DEVELOPMENT AND CHARACTERISATION OF Ni-BASED ODS SUPERALLOY FOR HIGH TEMPERATURE APPLICATION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
METALLURGICAL AND MATERIALS ENGINEERING
(With Specialization in Physical Metallurgy)

By

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JULY, 2004

CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented is this dissertation entitled "**Development and Characterisation of Ni-Based ODS Superalloys For High Temperature Applications**" in partial fulfillment of the requirement for the award of the degree Master of Technology in Metallurgical and Materials Engineering with specialization in Physical Metallurgy, and submitted in the Department of Metallurgical and Materials Engineering of Indian Institute of Technology Roorkee, under the guidance of **Dr. P. S. Misra**, Professor, Department of Metallurgical and Materials Engineering of Indian Institute of Technology Roorkee, Roorkee, during the period July-03 to July-04 is genuine.

The matter presented is this dissertation has not been submitted by me for the award of any other degree of this or any other institute/University.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGEMENT

I take the opportunity to pay my regards and a deep sense of gratitude to my guide **Dr. P. S. Misra**, Professor, Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee, for his guidance, keen co-operation, and cheerful encouragement through out my dissertation work.

I am thankful to **Dr. Satya Prakash**, Professor and Head of Department of Metallurgical and Materials Engineering and all the faculty members (Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee) for providing me all the possible support and facilities for my dissertation work.

I wish my deep sense of gratitude to all staff of Metal forming Lab. I am thankful to Mr. Panday who was extremely helpful.

I am thankful to all my friends for their help and necessary support during my dissertation work.

Last but not the least, I wish to place on record my deep sense of gratitude to my parents without whose blessings I would not be at this prestigious place and pursue my higher studies.

SURESH KUMAR VUPPADA

ABSTRACT

Fabrication of Advanced Engineering Materials is one of the most progressive work in Research and Development of Metallurgy and Materials Engineering. Powder Metallurgy route is one of the preferable advanced manufacturing route to develop high temperature alloys with ODS strengthening technique.

ODS alloys attract great attention as advanced high temperature materials, because they retain useful strength up to relatively high fractions of their melting points. Presently, ODS alloys are often produced through Mechanical Alloying (MA) via the P/M route with extrusion or hot isostatic pressing and are known for their excellent high temperature strength and excellent resistance to Oxidation and Hot corrosion. An in-depth analysis of the literature and state of the art technology on high temperature materials revealed that a considerable scope exist in developing ODS alloys provided low cost raw materials could be utilized. Ni-base ODS superalloys produced by mechanical alloying process (ex:- INCONEL MA 754) produced by extrusion technique have been used as a turbine vane alloy in advanced Jet engines produced.

In our present work encapsulated powder has been forged and thermo mechanically treated with hot rolling technique as in conventional P/M route. The powder with wide range of size variation and non reduced environment has not shown much effect on high temperature oxidation resistance. The final alloys thus developed compare favorably with Inconel MA 754 in oxidation and cyclic oxidation resistance. On the basis of oxidation resistance result, it can be conclude that alloys developed through a combination of P/M and forging technique result in extremely good oxidation resistance. This new technique highlighted in the present investigation opens up entirely new area for the economical production of all types of ODS alloys.

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Chapter 1

INTRODUCTION

The major objective in the design of new material development, whether for industrial, marine or aero application, are improved performance of the component and reduced cost of ownership [1]. Alloy development alone was sufficient to meet the design needs, with relatively little contribution from the component manufacturing process other than the required shape. In materials technology terms, the requirements for high temperature materials are:

1. increased strength and stiffness
2. reduced density
3. increased temperature and capability
4. increased corrosion resistance
5. improved manufacturing process capability in terms of properties and yield.

In this way the present R&D has been developed so many type of materials existence for various applications like Superalloys, Cermets, and Ceramics for High Temperature applications. In that, Superalloys play a major role for Aero and Industrial Power applications. The Superalloys have contain various alloying additions to attain the distinct properties. The latest technologies such as Directional Solidification and Mechanical Alloying are presently dominated manufacturing processes for Superalloys [1]. So in our present work we have been used the Mechanical Alloying for developing the alloy mixture.

The Superalloys can be classified into three groups such as Fe-based, Ni-based and Co-based Superalloys based on the major base metal present. Among these the Ni-based Superalloys are superior for high temperature applications. Ni-based Superalloys operating closer to their melting temperature than any other structural material. The Co-based Superalloys have inferior mechanical properties because the Co-matrix is not stable as the Ni-matrix. Nickel base Superalloys are used extensively for manufacturing the hottest parts of aircraft jet engines and also in industrial power plants. The Ni-based superalloys attain high temperature strength due to high volume fraction of hardening phase gamma prime. Previously the Ni-based superalloys are processed through casting and wrought practice.

Ni-based Superalloys by powder metallurgy route gives high performance to the components. In powder metallurgy since the starting material is homogeneous, the product also has a uniform microstructure and thus uniform mechanical properties.[2].

Nowadays the Ni-based ODS alloys are developed for high temperature applications. These ODS alloys are having better properties compared with cast alloys. The yttrium oxide is used as a dispersion strengthening element. The elevated temperature strength of ODS alloys is due to the presence of inert, finely dispersed oxide particles, which serve to inhibit the motion of dislocations. In addition to this direct strengthening by oxide particles, the most important microstructural feature affecting elevated temperature strength of ODS alloys is a very coarse grain structure. The ODS alloys can only be produced by powder metallurgy. Conventional melting and casting techniques are not useful for production of dispersion strengthened materials because of the very high interfacial energy between the molten metal and oxide, which leads to flocculation and disparities in densities between the matrix metals and dispersoids, which lead to segregation in the melt.

Ni-based ODS Superalloys contain around 78% of Ni and Cr, Al, Y_2O_3 as alloying elements. Mechanical alloying technique is used for efficient mixing of the alloying elements and to get the uniform distribution of the Y_2O_3 particles. Mechanical alloying is a unique process for fabrication of several alloys and advanced materials at room temperature[3].

Hot Isostatic Pressing (HIP) and Cold Compaction-Extrusion processes are most commonly used manufacturing techniques for ODS alloys. ODS alloys are strain rate sensitive, and therefore high speed deformation associated with process like forging is not suitable for manufacture of these alloys. The extrusion process gives dense products. Dense products increase the weight of the product. But these HIP and Extrusion processes are costlier than Forging technique. So In our present work to optimize the cost of the process of ODS alloy development, the forging technique have been used but strain rate sensitivity of these alloys has been carefully controlled to minimum level.

