain boundaries [8]. Carbides affect both the mechanical and fracture properties. They are mostly found as MC carbides, segregated along the grain boundaries, and act as stress-raisers and initiate cracks in the material. Misfit between matrix and carbide leads to crack nucleation [9]. Under certain conditions, plate like phases such as sigma, μ and Laves are formed which leads to lowered rupture strength and ductility.

1.5 Development of Microstructure

IN738LC was patented in August, 1969 by C.G.Vieber and J.J.Galka [10] of International Nickel Company, Inc., NY. It is a polycrystalline Ni-based superalloy, investment cast to desired design for industrial applications. LC represents that the alloy is low in carbon, ~0.1 wt%. As stated before, it contains phases like γ' precipitated in the γ solid solution matrix and carbide phases at the grain boundaries. The alloy contains about 43 % γ' intermetallic precipitate phase. IN738LC has an FCC crystal structure with γ' precipitates having the L₁₂ ordered superlattice.
1.6 Investment Casting

Investment casting produces near net shape configurations, allowing freedom of design for wide range of alloys with precise details and dimensional accuracy. Wax patterns are obtained by injection molding. An assembly is formed by attaching the patterns and the sprue (central wax stick). The assembly is then immersed in a liquid ceramic slurry and then into fine sand bed to form a shell. This is repeated several times to form layers and then the wax is melted off, leaving a negative impression of the assembly within the shell.

The molten alloy is cast in the mould; then the alloy is subjected to a hot isostatic pressing process called HIPing, which helps to remove microporosity developed during the casting process. In a neutral environment, HIPing is done for 2 hrs at 1200°C and then the alloy is subjected to an aging treatment. Solutionizing and aging are the two steps involved in the commercial aging treatment of IN738LC.

In the solution treatment process the alloy is placed at 1200°C for about 2 hours and then is cooled either by accelerated air cooling (AAC) or water quenching (WQ). Then it is reheated to a temperature of 850°C and held there for 24 hours and furnace cooled to room temperature. Better heat treatments are developed to obtain a unimodal precipitate microstructure and decrease the formation of spheroidal precipitates [11]. Thus a two step aging process is given. Solution treatment at 1130-1250°C for 2-4 hours is followed by an initial aging in a temperature range of 650-950°C for a time period and cooled to room temperature. Holding time of 12 to 200 hours and different cooling rates during the aging has been reported in the literature [12]. Material scientists observed that slow cooling during the final aging process and long periods of holding time (100-200 hours) at 1000°C changes the spheroidal precipitates to unimodal cuboidal precipitates.
1.7 $\gamma'$ Precipitate Coarsening and Coalescence

Many theoretical studies and experiments have been undertaken in the past to understand the coarsening features and coalescence of $\gamma'$ [19, 13-24]. The $\gamma'$ precipitates evolve in the process of minimization of the total free energy of the system. During this process interfacial surface energy and elastic misfit strain energy play an important role [25]. Interfacial energy leads the initial stages of the coarsening and later, when the particles reach a critical size, the elastic strain energy takes over. Precipitate coarsening along elastically soft $<100>$ directions in Ni based alloys have been reported [9]. This also is a tendency to minimize the free energy of the system.

Stabilized microstructure is good for high temperature industrial applications. So control of size and growth of the precipitate helps to improve the mechanical properties of the material at high temperatures [5]. Thermo-mechanical processes give refined grain size yielding to a recrystallized microstructure through interactions between the precipitate and the grain boundary. Dissolution or reformation of the precipitate and thermal cycling gives rise to the final microstructure. Different mechanisms [26-27] have been proposed for precipitate dissolution in the matrix.

Aaron and Kotler [28] considered that the concentration gradients and interactions between the precipitate and the matrix at the interface contribute to the precipitate dissolution. A three step model for the precipitate dissolution is proposed by Vermolen and Zwaag [29] considering decomposition of precipitate, solute crossing the boundary and finally, diffusion of solute to a long distance. Interface interactions are rate controlling processes for precipitate dissolution.

During the process of balancing the free energy in the system the shape, size and distribution of precipitates change. The size of $\gamma'$ precipitate range from a few nm for
cooling precipitate to 100-1000 nm for fine, medium and coarse size precipitates. Coarse precipitates dissolve again in the matrix in certain temperature range [9] or form rafts [29-31]. In this the Zener’s approximation was used for explaining the diffusion mode, and the growth rate is given by:

\[
\frac{dr}{dt} = \frac{D(Cm - Cr)}{r} \Rightarrow 1
\]

Here \( C_m \) is solute concentration in the matrix at equilibrium with precipitate of solute concentration \( C_r \) and infinite radius, \( r \). At increasing volume fraction this approximation becomes poor when inter-particle distance decreases and diffusion field overlaps. A modified version of LSW theory was proposed by Ardell [32] taking into account the volume fraction in the diffusion equation. Multi particle diffusion is addressed by many theories but particle coalescence was ignored [33-37].

Coalescence is the effect of volume fraction along with diffusion fields overlapping and was studied by Davies, et al. [38-39], using Lifshitz and Slyozov theory [40], and they came up with a modified Lifshitz-Slyozov Encounter Model (LSEM). At high volume fraction coalescence is very high in both the solid phase and liquid phase systems [41]. The mechanism of coalescence was interpreted in several ways. Davies, et al. [38] proposed that overlapping of the diffusion fields when the particles are close enough, not necessarily in physical contact in initial stages, causes the particles to coalesce. After coalescence the precipitate was considered to move rapidly to equilibrium shape through \( \gamma' / \gamma \) interface diffusion. Doherty [42] proposed that the process depends on lattice mismatch where the precipitates move towards each other and coalesce, which may be due to removal of elastically strained matrix between two adjacent particles. Kang and Yoon [24] explained that when grains touch each other, migration of the grain
boundary between them towards the smaller grain takes place. Thus, here, coalescence may be due to rapid diffusion at the $\gamma'$ / $\gamma$ interface immediately after the formation of a neck between the two grains. In this process the activation energy for coarsening remained constant with change in volume fraction indicating that the dominant coarsening mechanism is still volume diffusion through the matrix even when the particles are touching each other.

1.8 Texture Development

Texture formation during thermal or mechanical processing is an interesting phenomenon \[9\]. Variation in Properties was observed due to onset of preferred orientation (PO). Various studies only included two types of textures called annealing textures and cold work textures. Grains recrystallize after processing to align themselves in particular slip direction \[43\]. PO in FCC material can be related to interface mobility of the growing grain \[44\].

Selective growth of recrystallized grains due to higher mobility of certain planes and oriented nucleation and subsequent growth can be responsible for the formation of textures in annealed materials \[45\]. A texture develops and proceeds at the expense of some other possible texture with increase in temperature \[46\]. Texture formation would affect modulus of elasticity and the thermal expansion coefficient along specific directions in a given component made out of the oriented material. Interfacial mobility and solute segregation mainly contribute to PO. In some cases textures are also developed due to decrease in grain boundary energy, grain rotations, growth of twins, etc.\[47\].

1.9 Oxidation Kinetics of Superalloys

Oxidation is one of the important phenomena which plays an important role at high temperatures. Better understanding of the oxidation kinetics of the material helps us
to understand the process of degradation and the chemical reactivity of the material at high temperatures, thereby helping us to provide protective measures to keep the component working for longer period of time and minimize the maintenance costs [48].

Oxidation kinetics of superalloys follows the parabolic law [2, 18] and is diffusion controlled. The kinetic curves rose quickly at the beginning and then leveled off showing no weight gain after some time. Factors that may cause the high initial oxidation rate include micro-cracks and rough surfaces on the coatings. The stability is attained when the dense and protective oxide layers form on the oxide scale and restrict the diffusion of oxygen through the oxide layer to the alloy surface. However, oxidation can still continue if the protective oxide scale is spalled away or get cracked.

It is remarkable that some of these alloys can be utilized at 0.9T_m. The basic reason for this endurance must be attributable to the following:

- The high tolerance of Ni for alloying without phase instability owing to its nearly filled 3d- electron shell.
- The tendency of Cr additions to form Cr_2O_3-rich protective scales having low cation vacancy content, thereby restricting the diffusion rate of metallic elements outwards and oxygen, nitrogen, sulphur, and other aggressive atmospheric elements inward in the oxide scale layer.
- The additional tendency at high temperatures to form Al_2O_3-rich scales with exceptional resistance to oxidation.

The oxidation kinetics of superalloys near their melting temperatures affects the properties of the material. Thus, for safe operation of the components, it is necessary to study the oxidation kinetics at such high temperatures. Oxidation kinetics, microstructural
changes, phases present, and oxide scale morphology in the superalloy IN738LC at lower temperatures have been studied earlier [3].

According to the steady state scale morphology, the Ni-Cr-Al-Ti alloys were divided into 3 types [49]:

1. Alloy low in Cr and Al form no scale with Cr$_2$O$_3$ and Al$_2$O$_3$ subscale.
2. Alloys high in Cr (>15%) and low in Al (<3%) form Cr$_2$O$_3$ scale and Al$_2$O$_3$ subscale.
3. High Cr (>15%) and high Al (>3%) alloys form exclusively Al$_2$O$_3$ scale.

IN738LC belongs to types 2 and 3 depending on the oxidation conditions. Growth mechanism of the oxide scales is difficult to understand. Oxidation of primary carbides in IN738LC can lead to surface crack initiation and oxide intrusions along grain boundaries [12]. Morphological changes of MC carbides play a very important role. The quantity and size of primary carbides often determine the growth rate of creep or fatigue cracks in components and affect ductility and toughness of the alloy in general.

IN738LC has relatively large blocky MC carbides of the type (Ta, Nb, Ti, W)C which oxidize more rapidly than the other phases in the alloy system. There is a large volume increase during oxidation. Due to the formation of oxide layer on these phases and at carbide-oxide interface, shift of corrosion product from inside to outside takes place. High shear stresses are present between the Cr$_2$O$_3$ scale and the carbide oxidation products. These lead to scale cracking, favoring internal corrosion.

The metal matrix forms Cr$_2$O$_3$ protective layer while the carbides undergo selective oxidation and form a non-protective scale at oxide-carbide interface. At the beginning of the oxidation process the selective MC oxidation is limited to particles on the metal surface. The same applies to the carbide particles, which are affected by the
oxidation front. So local cracking continues during oxidation as long as the front moves deep into the metal matrix.

When MC particle is completely oxidized, Cr$_2$O$_3$ rich scale is formed beneath it and thus rapid oxidation stops in that area. So the corresponding products or oxides are incorporated in the scale. Internal oxidation [50] leads to the formation of Al$_2$O$_3$ in the subsurface layer and this is accompanied by the internal nitridation (TiN) beneath the Al$_2$O$_3$ subscale. N could not be identified unequivocally as the N-$K\alpha$ line overlaps with the first order Ti-$L\gamma$ and 2$^{nd}$ order Co-$L\alpha$ Line. Cr$_2$O$_3$ is formed beneath this layer, which has dissolved Ti in it. Beneath the scale an internal corrosion zone is formed that contained Al$_2$O$_3$ + TiN further into the substrate [49].

1.10 Intensified Plasma Assisted Nitriding (IPAN) of IN738LC

Many surface modification methods are available in recent years to enhance properties like wear, fatigue and corrosion resistance [52-60]. IPAN is a low temperature nitriding process patented by E.I.Meletis [61] and is used for surface modification of Ti and Ti alloys. This process enhanced the surface properties in Steels.

Liquid lubrication becomes ineffective at high temperatures and so solid lubrication is used in the form of thin films coatings. This prevents metal-to-metal contact and thus avoids severe wear [55]. Plasma vapor deposition and plasma assisted chemical vapor deposition are also widely used in industrial applications [57].

1.11 Research Motivation and Objectives

Power generation companies are meeting the need of new generation capacity by selecting natural gas-fired advanced gas turbine combined-cycle systems. These high efficiency turbines have high inlet temperatures, requiring the use of advanced materials and coatings which have desired properties.
Around the world the energy industry has to meet the demand of the increasing competition in energy markets along with the environmental protective regulations being imposed. To increase the efficiency at low costs with low emissions is a challenge to power industry. Methods like raising the firing temperature and using spray-cooling process with compressed air are being used. The latest models of gas turbines have improved materials with coatings and advanced cooling designs to allow rotor inlet temperatures of 1300°C-1400°C.

Power generation industries used Inconel alloys extensively for their excellent mechanical properties at high temperatures. Having good strength at elevated temperatures, creep properties and weldability proved to be good for High Temperature Gas Cooled Reactors (HTGR) [62]. Previous studies emphasized mainly the reaction kinetics of the process and identification of morphology of oxide scale at lower temperature where phenomenon of oxide volatilization has been largely ignored.

Weight loss is observed during the oxidation process at temperatures starting around 1100°C. This can be attributed to volatile oxides formed on the metal surface at such high temperatures. Certain oxides like Cr2O3 and oxides of Nb, Mo, W volatilize at higher temperatures. The scales formed on the superalloy IN738LC at 1000°C, 1090°C, 1140°C and 1190°C in dry air have been investigated in the current study by scanning electron microscopy, X-ray diffraction, EDXS and XPS.

With a view to improve reliability and performance in service and in environmental conditions, nitriding characteristics of IN738LC were also studied in the present study. Intensified plasma assisted nitriding process was used to modify the surface of IN738LC. Investigation of variation of hardness, diffusion of nitrogen in the alloy, structural changes and friction coefficient variation were carried out using different experiments.
The nitriding characteristics were studied using SEM, XRD, XPS, wear testing and microhardness testing. From the XRD analysis it was determined that the nitrided samples have preferred orientation. The wear test of the nitrided samples showed that the friction coefficient is approximately 1.15. The microhardness tests on the 3 nitrided samples showed that as the current density was increased the hardness value of the surface layer increased, indicating the improvement in surface mechanical properties.
Chapter 2. Experimental Background and Procedures

2.1 Materials

The material used in this study was IN738LC which is a polycrystalline Ni based superalloy with low carbon content. The material was obtained from Howmet Corporation, Whitehall, MI in the form of rods of length 110 mm and 15 mm in diameter. In a neutral environment, the investment cast superalloy was subjected to HIPing at 1185°C for 2 hours to remove any micro-porosity in the alloy due to investment casting and then cooled to room temperature by argon-backfill cooling, whose cooling rate was the same as that of air cooling. HIPing, solution treatment and aging were carried out by the company that supplied the material. The chemical composition of the as-received material is given in Table 1.