The Ni-based ODS superalloys are developed through powder forging route. The powder forging technique was evolved in this department for the first time in the year 1991 for the production of ferritic base ODS alloy mainly MA956 and was patented under Indian patent no. 184576/92. This technique could successfully produce this alloy to near density and the properties obtained were of high quality in comparison to MA956 alloy produced by costly extrusion process by M/s. INCO alloy company.

the Ni-based ODS alloys are developed by mixing the powder particles through mechanical alloying. The mechanical alloying done in attriors. The mechanical alloying process permits the uniform distribution of the yttrium oxide dispersion particles. The mixed alloy made into compact by friction screw forging press. After forging the thermo-mechanical treatment was given to the component. The general aim of thermo-mechanical processing (TMP) is to achieve coarse grain morphologies by means of secondary recrystallisation and is to increase the availability of the necessary product forms [4-5].

The developed Ni-based ODS Superalloy was characterized to check the suitability of the material for high temperature applications. The present investigation is to estimate the influence of deformation porosity on the final product properties namely its oxidation resistance. The cyclic oxidation test was conducted to know the stability of the weight gain of the material at high temperatures. The oxidation testing is the preliminary test to assess the high temperature characteristics of the product.

Here the effort was made to assess the response of the formation on microstructure particularly porosity on the final properties of the product. The microstructural aspects were also studied to know the amount of porosity in the product. The hardness values are also evaluated for the material.

LITERATURE REVIEW

2.1 History of Superalloys

A Superalloy is an alloy developed for elevated temperature service, usually based on group VIIIA elements, where relatively sever mechanical stressing is encountered and where high surface stability is frequently required [6]. Classification based on base material as three groups of superalloys: Cobalt base, Nickel base and Iron base.

Superalloys are most commonly used for aircraft gas turbine engine and industrial gas turbine engines components. In addition to aircraft, marine, industrial and vehicular gas turbines, superalloys are now used in space vehicles, rocket engines, experimental aircraft, nuclear reactors, submarines, steam power plants, petrochemical equipments and other high temperature applications.

Evolution:

Austenitic Stainless Steel of the 18/8 type and related varieties are unsuitable for many applications above 700°C, e.g. for manufacturing components of gas and Jet engines and steam turbines. Therefore, a need was felt to design and develop new materials having the ability to sustain high strength at elevated temperature.

Types of Superalloys

Fe – based Superalloys

The utilization of iron – base superalloys dates back to the 1940s with the development of 16-25-6 (Cr-Ni-Mo). This alloy quickly achieved widespread use in turbine wheels and remained the dominant disk alloy for more than a decade. These are the solid solution strengthened single phase Fe – based alloys. Most of the alloys in this system contain about 15% chromium to provide corrosion resistance and 25% Nickel to stabilize the corrosion resistance. Nickel to stabilize the austenitic structure.

Molybdenum is added in moderate amounts for solid – solution strengthening. More recent alloys contain a total of 2 – 3 %. Aluminium plus titanium for precipitation hardening. Table 2.1 shows that typical alloys of Fe-based superalloys.

Table 2.1 The Iron Base alloys compositions

Alloy	Al+Ti+Ta+Cb	Mo+W	Cr	Fe	Ni
16-25-6	-	6	16	51	25
DISC ALLOY	1.8	2.7	14	54	26
A–286	2.4	1.3	15	55	26
V–57	3.2	1.2	15	52	27

High temperature conventional wrought alloys of Fe–based appear unlikely to be accepted by industry because of a tendency towards phase instability as alloy content is increased. The stability of such alloys can be improved by replacing part of the iron with nickel, thus making possible more highly alloyed and stronger material without the formation deleterious phase.

Ni-based Superalloys

Ni-base superalloys, on the basis of chemical composition are fairly complex alloys. The elements which are added to Ni can be divided into different groups depending upon their contribution to strengthening and corrosion resistance. Table 2.2 shows the alloying elements in the Ni-base Superalloys.

Gamma prime phase forming elements

Although Al and Ti serve as potential solid solution strengtheners in superalloys, their main function is to combine with Ni and in conjunction with Nb and Ta to form the gamma prime precipitate, which provides the main strength to precipitation – hardened Superalloys.

The gamma prime phase has a FCC structure and lattice constant which shows only small deviations from that of matrix (range 0 – 1.5%) where as most alloys have a difference of much less than 1.5%. Coherence with the matrix is maintained by tetragonal distortion. As a consequence of this, there is an easy homogeneous nucleation of the precipitate and because of the low values of interfacial energy. However, at very high temperatures a part of the precipitate is dissolved and the strengthening effect gradually decreases.

Table 2.2 Alloying elements in Ni-base superalloys.

	Elements	**Function**
Matrix class elements	Co, Fe, Cr, Mo, W, V, Ti, Al	Solid – solution strengthening
Gamma prime – phase forming elements	Al, Ti, Nb, Ta	Precipitation hardening
Carbide forming elements	Cr, MO, W, V, Nb, Ta, Ti, Hf	Reduction of grain boundary sliding
Grain – boundary active elements	Zr, B	Enhancements of Creep strength and rupture

Gamma double prime, Ni_3Nb

In constant to Ni-based Superalloy, Al is only a minor Gamma double prime – forming element. The gamma double prime Ni3Nb precipitate is unique in Fe-Ni base superalloys. An important characteristic of gamma double prime is its slow precipitation kinetics, which explains its reduced tendency to post – weld strain age cracking.

Carbide forming elements

The carbide – formers are Cr, Mo, W, V, Nb, Ta, Ti and Hf. The role of carbide in superalloys is far more complex and less well understood compared to that of gamma prime – precipitate.

a) Which have a beneficial effect on rupture strength by reducing grain – boundary sliding, while carbides of certain morphologies can have adverse effect on ductility,

b) Chemical effect due to the removal of carbide forming elements from the matrix surrounding the grain – boundary.

In alloy development the aim is to utilize carbides to improve the high temperature mechanical properties and to reduce their detrimental effect on ductility by selecting suitable morphologies.

There are four types of carbides:

MC Carbides

$M_{23}C_6$ Carbides

Cr_7C_3 Carbides

M_6C Carbides

Cobalt-base alloys:

Co-base alloys have played a very important role in the early stages of super alloys development. However, they have failed to match the good high-temperature mechanical properties of advanced Ni-base super alloys. Co-base alloys show superiority over Ni-base superalloys in hot corrosion resistance and offer better structural stability at elevated temperature albeit at low stresses. This makes them attractive for non-rotating applications. Table 2.3 shows the function of alloying elements in Co-base superalloys. Table 2.4 shows the typical Co-base superalloys compositions.

The inferior mechanical properties are because the Co-matrix is not as stable as the Ni-matrix. All attempts at introducing a coherent γ precipitate, which would remain stable at elevated temperatures, have not succeeded. The coherent Gamma double prime, CO_3Ti precipitate, formed as result of Ti additions to Co-alloys, exhibits poor thermal stability due to matrix transformation. The principal function of Ni is to stabiles the FCC matrix W is most important element added Te affect solid solution strengthening.

Table 2.3 Function of alloying elements in Co-base Superalloys

	Ni	Cr	W	Ti, Zr, Cb, Ta	C
Principal function	Austintic Stablizer	Surface Stability, Carbide former	Solid Solution Strengthner	MC former	Carbide formation
Problems	Lowers Corrosion resistance	Forms TCP Phase	Forms TCP phase	Forms Surface Stability	Decreases Ductility

Table 2.4 The Typical Cobalt-Based Super Alloy Composition

	Ni	Cr	W	Ti, Zr, Cb, Ta	C
IX X-40	10	25	7.5	-	0.4
MM-509	10	24	7.0	3.5Ta, 0.5Zr, 0.2Ti	0.60
L-605	10	20	15.0	-	0.10
HS-188	22	22	14.0	-	0.08

The major contribution to strengthening in Co-alloys comes from the carbides. For this reason, the carbon content in quite high (0.25 – 1.0 % compared with 0.05 – 0.2 % in Ni-base superalloys). $M_{23}C_6$ carbides are the most commonly found in Co-alloys. The above mentioned elements, with the exceptions of Ni, contribute to carbide formation.

The development of Co-base alloys has suffered a severe set back because of the escalation of cobalt prices and subsequent drive to substitute Co-based alloys by Ni-base Superalloys.

2.2 History of Ni-based superalloys

Though Ni-Cr alloys have been known from the onset of the present century [Nichrome-V (80Ni-20cr)] [7], their commercial developments occurred in 1930s and first set of heat-resistant alloys was produced in 1940. The first Ni-based Superalloys (Nimonic-75) was developed from Nichrome-V by the addition of 0.3% Ti and 0.1%C.

In Britain a number of Nimonic alloys [8] were developed in rapid succession. Increased Ti content led to the development of Nimonic 80, whereas Al additions to the Ni-base alloys resulted in the first γ^1 -hardened Nimonic-80 Alloys. In an effort to raise the temperature stability further, Co and Mo were added to produce Nimonic-90 and Nimonic-100 respectively.

Inconel-Z was the fist Ni-based Superalloy to be developed in the united states. This was a modification of Inconel (15Cr-7Fe-78Ni), through controlled additions of Al, Ti, Nb and C. Further modifications in this system led to the development of Waspalloy.

Soviet alloy development methodology differs from that adopted in the US as W is added in place of Mo due to its larger availability. Co is used with reluctance. Al and Ti concentration are maintained at lower levels but V is added to improve forgeability [9]. However, a point common to all the developmental efforts has been to increase the γ content. To start with, air-melting techniques were used. This acted as hindrance to further development because of the difficulties of vacuum induction melting in the mid sixties provided a break through due to the attainment of improved stress rapture life. Waspalloy was one of the earliest examples of product development through vacuum melting.

Second generation Superalloys

A major drawback of the materials used in the land based gas turbines was their poor hot corrosion resistance over prolonged use. The second generation alloys were developed in 1965 in response to this. They exhibited superior hot corrosion resistance although this rupture strength was equivalent to those of the earlier alloys. This was achieved by incorporating higher Cr contents as in IN-738 and IN-939 alloys. The rationale behind developing such alloys was that refracting elements W and Ta stabilizing MC carbides thereby delaying $Cr_{23}C_6$ formation in service. Thus allowing Cr to remain in the matrix and therefore, enabling it to continue with its role of providing protection against hot-corrosion [9].

Besides altering the alloys chemistry, an equally important aspects is to affect changes in the processing. This has undergone major changes starting from the normal solidification techniques, in the late 60s to the more recent techniques such as directional solidification and single crystal solidification mainly with a view to enhances thermal fatigues and creep rupture properties.

After that the powder metallurgy processing route developed for producing superalloys. The availability of novel powder consolidation processes which can guarantee densities close to the theoretical values has revolutionized the powder metallurgy field. In powder metallurgy since the starting material is homogeneous, the product also has a uniform microstructure and thus uniform mechanical properties. Powder metallurgy route also permits creation of alloys which are non-castable, or non-workable or non-alloy-able by conventional processes. The production of dispersion strengthened superalloys is possible by powder metallurgy route because in the conventional melting and casting techniques the following problems occur:

- The very high interfacial energy between the molten metal and oxides, which leads to flocculation.
- Disparities in densities between the matrix metals and dispersoids, which leads to segregation in the melt.

The typical compositions for Ni based P/M Superalloys and ODS alloys are given in table 2.5 and table 2.6 respectively. The oxide dispersion strengthened Ni-based superalloys are INCONEL MA6000, and INCONEL MA754.

These ODS Superalloys are superior in terms of high temperature applications. These are generally used in the temperature greater than 0.5 Tm, i.e. equicohesive temperature. Equi-cohesive temperature is the temperature where the strength of grain & grain boundary are equal. These alloys were developed for spacecraft engine components and Industrial gas turbine components. Table 2.7 shows typical applications of INCONEL MA754 and MA6000.

Table 2.5 The Typical Cobalt-Based Super Alloy Composition

	Ni	Cr	Co	Mo	W	Cb	Al	Ti	Hf	Ta	C	B	Zr	V
Rene 95	Bal	13.0	8.0	3.5	3.5	3.5	3.5	2.5	-	-	0.05	0.01	0.05	-
IN-100	Bal	12.4	18.5	3.2	-	-	5.0	4.3	-	-	0.07	0.02	0.06	0.8
MERL-76	Bal	12.5	18.5	3.2	-	1.4	5.0	4.4	0.4	-	0.04	0.2	0.6	-
APK 1	Bal	15.5	17.0	5.0	-	-	4.0	3.5	-	-	0.03	0.025	-	-
NiAlMo	Bal	0.10	-	10-14	6-10	-	7.8	-	-	0-6	-	-	-	-

Table 2. 6 Typical Chemical Composition for ODS alloys

	Ni	Cr	Mo	W	Al	Ti	Ta	B	Zr	C	Y_2O_3
MA754	Bal	20.0	-	-	0.3	0.5	-	-	-	-	0.6
MA6000	Bal	15.0	2.0	4.0	4.5	2.5	2.0	0.01	0.15	0.05	1.1

Table 2.7: typical applications of INCONEL MA754 and MA6000[10]

Alloy	composition wt%	Major application
Inconel MA754	Ni-20Cr-0.6Y_2O_3	Gas turbine Stator Vanes and Shroud Bands
Inconel MA 6000	Ni-15Cr-4W-2Mo 4.4Al-2.5Ti-2.0Ta –1.1 Y_2O_3	Gas Turbine Rotor Blades

The largest use of MA 754 is as Vanes and bands for aircraft gas turbine engines. For applications requiring good resistance to thermal fatigue, such as gas turbine Vanes, Inconel MA 754 is given a strong texture. Alloy MA 758 is used in a number of industrial applications where its high chromium content makes it resistant to extremes of temperatures and environment. The alloy is used in the glass industry for high temperature components requiring both elevated temperature strength and resistance to extremely corrosive molten glass.