Table 1 Chemical Composition of As-Received IN738LC (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Nb</th>
<th>Al</th>
<th>Ti</th>
<th>B</th>
<th>Zr</th>
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<tbody>
<tr>
<td>Min</td>
<td>Bal</td>
<td>15.7</td>
<td>8.00</td>
<td>1.5</td>
<td>2.4</td>
<td>1.5</td>
<td>0.6</td>
<td>3.2</td>
<td>3.2</td>
<td>0.007</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Max</td>
<td>Bal</td>
<td>16.3</td>
<td>9.00</td>
<td>2.0</td>
<td>2.8</td>
<td>2.0</td>
<td>1.1</td>
<td>3.7</td>
<td>3.7</td>
<td>0.012</td>
<td>0.08</td>
<td>0.13</td>
</tr>
</tbody>
</table>

2.2 Sample Preparation for Oxidation

Investment cast rods of polycrystalline, low carbon, Ni-based superalloy of IN738LC was provided by Howmet Corporation, Whitehall, MI. The rods were 110 mm long and 15-16 mm in diameter. They were cut into 2-3 mm thick samples using STRUERS-ACCUTOM-5 cutter and an aluminum oxide cut-off wheel, STRUERS 456 CA. The speed and feed parameters used are given in Table 2.

A hole was drilled into the sample somewhat near the edge to suspend the sample from an electric digital balance to the middle of a furnace. Two samples were oxidized at each chosen temperature. For the study of microstructure, the oxidized samples were first
ground from 240 to 600 ASTM grit size, then were polished up to 1000 ASTM grit size and further down to 0.05 μm. Selected mirror polished samples were etched with a solution made up of 33% HNO₃ + 33% acetic acid + 33% H₂O + 1% HF, and studied in an SEM.

Table 2 Speed and Feed Parameters for Cutting Samples

<table>
<thead>
<tr>
<th>Operational Speed</th>
<th>3000 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>0.01 mm/sec</td>
</tr>
<tr>
<td>Force</td>
<td>Low / Medium</td>
</tr>
<tr>
<td>Coolant</td>
<td>STRUERS coolant</td>
</tr>
</tbody>
</table>

2.3 Experimental Procedure for Oxidation

With the help of a Pt wire of required length, the sample was suspended into a box furnace from an electronic scale kept suitably above the furnace. The weight of the sample along with that of the Pt-wire was continuously noted to study the mass change of IN738LC due to oxidation at a specific temperature. This was repeated several times at different elevated temperatures. After certain period of time when there was no mass gain, i.e. when the mass of sample remained nearly constant, the sample was removed from furnace and air cooled. This procedure was followed for the two samples each at 1000°C, 1090°C, 1140°C and 1190°C, respectively.

2.4 Sample Preparation for Microstructural Study

The cut out edges along the circumference of the thin cylindrical specimen of samples subjected to high temperature oxidation were ground from 240 to 600 ASTM grit size, then were polished up to 1000 ASTM grit size, and further down to 0.05 μm using aluminum oxide suspension in water. The morphology of the oxide, metal and metal-oxide interface was observed along the edge at the flat region of the polished circumference of the oxidized samples, using an SEM. EDAX spectrum analysis of the
oxide layer was carried out to have an idea of elements present in the phases observed. For this purpose an SEM with EDAX capability was used. The surface morphology of the oxide on the radial plane was also examined in the same manner.

2.5 Sample Preparation for X-Ray diffraction study

The specimens oxidized at 1000°C, 1090°C, 1140°C and 1190°C were subjected to XRD studies to identify the phases from their respective diffraction patterns. A Rigaku X-Ray diffractometer was used for X-ray diffraction analysis. The incident CuKα X-rays have a wavelength $\lambda = 1.5418$ Å. Diffraction pattern was detected over the 2θ range from 30° to 105°, at a scanning rate of 1°/min, for all the samples. This study helped to identify the major oxide phases in the oxide scale, formed on the surface of the superalloy. It was interesting to observe preferred orientation in the metal under the oxide scale.

2.6 Sample Preparation for XPS Study

The high resolution XPS determinations were carried out on an AXIS 165 instrument which is capable of performing X-Ray photoelectron spectroscopy (XPS), also known ESCA, XPS imaging, XPS sputter depth profile, angle-resolved XPS, Auger electron spectroscopy (AES), scanning Auger microscopy (SAM), and AES sputter depth profile.

XPS spectrum analysis was done on the samples oxidized at 1000°C, 1090°C, 1140°C and 1190°C. In this study the oxide layer was sputtered off for one minute at a time. The sophisticated XPS machine was capable of picking up signals in the form of kinetic energy corresponding to the absorption of elements in pure form or in combined form with other elements. From the latter the prevalent compound can be identified in the
oxide scale. This process could identify oxide phases that were present in the samples, but not identified in XRD analysis.

2.7 Sample Preparation for Microhardness Testing

Microhardness testing was done on the samples oxidized at 1000ºC, 1090ºC, 1140ºC and 1190ºC and air-cooled. This study helps us to see how the hardness of the material was affected by oxidation at various high temperatures. For this purpose the specimens were ground to 1000 grit size and polished using aluminum oxide powder up to 1 micron size. A Knoop indenter was used to measure the microhardness with loads of 25, 50 and 100 gm.

2.8 Sample Preparation for Nitriding

The rods of IN738LC, 15-17 mm diameter, were cut into 5-6 mm thick slices using STRUERS–ACCUTOM-5. An aluminum oxide cut-off wheel, STRUERS 456 CA was used for this purpose. The speed and feed parameters are given in Table 2.

The cylindrical specimen was drilled half way through along the axis of the rod and threads were machined on the hole surface to give good grip while fixing it safely to the vacuum chamber lid. The six samples forming two sets to be nitrided were ground from 240 to 600 ASTM grit size, polished up to 1000 ASTM grit size on grinding papers and then were further polished down to 0.05 µm using regular polishing wheels with felt cloth. The samples were subjected to ultrasonic cleaning in acetone to remove any grease from the specimen surface prior to nitriding. They were kept in air to dry and then fixed in the vacuum chamber.
2.9 Experimental Procedure for Nitriding

2.9.1 Experimental Setup

The IPAP system is built around a water-cooled non-magnetic stainless steel vessel. Figure 1 shows the experimental setup of the IPAP system used for intensified plasma assisted nitriding.

![Experimental setup for IPAN process](image)

**Fig.1. Experimental setup for IPAN process**

The negative biased filament emission source and a DC powered positive plate were positioned facing each other inside of the vessel and were controlled separately. The system was continuously pumped and included a heating and pre-mixing nitrogen-argon container. Plasma was sustained in the system at a pressure of 50 mTorr.

2.9.2 IPA Nitriding Procedure

The ultrasonically cleaned sample was screwed in the place shown for work piece. The internal threads machined in the sample help in getting the sample screwed into the pressure chamber. The sample is held firmly throughout the process.
The chamber was closed tightly and pumping was started to evacuate the chamber. Mixture of N₂ and Ar in the ratio of 4 : 1 was pumped into the vacuum chamber when the required low pressure was reached. The sample served as cathode and was heated with the help of the hot filament. Setting up the various parameters, the nitrogen gas introduced was ionized and the sample was bombarded with nitrogen ions. A triode glow discharge system was used to control the thermionic emission. This intensifies the plasma for added effect on the work piece at a low pressure.