Alloy MA 758 is also used for internal combustion engine components, mainly in critical fuel injection parts. One novel industrial application of alloy MA 754 is a high-temperature atmosphere – circulation fan in a "floating" furnace designs. Large diameter, thin wall tubing of alloy MA 754 has been produced and elevated for radiant tube applications and alloy MA 758 has been used as tubing in heat exchangers and process equipment operating at very high temperatures. The alloy MA 754 is used for brazed nozzle guide vane and band assemblies in U.S military aero engines.

The MA 6000 alloy is a more complex alloy developed as a blade material for advanced gas turbines. It is used for first and second stage turbine Vanes and blades machined from solid bar. MA 6000 exhibits nearly flat rupture – life curves at temperatures due o the combination of oxide – dispersion strengthening and high grain – to width ratios (typically > 10 to 1).

2.3 Microstructural aspects: Nickel-base Superalloys

The evolution of high efficiency turbine engines has resulted in the extensive use of nickel-based Superalloys to accommodate the ever-higher temperatures. Superalloys appears to have deceptively straightforward structures, but details can be quite complex. A number of microstructural features control the level of properties, and a detailed knowledge of the spatial distributions, morphologies, volume fractions and chemical constituents of the phases is essential for the prediction of alloy performance. The major phases are an ordered γ^{l} (Ni_3Al type) phase, and a disordered solid-solution face centered cubic γ matrix. Carbides and borides occur as minor phases and, under certain conditions, the topologically close-packed (TCP) phases such as σ, μ, and Laves can also form. Nickel-based Superalloy components can be produced as castings or wrought products made from ingot or powder metallurgy pre-forms. The above phases are controlled in amounts to get good rupture strength and ductility, but the TCP phases are avoided because these can result in lowered rupture strength and ductility.

Chemical composition:

Generally Nickel-based Superalloys contain Ni, 10-20% Cr, 8% Al and Ti, 5-10% Co. Trace elements like Silicon (Si), Phosphorous (P), Sulfur(S), Oxygen (O), and Nitrogen (N) must be controlled through appropriate melting practice. Trace elements like Selenium, thallium, lead and bismuth must be held to very small (ppm) levels in critical parts. Small amounts of Boron (B), Zirconium, and Carbon (C) included. Optional additions like Molybdenum (Mo), Tungsten (W), Columbium (Cb) and Hafnium (Hf) are added.

Classification of alloying elements:

Matrix class elements, that prefer and make up the face centered cubic (FCC) austenitic (γ) matrix which include Nickel, Cobalt, Iron, Chromium, Molybdenum, and Tungsten. The elements make up the γ^{l} precipitate are Aluminium, Titanium, Columbium, Tantalum, and Hafnium. Boron, Carbon and Zirconium elements tend to segregate to grain boundaries.

The major phases present in Nickel Superalloys:

A. **Gamma Matrix (γ):** The continuous matrix is an FCC Nickel-base austenitic phase called gamma that usually contains a high percentage of solid solution elements such as Cobalt, Chromium, Molybdenum and Tungsten.

B. **Gamma Prime (γ^{l}):** Aluminium and Titanium are added in amounts and mutual proportions to precipitate high volume fractions of FCC γ^{l}, which invariably precipitates coherently with the austenitic γ matrix.

C. **Carbides:** Carbon combines with reactive and refractory elements such as Titanium, Tantalum and Hafnium to form MC carbides.

D. **Grain Boundary γ^{l}:** For the stronger alloys, heat treatments and service exposure generate a film of γ^{l} along the grain boundaries, this is believed to improve rupture properties.

E. **Borides:** Occur as infrequent grain boundary particles.

F. **TCP-Type phases:** Under certain conditions, plate like phases such as σ, μ, and Laves form, this can result in lowered rupture strength and ductility

➢ Gamma Prime Phases

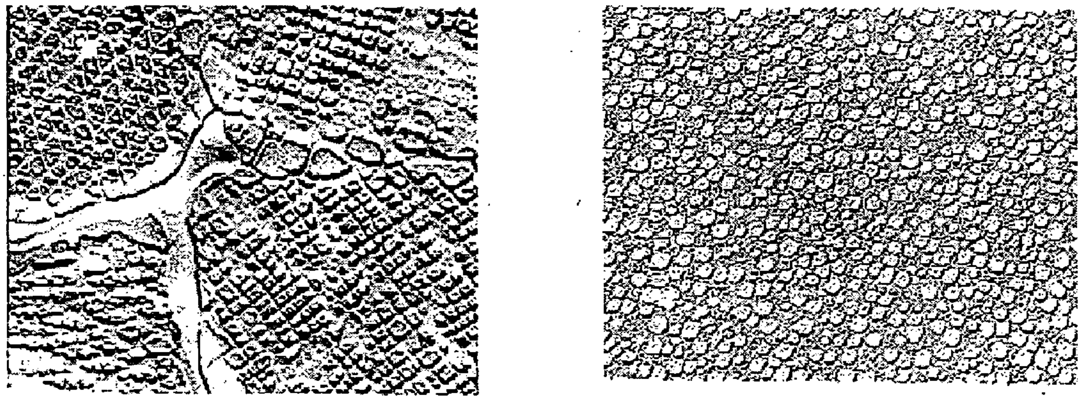
High nickel matrix favors precipitation of γ^{l}, which requires little size change. The compatibility of the γ^{l} FCC crystal structure and lattice constant (approximately 0.1% mismatch) with γ alloys homogeneous nucleation of a precipitate with low surface energy and extraordinary long time-stability. Coherency between γ^{l} and γ is maintained by tetragonal distortion.

In the γ^{l} type A_3B compound relatively electronegative elements such as nickel, cobalt or iron compose the A, and more electropositive elements such as aluminium, titanium, tantalum, or columbium compose the B. Typically, in a nickel-base alloy, γ^{l} is $(Ni,Co)_3(Al,Ti)$ with nickel and aluminium dominating, although it is common to add at least as much titanium as aluminium.

The γ^{I} is a unique intermetallic phase. It contributes remarkable strengthening by dislocation interaction to force, by passing or particle cutting to the γ - γ^{I} alloy. More remarkable, the strength of γ^{I} increases as temperature increases. Further more the inherent ductility of γ^{I} prevents it from being a source of fracture.