The IPAN was done for 3 hours after which the power supply was cut off, the pressure was brought back to normal by introducing argon into the chamber and the sample was allowed to cool in the chamber itself. Later, the sample was unscrewed and removed carefully from the chamber.

The parameters involved in the intensified plasma nitriding were bias voltage, pressure, current density and time. 1000 V of bias voltage was given at varying current densities as shown in Table 3 and the pressure of the gas mixture of N₂ and Ar was maintained at 50 mTorr. Time of processing was fixed for 3 hrs. The approximate temperature of the sample inside the pressure chamber is also shown in Table 3.

<table>
<thead>
<tr>
<th>Nitrided Sample</th>
<th>Current Density(mA/cm²)</th>
<th>Temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.5</td>
<td>~500</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.0</td>
<td>~550</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1.5</td>
<td>~650</td>
</tr>
</tbody>
</table>

The thickness and quality of the nitrided layers were greatly affected by the processing parameters. Both the thickness and the surface roughness increase with increase in discharge power. This implies that more material was melted and solidified on
the surface. The amount of N deposited in every discharge was small and led to in a more compact and uniform nitrided layer.

2.10 Sample Preparation for Microstructural Study

Morphological study of the nitrided samples was done using the JEOL 840A Scanning Electron Microscope. The spectrum study of the amount of different elements present in the samples was done by the EDS system attached to the SEM. The digital output was collected into a Mac computer connected to the SEM for data acquisition and analysis.

2.11 Sample Preparation for X-Ray Diffraction Study

The specimens nitrided at current densities of 0.75, 1.0 and 1.5 mA/cm² respectively, were subjected to XRD studies to identify their respective diffraction patterns. The Rigaku X-Ray diffractometer was used for X-ray diffraction analysis. The incident CuKα X-rays with a wavelength $\lambda = 1.5418\text{Å}$ were used. Diffraction pattern was recorded over the $2\theta$ range from 30° to 105°, at a scanning rate of 1°/min, for all the six nitrided samples.

2.12 Sample Preparation for XPS Study

AXIS 165 machine which is capable of performing X-Ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), XPS imaging, XPS sputter depth profile, angle-resolved XPS and Auger electron spectroscopy (AES) was used.

XPS spectrum study was done on the as-received sample and on the samples nitrided at various current densities. The XPS machine was capable of picking up signals in the form of kinetic energy corresponding to absorption of elements in pure form or in
combined form with other elements. From the latter prevalent compounds can be identified in the nitrided samples.

2.13 Sample Preparation for Microhardness Testing

Microhardness testing also was done on the intensified plasma assisted nitrided samples. This study helps us to see how the microhardness of the material was affected upon nitriding with different current densities. A Knoop indenter was used to measure the microhardness using loads of 25, 50 and 100 gm.

2.14 Sample Preparation for Wear Testing

The tribological behavior of the as-processed nitrided samples and the unprocessed sample of IN738LC has been studied using the Falex ISC200 PC Pin-on-Disc system with data acquisition. The system provides information on wear resistance and friction of the material and allows comparison of the quality of thin coatings. During testing, specimens can be heated up to 650°C. Wear test on each sample was done in air with a load of 100 gm and the distance traveled by the steel ball was 1000 m. The atmospheric conditions are also included in Table 4.

Table 4. Details of Wear Testing

<table>
<thead>
<tr>
<th>sample</th>
<th>Load (gm)</th>
<th>pin no.</th>
<th>Radius of pin</th>
<th>rpm</th>
<th>Distance travelled (m)</th>
<th>Temperature (°C)</th>
<th>R.H.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asreceived</td>
<td>100</td>
<td>440C-1</td>
<td>5 mm</td>
<td>190</td>
<td>1000.09</td>
<td>27</td>
<td>52</td>
</tr>
<tr>
<td>Nit.1</td>
<td>100</td>
<td>440C-1</td>
<td>5 mm</td>
<td>191.2</td>
<td>1000.3</td>
<td>27.4-28.4</td>
<td>34.6-37.6</td>
</tr>
<tr>
<td>Nit.2</td>
<td>100</td>
<td>440C-3</td>
<td>5 mm</td>
<td>191.3</td>
<td>1000.05</td>
<td>25.1-28.4</td>
<td>54.4-41.2</td>
</tr>
<tr>
<td>Nit.3</td>
<td>100</td>
<td>440C-3</td>
<td>5 mm</td>
<td>191.5</td>
<td>1000.07</td>
<td>25.1-28.4</td>
<td>54.4-41.2</td>
</tr>
</tbody>
</table>
Chapter 3. Results and Discussion - Oxidation of IN738LC

3.1 Oxidation Kinetics

3.1.1 Oxidation at 1000°C

The sample was loaded in the furnace at 1000°C and the weight gain as a function of time was observed. The sample at 1000°C showed sharp increase in weight and then it became stable. There was a weight gain of 11 mg/cm². The process was again repeated with a second sample and similar results were found. The sample heated for 285 hours approximately showed that there was no weight gain after certain period of time. Therefore the second sample was just tested until the sample stabilized, i.e. for 225 hours of isothermal oxidation. The slope of the oxidation curve in Fig. 2 for IN738LC at 1000°C indicated high oxygen diffusion into the alloy. Table 5 gives the data for the plot of the oxidation curve.

![Oxidation kinetics of IN738LC at 1000°C & 1090°C](image)

Fig. 2. Oxidation kinetics of IN738LC at 1000°C & 1090°C
3.1.2 Oxidation at 1090°C

The oxidation kinetics of the IN738LC at 1090°C seemed to follow the parabolic growth rate law after about 75 hours. The metal oxidized linearly up to this point. After 285 hours of heating of the specimen at such high temperature there was no more weight gain and the weight of the sample remained constant. This shows that the oxidation rate decreased with time and oxygen penetration to the metal through the oxide scale reduced considerably with time. It can be verified from Table 5 that there was 5.5 mg/cm² of weight gain and it was gradual. The oxidation rate at 1000°C was higher than that of 1090°C. The weight gain at 1090°C was almost half the amount and this and the initial linear oxidation kinetics indicate that volatilization of certain oxides from the oxide scale might have been taking place initially during the first 75 hours prior to the formation of stable and sealing oxide species.
3.1.3 Oxidation at 1140°C

The oxidation of IN738LC at 1140°C seems to follow the parabolic growth rate mechanism initially till about 6 hours, beyond which weight loss was observed after gaining a maximum weight of about 2 mg/cm². Oxidation at 1140°C was much faster and so the maximum weight gain took place within 5 hours and at 24 hours the weight gain dropped to zero. The weight loss in the oxidation process continued until 29 hours after which it seemed to stabilize. At this stage the metal was perhaps losing as much oxide by evaporation as it formed. It is suggested that Cr₂O₃ formed in the scale changes to CrO₂ and then to CrO₃. In CrO₃, Cr is in hexavalent state which leads to high vapor pressure and the oxide phase evaporates leading to weight loss. The oxides of W, Ta and Mo may be evaporating too, if formed. On the contrary, oxides of Ni, Co and Al are not volatile at high temperatures. Volatilization destroys or modifies the protective nature of the oxide scales. It increases with temperature and gas rate flow. Thus its detrimental effects become more important in advanced high temperature, high flow and air breathing propulsion systems. Tables 5 and 6 give more insight into the kinetics.

3.1.4 Oxidation at 1190°C

IN738LC oxidized at 1190°C in dry air was at a much faster rate than at 1140°C following the parabolic growth law initially during the first hour. Thereafter it lost weight at an equally fast rate in the next 1.5 hours. All the changes during oxidation were observed during the first three hours. There was a weight gain of 0.6 mg/cm² in the first hour and then there was a drop in the weight to about 1 mg/cm² as shown in Tables 5 and 6. Slightly after 2.5 hours of oxidation the sample reached its initial weight and after 3.5 hours of oxidation the sample had lost weight by about 1 mg/cm² and the weight of
sample stayed constant indicating stabilization of the oxidation and volatilization process. The Cr₂O₃ might have changed to CrO₃ at a faster rate at this high temperature of 1190°C. Volatilization of other oxides of Ta, Nb, W and Mo might have taken place along with Cr₂O₃. Volatilization removes the protective layer of Cr₂O₃, thus allowing more oxygen to diffuse to the metal through the oxide layer. The oxidation may have been restricted by the thick protective oxide layer of Al₂O₃ (as found from SEM analysis) which does not volatilize at high temperatures from the oxide scales. Tables 5 and 6 give more details of the weight gain/loss at 1190°C.

**Table 5 Mass Gain and Loss Observed as a Function of Time at Various Temperatures**

<table>
<thead>
<tr>
<th></th>
<th>1000°C</th>
<th>1090°C</th>
<th>1140°C</th>
<th>1190°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Time (hr)</strong></td>
<td><strong>Mass gain (mg/cm²)</strong></td>
<td><strong>Time (hr)</strong></td>
<td><strong>Mass gain (mg/cm²)</strong></td>
<td><strong>Time (hr)</strong></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>8.70</td>
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<td>1.04</td>
<td>1</td>
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<tr>
<td>50</td>
<td>9.14</td>
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<td>2.38</td>
<td>3</td>
</tr>
<tr>
<td>75</td>
<td>9.97</td>
<td>75</td>
<td>4.91</td>
<td>5</td>
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<tr>
<td>100</td>
<td>10.19</td>
<td>100</td>
<td>4.97</td>
<td>7</td>
</tr>
<tr>
<td>125</td>
<td>10.54</td>
<td>125</td>
<td>5.18</td>
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<td>150</td>
<td>10.79</td>
<td>150</td>
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<td>175</td>
<td>10.74</td>
<td>175</td>
<td>5.81</td>
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<tr>
<td>200</td>
<td>11.57</td>
<td>200</td>
<td>5.96</td>
<td>15</td>
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<td>225</td>
<td>11.65</td>
<td>225</td>
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<tr>
<td>-</td>
<td>-</td>
<td>250</td>
<td>6.40</td>
<td>19</td>
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<tr>
<td>-</td>
<td>-</td>
<td>275</td>
<td>6.40</td>
<td>21</td>
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<td>-0.96</td>
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<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29</td>
<td>-1.10</td>
</tr>
</tbody>
</table>

**Table 6 Analysis of Oxidation of IN738LC at Various Temperatures**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time for stabilization of the process (hr)</th>
<th>Mass gain / mass lost (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C</td>
<td>225</td>
<td>11.7</td>
</tr>
<tr>
<td>1090°C</td>
<td>275</td>
<td>6.4</td>
</tr>
<tr>
<td>1140°C</td>
<td>29</td>
<td>-1.11</td>
</tr>
<tr>
<td>1190°C</td>
<td>3.5</td>
<td>-1.12</td>
</tr>
</tbody>
</table>
3.2 Morphological Study Using SEM

Fig. 4. IN738LC oxidized at 1000°C a) showing oxide scale/alloy interface and b) Carbide oxidation

Oxide scale, $\gamma'$ depleted zone and $\gamma / \gamma'$ matrix can be clearly identified from Fig. 4a. The bright oxide on the oxide layer is Cr$_2$O$_3$, below which Al$_2$O$_3$, a secondary protective (black) layer was seen. The oxidation of an MC carbide particle can be seen in Fig. 4(b).

At 1090°C the oxidation was linear initially ending in parabolic kinetics, which formed a thick oxide layer. $\gamma'$ depleted layer below the oxide scale and the $\gamma - \gamma'$ matrix are seen in Fig. 5(a). Fig. 5(b) shows the Al$_2$O$_3$ oxide channels below the top bright layer, whereas Fig. 5(c) shows the formation of rafts at grain boundaries. Fig. 5(d) shows the particle agglomeration and coarser particles in the metal below the $\gamma'$ depleted zone. The particle agglomeration leads to equi-axed grains varying from 0.5 to about 2 µm in size, Fig. 5(d). Likewise in the specimen oxidized at 1140°C, the oxide layer (bright), $\gamma'$ depleted zone and $\gamma$-$\gamma'$ mixed zone can be seen in Fig. 6(a). Fig. 6(b) and (c) show the precipitate particles becoming spherical in shape.
Fig. 5. IN738LC oxidized at 1090°C:

a) Metal-oxide interface  b) Al₂O₃ oxide layer  c) Growth of γ'  d) coalescence of γ'

The remaining figures show the dissolution of the precipitates. Figures 6 d and e indicate the formation of oxide channels in what appear to be sub grain boundaries. Preferential internal oxidation seems to be occurring along the normal grain boundaries in the γ matrix, Fig. 6(f-h).
Oxidation at 1190°C shows internal oxidation (dark oxide) again in the metal beneath the oxide layers. Internally there is lack of precipitates in the metal; the $\gamma'$ precipitates should have dissolved into the matrix (It is known that in a span of less than 1 minute the precipitates would dissolve completely into the matrix at any temperature at and above 1160°C [9]). Formation of a continuous dark oxide layer ($\text{Al}_2\text{O}_3$) below the bright exterior oxide layer (Cr-Oxide, Ni-Cr-oxide, etc.) in Fig. 7(a) is indicative of resistance to oxidation provided by $\text{Al}_2\text{O}_3$ sub-oxide layer. However, this may not stop internal oxidation of the metal in grain boundaries. Any subsequent small weight gain could be due to internal oxidation.

3.3 EDX Spectrum Analysis

Figure 8 (a–d) show the EDX spectra of matrix, normal precipitate, precipitate at the boundary and the MC carbide in the as-received IN738LC. The oxidized sample had similar spectra for different phases that are shown in Fig. 9(a-h).