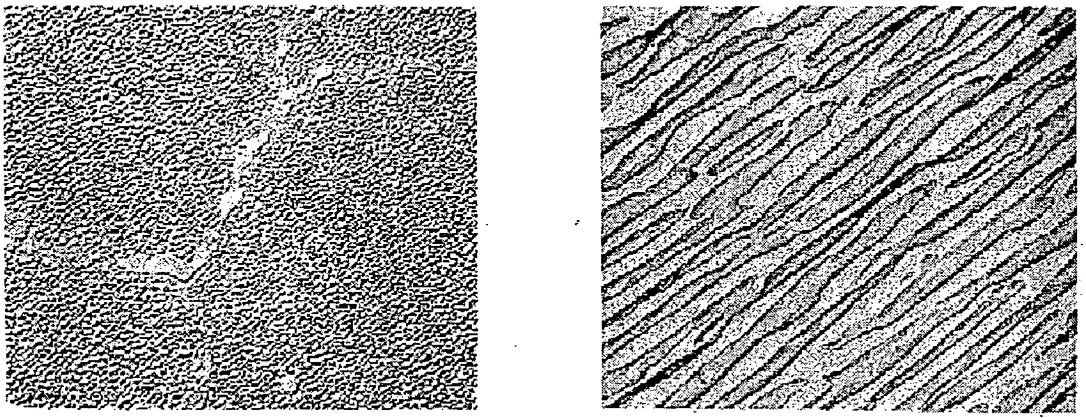
Microstructure:

The γ^{I} was first observed as a spherical precipitate and then as cubes, its shape was later found to be related to matrix-lattice mismatch. Hagel and Beattie observed that γ^{I} occurs as spheres at 0-0.2% lattice mismatch, becomes cubes at mismatches around 0.5-1.0%,and then becomes plates at mismatches above about 1.25%.



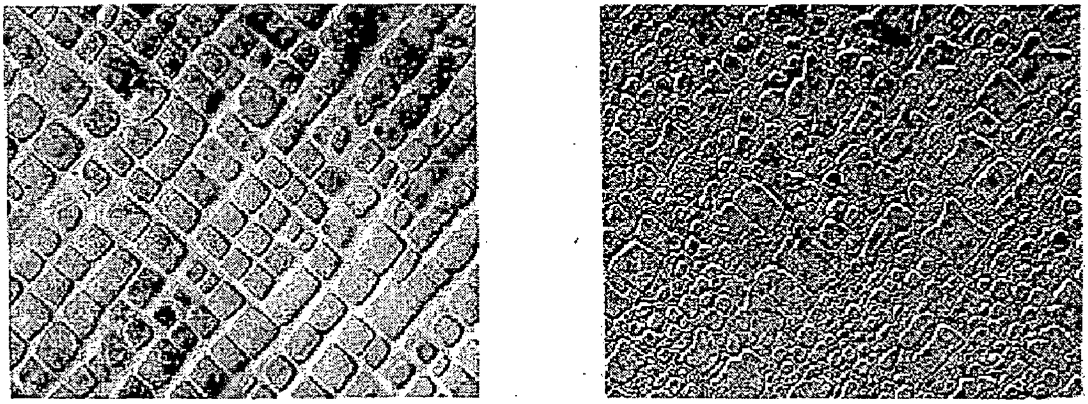
Cubical and trigonal γ' in NASA S-R Tested at 1900^0F (1040^0C).2725X.

Typical Spherical and Cooling γ' in S-R Tested U500.5,450X.



Very Fine γ' in AF-1753.S-R Tested at 1350^0F(735^0C).4,100X

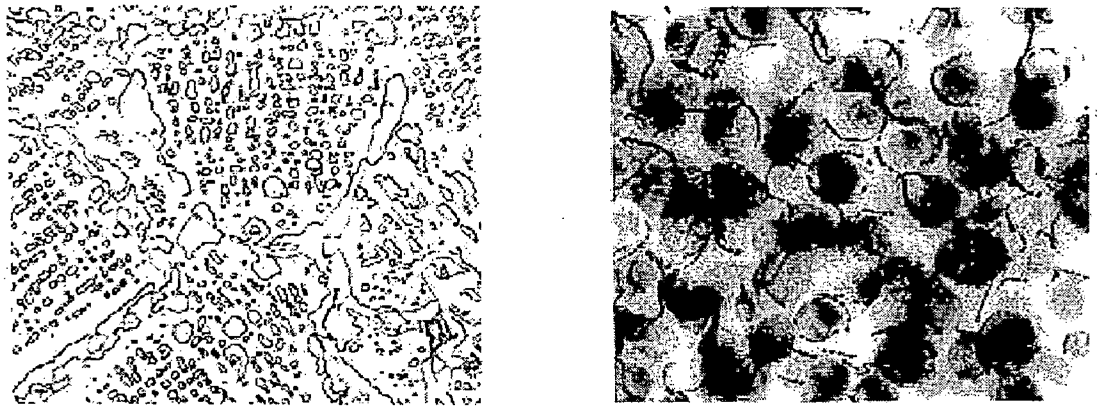
Elongated γ' in Alloy 713 C Tested at 1500^0F (815^0C).



Typical Cubical γ' in IN-100 S-R Tested at 1500^0F(815^0C).13,625X.

Fine, Medium and Coarse γ' in Heated –treated IN-738.5,450X.

Figure 2.1 Microstructures of gamma prime phases. Contd...



Condensed γ^{1} in U700 Aged 180 Days 1900^{0}F (1040^{0}C).545X.

Dislocations Decorating γ^{1} in U500 Tested at 1450^{0}F (790^{0}C). Transmission,4,800X

Figure 2.1 Microstructures of gamma prime phases.

➢ CARBIDES

The role of carbides in Superalloys is complex. First, carbides appear to prefer grain boundaries as location sites in nickel alloys. Carbides exert a beneficial effect on rupture strength at high temperature .In addition, it is clear that carbide morphology can influence ductility and that carbides can influence chemical stability of the matrix through the removal of reacting elements. Therefore, understanding of the desirable chemistry, class, and morphology of carbides is critical to the alloy designer in the selection of compositions and the heat treatments.

Class of carbides and typical morphologies

The common nickel-base alloy carbides are MC,$M_{23}C_6$,and M_6C..MC usually takes a course random cubic or script morphology..$M_{23}C_6$,shows a marked tendency for grain boundaries, it usually occurs as irregular discontinuous blocky particles, although plates and regular geometric forms have been observed.M_6C can also precipitate in blocky form in grain boundaries and more rarely in a Widmanstatten intergranular morphology. It is apparent that continuous and/or denuded grain boundary $M_{23}C_6$ and Widmanstatten M_6C are to be avoided for best ductility and rupture life.