Fig. 6 (a-b). IN738LC oxidized at 1140°C a) Oxide-Metal interface b) Precipitate dissolution
Fig. 6 (c-g) IN738LC oxidized at 1140°C

c) spheroidal γ' particles
d) solute migrating to channels, possibly (sub) grain boundaries
e) interconnected oxide channels
f) dissolution of γ' after solute is removed
g, h) oxidation along grain boundaries
The outermost layer indicates the presence of Al, Cr, Ni, Ti, and traces of Nb, Mo, W are present. Traces of Co are also present. Cr was more here than the inside layer, Fig.9 (g) indicating Cr$_2$O$_3$ phase. Just below the outermost level the Cr content slightly decreased.
The carbide in the matrix (Fig. 9(e)) indicated presence of Ta, W to be very strong along with Ti which was present also strong, with less Al and Cr, while Ni was moderate. Thus the carbide should be that of mixer of large amount of Ta, W, Nb and Mo. Above 1090°C, the oxide channel in Fig. 5(b) had large amount of Al, also considerable amount of Ti, Ta, W and Traces of Nb, Mo, Ta were present. The matrix beside the channel had all elements with Al very strong, Cr and Ni strong, with small amount of Ti and Ta, W less in amount, and Nb, Mo, Ta being present in traces. Further below the scale and into the solute depleted layer the Cr and Ni content increases indicating the matrix, but it is still rich in Al. Ti and Co of equal amount and other refractory metals are also present in considerable amount.

The dark area in the scale represents Al₂O₃ and it formed a thick layer with traces of all other elements being present in it. Carbide particles might be embedded in the Al₂O₃ layer. Away from the Al₂O₃ layer, the Cr and Ni contents continues to increase, while the amounts of Ti, Co, Ta remain the same, the Al content decreases to the level of Ti, Co and Ta. Below the scale there are dark areas which were rich in Ni and Cr as well as Ta and W to a considerable extent. Al, Ti, Co, and Ta remain the same. Ta, W, Nb, Ti are present in the Al₂O₃ layer and it may be due to carbides that are getting oxidized on the surface. The white area in the Al₂O₃ is probably due to presence of Ti, Cr and refractory elements. Near the carbide the matrix tends to have Ta, W, a bit more and equal to that of Al, Ti. Carbides have Ta, W, Ti, Nb, Mo and Ni and Cr are also included. Traces of Co and Ta are also present.
Fig. 8 EDX Spectra in as-received IN738LC
a) $\gamma$ b) $\gamma'$ c) $\gamma'$ at grain boundary and d) MC carbide
Fig. 9 EDX Spectra of oxidized samples

a) γ  b) γ' precipitates  c) γ beside carbide particle  d) oxide layer of Al₂O₃  e) MCx carbide  f) Dark area beneath Al₂O₃  g) outermost oxide layer  h) under the outermost oxide layer
3.4 XRD Analysis

X-ray diffraction patterns of the oxidized samples were generated before and after removing the oxide layer. The following figures (Fig.10 (a-d)) show the diffraction peaks of phases in oxidized samples at 1000°C, 1090°C, 1140°C and 1190°C, respectively.

It was previously observed that the matrix which was in supersaturated solid solution condition tended to form fine precipitate and during this process the (131) orientation of the SSS matrix changed to (111) orientation showing tendency to form the precipitate [9]. These two preferred orientations were observed only for the supersaturated solid solutions phase.

After oxidation at 1000°C it was observed that the surface which was depleted from precipitates had only the {111} peak visible. During oxidation the precipitate dissolves into the matrix enriching it with solute. Its lattice parameter thereby increases. The strong {111} peak is inferred to be that of solute enriched matrix. The somewhat larger lattice parameter $a = 3.585 \text{ Å}$ derived from its location can be inferred to be due to enrichment of the matrix with the solute from the dissolved precipitate. The dissolution of precipitate itself can be induced by the oxidation process taking place on the surface, requiring preferential diffusion of solute atoms, mostly from the precipitate, thus denuding them of solute and enabling them to dissolve.

The strong {111} and {131} preferred orientations of the matrix with the increased lattice parameter are also indicated in the 1090°C oxidized sample. The sample oxidized at 1140°C seems to show again dissolution of the precipitate into the matrix enriching it with the solute. It is interesting to see a second FCC phase, with a somewhat lower lattice parameter with a {200} PO, forming along with the matrix FCC phase with the {131} PO.
Fig. 10 XRD patterns of oxidized samples

a) 1000°C  b) 1090°C  c) 1140°C  and  d) 1190°C

(Fig. Cont.)
It can be inferred to be the precipitate phase, in coherence with the matrix phase surrounding it. It could very well be that at high temperatures the solute enriched matrix decomposes into two FCC solid solutions, one rich in solute and the other one lean, which could again explain the results obtained in X-ray diffraction.
On the contrary, XRD data from the sample oxidized at 1190ºC seems to show an FCC phase with a larger lattice parameter having a \{220\} and \{131\} strong preferred orientation along with another FCC phase of reduced lattice parameter with strong \{111\} and \{220\} preferred orientation. These can be inferred to be the two solid solution phases formed, again by the splitting of the matrix as at 1140ºC.

**Table 7 Results of XRD analysis after oxidation of IN738LC at different temperatures**

<table>
<thead>
<tr>
<th>Oxidation Temperature °C</th>
<th>Phases Identified</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C</td>
<td>FCC (a = 3.585 Å) {111} very strong + NiCr₂O₄, TiO₂, Cr₂O₃</td>
<td>Very strong {111} preferred orientation</td>
</tr>
<tr>
<td>1090°C</td>
<td>FCC (a = 3.585 Å) {111}_m very strong and {131}_m strong + Co₂NiO₄, CoAl₂O₄, Co₃O₄ and Al₂O₃</td>
<td>Indicates very strong preferred orientation of matrix</td>
</tr>
<tr>
<td>1140°C</td>
<td>FCC (a=3.580 Å) {131}_m very strong along with FCC (a=3.565 Å) {200}_m strong + strong NiCo₂O₄, NiAl₂O₄, NiCr₂O₄, Co₂O₃ (trace), Al₂O₃</td>
<td>Indicates {131} preferred orientation of matrix and {200} preferred orientation of another solid solution phase.</td>
</tr>
<tr>
<td>1190°C</td>
<td>FCC (a = 3.58 Å) {220}_m very strong and {131}_m very strong + FCC (a=3.53 Å) {111}_m and {220}_m orientations + TiO₂ (moderation), NiCr₂O₄, CoAl₂O₄ and Al₂O₃.</td>
<td>FCC indicates strong preferred orientation of the matrix with {220} orientation FCC (seems to show preferred orientation {111} of the matrix along with {220} preferred orientation weak {200} and {131} are still present.</td>
</tr>
</tbody>
</table>

Prior X-Ray work on vacuum annealed samples of IN738LC had established the preference of \{131\} and \{111\} preferred orientations by the matrix and the \{220\} and \{200\} preferred orientations by γ’ precipitate, the former by fine ones and latter by the coarse ones. The formation of \{200\} preferred orientation at 1140ºC cannot be reconciled as due to the formation of coarse precipitate, since no precipitate was observed in the metal below the outer oxide scale. Similarly two FCC phases are observed at 1190ºC.
Thus a miscibility gap type decomposition of the matrix phase into two solid solution phases is inferred from the XRD results.