MC carbides usually form in Superalloy during freezing, they occur as discrete particles distributed heterogeneously throughout the alloy, both in inter-granular positions, often inter-dendritically. Little or no orientation with the alloy matrix has been noted. MC carbides are a major source of carbon for the alloy to use later during heat treatment and service.

These primary carbides are FCC. Their dense, closely packed structures are very strong and, if pure, they are same of the most stable compounds in nature. They occur from simple combination of carbon with reactive and refractory metals, classically possessing a formula such as TiC or TaC. The preferred order of formation in Superalloys for these carbides is HfC, TaC, CbC, and TiC in order of decreasing stability. This order is not the same as dictated by thermodynamics, which is HfC, TiC, TaC, and CbC.

Obviously, M atoms can substitute for each other, as in (Ti, Cb)C. However, the less reactive elements, principally molybdenum and tungsten, also can substitute in these carbides. For instance, one will find (Ti, Mo)C in U-500,M-252.and Rene 77.In the latter alloy it has been analyzed to be $(Ti_{0.8}\ Mo_{0.2})C$ plus traces of nickel and chromium. It is reasonably certain that the change in stability order cited above is due to the molybdenum or tungsten substitution, which so weakens the binding forces in MC carbides that degenerations, can occur. The leads typically to formation of $M_{23}C_6$ and M_6C- type carbides as the more stable compounds in the alloys after heat treatments and/or service.

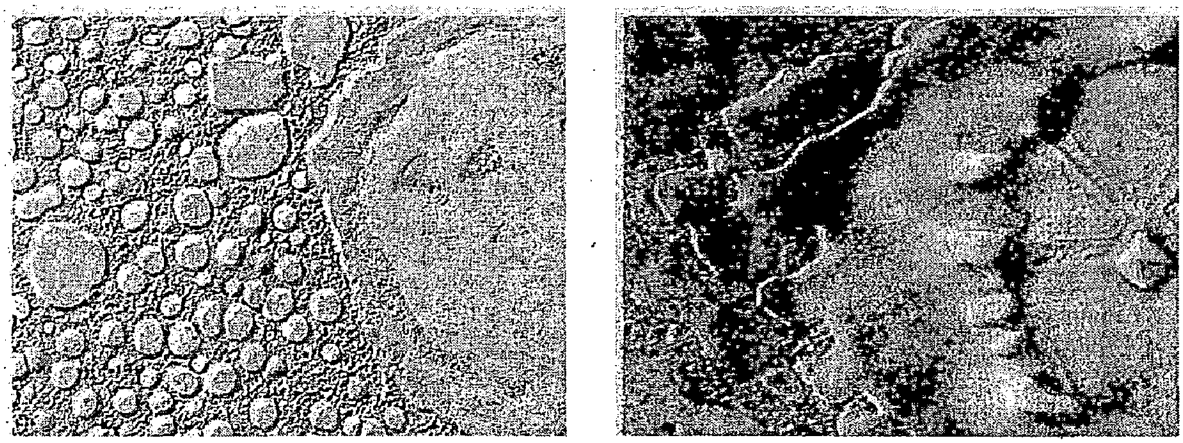
Additions of columbium and tantalum tend to counteract this effect. Modern alloys with high columbium and tantalum contents contain MC carbides that do not break down easily during solution treatment at, for instance,2200-2300^{0}F(1200-1260^{0}C).One such carbide, from MAR-M200,has been analyzed to have an approximate composition of $(Ti_{0.53}Cb_{0.31}W_{0.16})C$.

$M_{23}C_6$ Carbides are profuse in alloys with moderate to high chromium content. They form during lower temperature heat treatment and service, that is, 1400-1800^{0}F (760-980^{0}C), both from degeneration of MC carbides and from soluble carbon residual in the alloy matrix. Although usually forming at grain boundaries, they occasionally occur along twin lines, stacking faults, and at twin ends. In MAR-M200, it was found that $M_{23}C_6$ precipitated inter-granularly as platelets parallel to (110) planes of the austenite and that the $M_{23}C_6$ may be initially coherent. $M_{23}C_6$ carbides have a complex cubic structure, which, if the carbon atoms were removed, would closely approximate the structure of the TCP σ phase.

When tungsten or molybdenum are present, the approximate composition is Cr_{21} (Mo, W)C_6 and generally appears rigidly fixed as such $M_{23}C_6$ Carbides have a significant effect on nickel alloy properties. Then critical location at grain boundaries promotes a significant effect on rupture strength, apparently through inhibition of grain boundary sliding. Eventually, however, rupture failure can initiate either by fracture of these same grain boundary $M_{23}C_6$ particles or by de-cohesion of the $M_{23}C_6$ interface. In certain alloys cellular structures of $M_{23}C_6$ have been experienced but can be avoided by heat treatment and chemistry control. Cellular $M_{23}C_6$ has shown to initiate premature rupture failures.

Fig 2.3. (B) shows $M_{23}C_6$ particles forming from a degenerating MC particle in 713C.The only remaining MC appears to be the typical diamond in the center; it is surrounded by matrix, replacing the originally large MC particle. At the original MC surface $M_{23}C_6$ particles have formed in a ring and are encased in γ^1, another reaction product.

M_6C carbides have a complex cubic structure and form at slightly higher temperatures,1500-1800^{0}F(815-980^{0}C),then $M_{23}C_6$.They are similar carbide to $M_{23}C_6$ but are formed when the molybdenum and/or tungsten content is high, more than 6-8 a/o.M_6C forms as well as $M_{23}C_6$ in MAR-M200, B-1900, Rene80, Rene 41,and AF-1753. Typical formulas for M_6C are $(Ni,Co)_3$ Mo_3C and $(Ni,Co)_2$ W_4C.Since M_6C carbides are stable at higher temperatures than $M_{23}C_6$ carbides, M_6C is more beneficial as a grain boundary precipitate to control grain size in processing wrought alloys.



(A) Typical MC particles in γ^{1} strengthened alloy; Degeneration commenced.4,900X.

(B) Degenerated MC(Diamond) surrounded by $M_{23}C_6$ practices and matrix in IN-100. 2450X

Figure 2.3 Typical microstructures of carbides in Ni-based Superalloys

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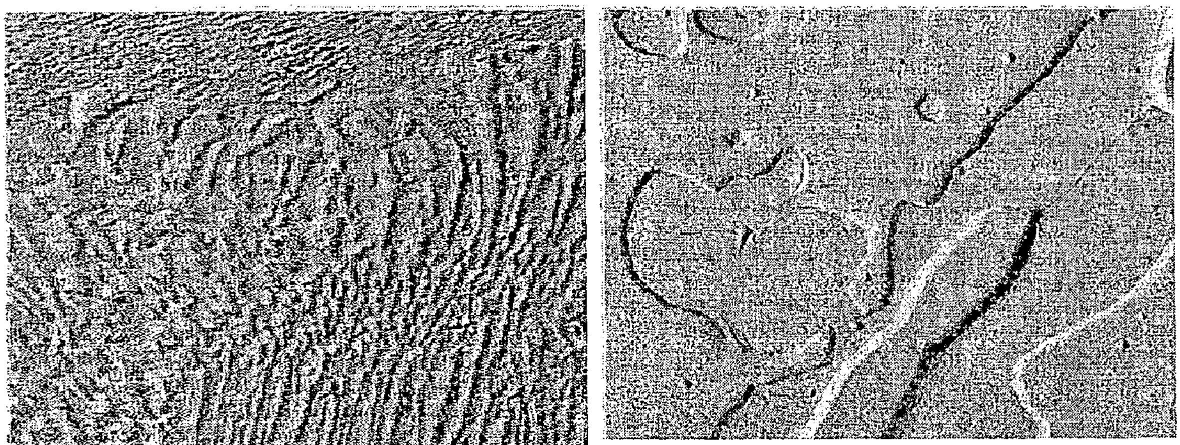
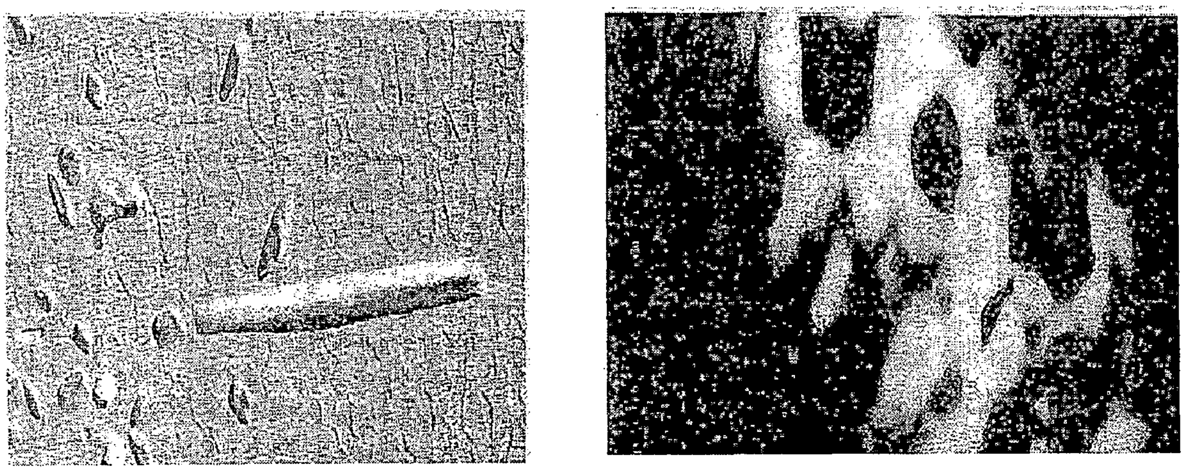


Cellular M23C6 formed in Nimonic 80A at 12000F(6500C) 4,900X

Blocky M6C surrounded by γ| at grain boundary of AF-1753.4,900X.



Widmanstaten M6C in γ|-strengthened alloy,4,900X.

Grain-boundary M23C6 in particles in Rene080.

Figure 2.3 Typical microstructures of carbides in Ni-based Superalloys

- **BORIDES**

➢ BORIDES

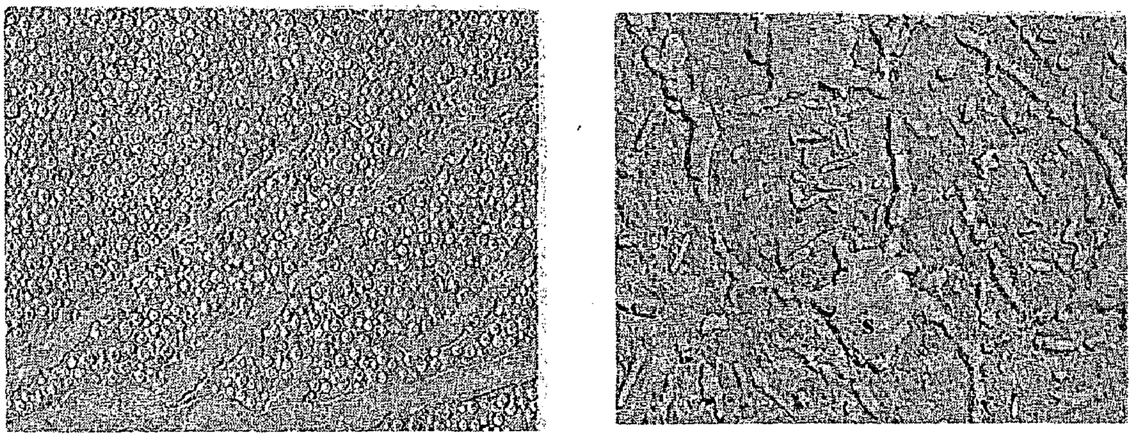
Boron is generally present to the extent of 50-500ppm in Superalloys; it is an essential ingredient. It goes to grain boundaries where it blocs the onset of grain boundary tearing under creep rupture loading. In U-700,for instance, more than 1200ppm boron reacts to form two types of M_3B_2 borides depending on thermal history; one is approximately $(Mo_{0.48}Ti_{0.07}Cr_{0.39}Ni_{0.03}Co_{0.03})_3B_2$ and the other is $(Mo_{0.31}Ti_{0.07}Cr_{0.49}Ni_{0.06}Co_{0.07})_3B_2$. Borodies are hard refractory particles observed at grain boundaries with shapes varying from blocky to half-moon in appearance, they act as a supply of boron for the grin boundary.

➢ TCP PHASES

In certain alloys where composition has not been carefully controlled, undesirable phases, can form either during heat treatment or more commonly during service. These precipitates, called TCP phases, are characterized as composed of close-packed layers of atoms forming in "basket weave" nets aligned with the octahedral planes of the FCC matrix. Generally detrimental, they may appear as thin linear plates, often nucleating on grain boundary carbides. Those commonly found in nickel alloys are σ and μ.