The results also indicate formation of Cr$_2$O$_3$ and NiCr$_2$O$_4$ at 1000°C, whereas Co$_3$O$_4$, Co$_2$NiO$_4$, CoAl$_2$O$_4$ were formed at 1090°C. The latter ones along with NiAl$_2$O$_4$ seem to form also at 1140°C, whereas TiO$_2$ was found abundantly at 1190°C, with traces of CoAl$_2$O$_4$ and Al$_2$O$_3$. Lack of strong presence of Cr$_2$O$_3$ and NiCr$_2$O$_4$ in samples oxidized at higher temperatures 1090°C - 1190°C can be correlated to the loss of Cr$_2$O$_3$ from the oxide layer through evaporation.

3.5 XPS Analysis

- **Spectrum of oxide layer formed at 1000°C (Fig.11(a))**

  At 1000°C the oxides present in the scale are shown in Fig.11(a). Ni was observed in both elemental state and in the form of NiO, Ni$_2$O$_3$, Ni(NO$_3$)$_2$ and NiAl$_2$O$_4$. Since Ni was about 56% by atomic fraction, it formed all of the above basic oxides easily. Co oxides like Co$_3$O$_4$, Co$_2$O$_3$, CoCr$_2$O$_3$, CoAl$_2$O$_4$ were also observed in the scale. Cr$_2$O$_3$, clearly indicated in the XRD patterns, was also the oxide of Cr observed in the scale. Ti in the alloy got oxidized and was found as TiO$_2$ (rutile), which was also indicated in XRD. Certain nitrides and carbides like WN, BN, TiC, WC were found. Ta forms Ta$_2$O$_5$ oxide. Mo forms traces of different oxides like MoO$_2$, MoO$_3$ and CoMoO$_4$. Traces of Al$_2$O$_3$ were observed.

- **Spectrum of oxide layer formed at 1090°C (Fig.11(b))**

  Co was present in the form of oxides like Co$_3$O$_4$/CoAl$_2$O$_4$, which were observed in the XRD pattern also. Here the amounts of Cr$_2$O$_3$ and Al$_2$O$_3$ were about as much as at 1000°C, and Ni oxides, especially NiAl$_2$O$_4$, were the basic oxides present. TiC and WC appeared to have increased when the oxidation temperature was increased. No nitrides
were deducted. Mo formed its oxides as well as the possible combined oxides with CoO and Al₂O₃.

- **Spectrum of oxide layer formed at 1140°C (Fig.11(c))**

  Most of the Ni, Co, Al and Cr oxides were found. Al₂O₃ was also present. Detection of CrO₂ along with Cr₂O₃ indicates that Cr₂O₃ was converted to CrO₂, en-route to volatile CrO₃. Cr₂O₃ oxide present in the oxide layer was more compared to that at 1000°C and 1090°C, indicating formation of more Cr-oxide at this temperature.

- **Spectrum of oxide layer formed at 1190°C (Fig.11(d))**

  Presence of CrO₂ was observed and most of the Cr₂O₃ seemed to have converted to higher oxide through this intermediate phase. The smaller amounts of Cr-oxides detected indicates that much of them have evaporated. Al₂O₃ generally forms the basic protective layer, though its combined oxides with NiO, MoO₄ and WO₄ found at this temperature as well as at 1140°C. The nitrides of Ti and Cr seemed to have formed. Nb and Ta continued to form oxides as temperature increased. CoAl₂O₄ and NiCr₂O₄ were found to be the main constituents of the oxide scale along with Al₂O₃ and TiO₂.

### 3.6 Microhardness Results

Effect of oxidation of IN738LC at temperatures 1000°C, 1090°C, 1140°C and 1190°C on hardness of the precipitate depleted alloy was studied using the knoop indenter. Knoop microhardness testing was done at different loads of 25, 50 and 100 gm on the oxidized samples which were polished to 0.5 micron finish after oxidation. The results are shown in Figure 12.
Fig. 11 XPS spectra of IN738LC oxidized at various temperatures:

a) 1000ºC and b) 1090ºC, c) 1140ºC, and d) 1190ºC.

Spectra from the top surface of oxidized specimen after sputtering time of 1) 1 min. and 2) 4 min. respectively.
It was observed that even after oxidation at such high temperatures the hardness of the superalloy was mostly undisturbed and was even slightly better than in the as-received condition. This may be due to the possible formation of some nitrides.

![Hardness vs. Temperature Graph](image)

**Fig. 12.** Microhardness data of IN738LC for the as-received and oxidized samples
Chapter 4. Results and Discussion - IPAN of IN738LC

4.1 XRD Analysis

XRD patterns of the three nitrided samples are reproduced in Fig. 13(a, b, c). FCC phases with strong preferred orientations are detected in the nitrided samples produced with different, increasing current densities as given in Table 3. The nitrided sample 1 shows that fine precipitates having $a = 3.5924 \text{ Å}$ and preferred orientations of $\{220\}$ were probably formed in solute-rich matrix having $a = 3.919 \text{ Å}$ and $\{131\}$ preferred orientation (in line with the results of Dr.Balikci [9, 51]). The nitrided sample 2 shows only the fine precipitate and both the matrix and the $\gamma'$ precipitate have $\{220\}$ orientation. The nitrided sample 3 showed the $\{200\}$ PO which probably implies that the precipitates grew and became coarser due the higher current density.

![Nitrided Sample 1](image)

(a)

**Fig. 13.** XRD patterns (a, b, c) showing Preferred Orientation in IPAN samples (Fig. Cond.)
Nitrided Sample 2

Nitrided Sample 3

(b)

(c)
4.2 Morphological Study Using SEM

The N ions hit the sample on the alloy surface wherein the precipitates were at a temperature of at least 500ºC during the nitriding process. When hit by high velocity nitrogen ions, the precipitates seem to dissolve partially, Fig. 15(b), in the matrix forming fine cooling precipitates, Fig. 14(d).

![Fig. 14. (a-d) Morphology of intensified plasma assisted nitrided sample 1](image)

a) Nitrided surface with γ''
b) smoothening of γ''
c) breaking of cuboidal γ''
d) fine cooling γ'' formed along with breaking of cuboidal γ''
In the nitrided samples 2 and 3, the N ions bombarding the precipitates formed probably the nano nitride precipitates, which grew in size with increase in the nitriding current density. The intensity of nitriding increased with current density, which can be seen in figures 15(c) and 16(a).

Fig. 15 (a-d). Morphology of intensified plasma assisted nitrided sample 2

The current density for nitriding sample 1 was not perhaps sufficient to grow nitride particles. The cuboidal morphology seems to set in and dissolution of the precipitates seems to be initiated after growth of $\gamma'$ grains to around 1 $\mu$m size. Fine cooling precipitates seen in Fig. 14(d) are probably formed while cooling, after nitriding.
The nitrided sample 2 shows fine nano precipitates formed on the precipitates, Fig. 15(b, c). These nano precipitates formed on the precipitates of γ' are postulated to be the nucleated nitride particles.

The nitride precipitates apparently grow in size to occupy the entire volume of the original γ' precipitate, Fig. 17 (a, b). Thus, a thick nitrided layer with lots of nitride precipitates resulted. Eventually the surface became rough and TiN and TiO₂ were found on the surface.

4.3 XPS Analysis

XPS spectra of the as-received and the three nitrided samples 1, 2 and 3 are given in Fig. 18. In the intensified plasma-assisted nitrided sample the following compounds were identified from found with the XPS analysis. TiN, CrN and TiO₂ were found in trace quantities in the nitrided samples. Cr was mostly detected in elemental form and it corresponds to a peak with a binding energy of 574.1 eV. Co was detected in CoB.
The Ti and W carbides were present in the as-received sample, but were not detected in the nitrided samples at higher nitriding current densities. This may be due to the Ti and W forming their nitrides upon bombardment with high energy nitrogen ions. Chromium does not seem to form nitrides and prefers to stay in elemental state. WN and BN at 397.3 and 397.9 eV, respectively, were present in nitrided samples 2 and 3 but were not present in the as-received and nitrided sample 1. This indicates that the current density of 0.5 mA is not sufficient to form the nitrides. Al was generally present in elemental state.

Detection of Ni at locations of 870 and 852.5 eV indicates its preference to remain only in the elemental form. Nb was present in the as-received sample and in nitrided sample 1, while Nb oxides were found in the as-received sample, and nitrided samples 2 and 3 in the form of NbO and NbO₂. Ta with absorption energies of 23.5 and 21.7 eV was found to be in the elemental state in the as-received sample. As the nitriding current density increased, Ta was slightly converted to Ta₂O₅, as observed only in samples 2 and 3.

This shows that the sample 1 nitriding conditions were not adequate to oxidize Ta. MoB₂ and MoO₃ may be present in trace quantities in the nitrided samples. MoO₃ seems to have readily combined with Al₂O₃ and CoO. WN having an absorption energy of 33.3 eV was present and WO₂ with an absorption energy of 32.5 eV was found in traces in the samples.

Ti was detected in the form of TiN and TiO₂, with absorption edges at 455.5 eV and 459 eV, respectively, Fig.18 (a, b). This indicates that the Ti got nitrided and was mostly in the form of TiN.
Fig. 17 XPS of IPA nitrided samples and as-received IN738LC

The amount of TiN is found to increase with increasing nitriding current density which is as expected. A small amount of TiB$_2$ could also be detected in the as-received and in nitrided sample 3. Cr, on the contrary, is detected mostly in elemental form as shown in Fig.18 (c, d).

4.4 Wear Test Analysis

The tribological behavior of the nitrided and the unprocessed as-received IN738LC was studied using the Falex ISC200 PC Pin on Disc system. The response of friction coefficient and wear rate is shown in the Figure 19. It was observed that the as-received IN738LC has a coefficient of friction of 0.8-0.9. The wear friction coefficient increased slightly to about 1.0 with increase in current density in the IPAN setup.
Fig. 18. XP Spectra of as-received and nitrided samples variation of Ti (a, b) and Cr (c, d) content after sputtering for 0 sec. (a, c), 180 sec. (b, d), respectively

Wear Test Results

Fig. 19. Wear Profiles of as-received and nitrided 1, 2 and 3 samples of IN738LC
Coefficient of friction can thus be said to have increased by about 10% by the intensified plasma assisted nitriding process. This does not appear to be proportional to the vastly increased microhardness found, as discussed below.

4.5 Microhardness Test Results

Microhardness testing was done on the unprocessed and on the nitrided samples using different loads of 25, 50 and 100 gm. The knoop hardness results obtained for all of the samples were plotted, as shown in Figure 20. It was observed that the microhardness of the unprocessed sample was around 480 and there was about a 70% increase in hardness values for the nitrided samples to about 830 (measured with 25 gm load).

With an increase in the nitriding current density the hardness of IN738LC increased. The improvement in microhardness values can be attributed to the formation of nano nitride precipitates on the $\gamma'$ precipitates at higher current densities.

![Microhardness Test Results](image)

**Fig. 20 Microhardness of the as-received and the three nitrided IN738LC samples**
Chapter 5. Conclusions and Directions for Future Research Work

5.1 Conclusion

Oxidation of the as-received, duplex size precipitated superalloy IN738LC at high temperatures like 1000°C, 1090°C, 1140°C and 1190°C showed that parabolic oxidation kinetics prevails only at lower temperatures. Except at 1000°C, the diffusion mechanism cannot be related to the oxide layer growth, because at the higher temperatures some oxides phases evaporated and affected the oxide layer growth and the metal’s resistance to oxidation. At 1000°C and 1090°C, the oxidation process stabilized after gaining certain amount of mass, though with less overall weight gain at 1090°C. Overall weight gain at 1090°C was less than that at 1000°C. At 1140°C and 1190°C heavy volatilization of selected oxide phases seems to have occurred, leading to a net overall weight loss.

The loss of mass can be attributed to the volatile CrO$_3$ formed from the Cr$_2$O$_3$ protective layer. Al$_2$O$_3$, on the contrary, forms a stable protective layer, though it still enables the diffusion of O$_2$ into the alloy much faster at higher temperatures, thus enabling internal oxidation.

At 1140°C, partial precipitate dissolution and solute segregation and mobility can take place at the initial stages. However, in due course of time all of γ’ in the metal near the metal-oxide interface should dissolve, as at 1000°C, leading to a precipitate depleted zone. At 1190°C two FCC solid solutions were found for the matrix phase, resulting from a miscibility gap. The formation of the two solid solutions by the miscibility gap type transformation needs to be studied more thoroughly in the future. Al$_2$O$_3$, NiCr$_2$O$_4$, CoAl$_2$O$_4$, CoNi$_2$O$_4$, Co$_3$O$_4$ and TiO$_2$ were the main oxide phases present at high temperatures. Mo seems to form mixed oxides with Al$_2$O$_3$ and CoO. The evolution of
these oxides should be studied also more thoroughly. The microhardness of IN738LC was quiet stable at such high temperatures even after oxidation. It can be inferred that the superalloy can still retain its strength at such high temperatures after the formation of the oxide layer, a key point in the application of this alloy at temperatures close to 1100°C.

IPA nitriding of IN738LC showed onset of different preferred orientations. The hardness was increased by 50-70% and the wear resistance by about 10%. The improvement in the surface properties is attributable to TiN formation in the form of nano precipitates on the γ' precipitates. It is TiN that mainly provides for increased hardness and wear resistance after nitriding the superalloy IN738LC.

5.2 Future Research Direction

- Study of high temperature oxidation can further be extended to nitrided samples to observe the oxidation kinetics of dissolved nitrogen and nitride containing surface layers.
- Oxidation studies can be extended to still higher temperatures, say to 1250°C.
- Oxidation can be studied on samples under stressed conditions, to study the effect of surface and internal oxidation and volatilization of oxides on the creep behavior of the alloy.
- The exact environment in practice can be imitated in these tests and analogous research can be undertaken.
- The IPAN pressure can be increased to 100 mTorr and above and the nitriding characteristics can be studied.
References


Vita

Mary Shanti Pampana was born on July 21, 1979, in Kakinada, Andhra Pradesh, India. She got her degree of Bachelor of Technology in Mechanical Engineering in 2001 from the Jawaharlal Nehru Technological University, Hyderabad, India. While studying, she worked as a supervisor in Murali Krishna & Brothers firm (1997-2001). Seeking advanced studies, she came to the United States of America to pursue her Master of Science degree program in Spring 2002. She has been pursuing her graduate education in the Department of Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana. She is currently a candidate for the degree of Master of Science in Mechanical Engineering to be awarded during the commencement in August 2004. After completing her master’s degree, she plans to pursue her doctoral program.