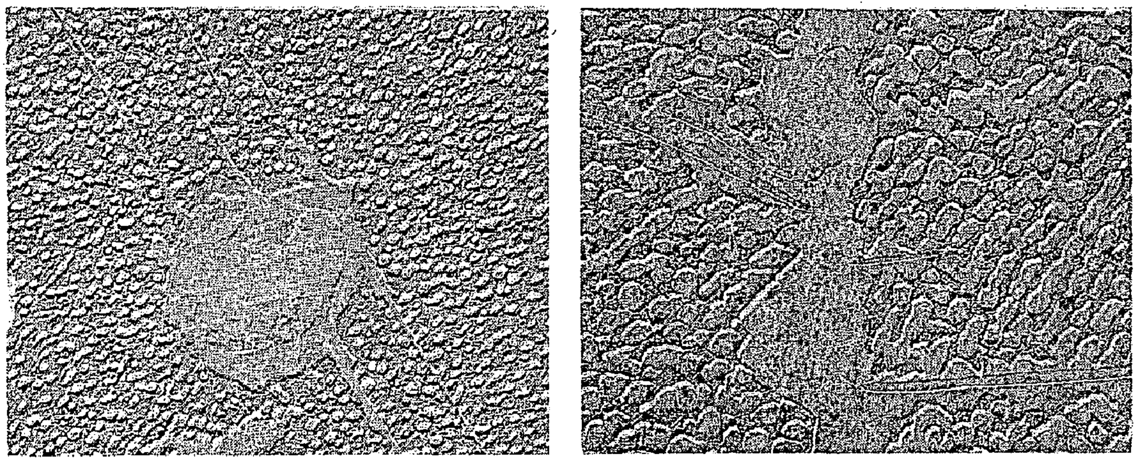
Although a TCP phase such as σ often seems to grow directly through γ^1 particles, it is logical that it must form from the nickel alloy matrix, since γ^1 and most carbides precipitate first. It's formula is $(Cr,Mo)_x(Ni,Co)_y$,where x and y can vary from 1 to 7.

Sigma has a specific and detrimental effect on alloy properties. It's physical hardness and plate like morphology is an excellent source for crack initiation and propagation, leading to low-temperature brittle failure. However, of perhaps more grave concern is the effect on elevated temperature rupture strength. Sigma contains a high refractory metal content sapped from the γ matrix of the Superalloy causing loss of solution strengthening. Also, high-temperature rupture fracture can occur along σ plates (inter-sigmatic fracture) rather than the normal inter-granular fracture, resulting in severe loss in rupture life. This was first shown by Ross for IN-100; excessive formation caused a 1500^0F, 40ksi rupture bar to fail in 967h versus an expected life of 8000h.Platelike μ also can form, but less is known concerning its detrimental effects.



Sigma plates in U-500,coherency with M23C6,5,625X.

Sigma plates in N-115,coherency with M23C6,5,625X.



M plates developing near degenerating MC particle in AF-1753,4225X.

Laves plates in S-590,with M6C and CbC,5625X.

Figure 2.3 Microstructures of TCP phases formed in austenitic alloys.

2.4. METALLOGRAPHIC TECHNIQUES

Department of Metallurgical and Materials Engineering
Indian Institute of Technology Roorkee

No. Met. /2313/PG

Dated: July 14, 2004

A.R. (PGS & R)
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Please find enclosed herewith M. Tech dissertation grade sheets of following M. Tech students alongwith the dissertation copy of each of the following :

Physical Metallurgy

Sl. No.	*Name of Student*	*Enrolment No.*
1.	Suresh Kumar Vuppada	025210
2.	M. Nageshwar Rao	025205

(G.C. KAUSHAL)
O.C. M. Tech Classes

14/7/04

2.4. METALLOGRAPHIC TECHNIQUES

The methods are different for microstructural characterization of powder processed nickel-based Superalloys. A three-step thermal cycle is relatively common to Superalloy heat treatment, solution treatment at high temperature, stabilization/stress relief at an intermediate temperature, and a low temperature age. After such a heat treatment, where the first step is at a temperature below the $\gamma^{'}$ solvus temperature. The two major phases present are the disordered γ phase and the ordered $\gamma^{'}$ phase. In this example three sizes of $\gamma^{'}$ precipitates are evident. Primary $\gamma^{'}$, the size and distribution of which is set by the solution treatment temperature. Secondary $\gamma^{'}$ formed during cooling from solution temperature and modified by the stabilization temperature and tertiary $\gamma^{'}$ formed during aging.

Preparation methods and results:

P/M IN-100 Superalloy forgings were subjected to a sub-solvus (1416K) solution heat-treatment, followed by a two-step aging sequence that involved holding at 1005K, respectively. This process cycle results in a fairly complex microstructure that consists of a fine grained γ matrix with three sizes of embedded $\gamma^{'}$ precipitates, usually designated primary, secondary and tertiary $\gamma^{'}$.

Metallographic preparation involved standard mechanical grinding at 800 grit followed by polishing using alumina powder suspensions. Due to the microstructural complexity of the alloy, separate techniques are developed for identification of each of the phases. Characterization was performed using optical microscopy, field emission scanning electron microscopy (FE SEM, Joel 6335F) and transmission electron microscopy(TEM, Philips EM420).

Matrix phase

Based on years of experience γ grain boundaries are typically examined by optical microscopy after electro-etching in a solution of 50%HCL and 50% Methanol at 4.5V by immersion etching in waterless Kalling's solution. Waterless Kalling's reagent coupled with SEM imaging proved to be very effective method of solving the γ matrix grain boundaries. Best practice involves etching by immersion for a period of 20-40s in a solution of 40ml HCL, 40ml ethanol, and 2 g cupric chloride. The primary γ grains are revealed as darker recessed areas due to preferential dissolution of this phase.

γ^{l} Phase

The γ^{l} phase is clearly defined after etching in Glycerygia, and such features as primary γ^{l} volume fraction, and secondary γ^{l} sizes can be measured. A two-step preparation of the etchant is necessary, firstly 15ml and 3ml HNO_3 are mixed and the solution is matured until the color turns orange(about 10 min).Then 18ml Glycerine is added. Specimens should be etched in this solution by immersion for 20-40s.Observations is best conducted by SEM. It illustrates the general structure of sample prepared using this procedure, the location of the γ^{l} phase is revealed as darker recessed regions because Glycergia is a highly selective etchant for structural constituent.

Carbides and borides:

General distributions of carbides can be evaluated through specimens are electro-polished in a mixture of 20ml $HclO_4$ in 80 ml methyl alcohol at 25V for 25s followed immediately by electro-etching in the same electrolyte at 5V for 3-5s.This procedure exposes carbide particles in relief and the strong constraint between y phase bright particles and the darker background in SE SEM images makes for effective demarcation. It shows of such surface and it may be clearly seen that angular $M_{23}C_6$ type of carbides are located at grain boundaries while spherical MC carbides lie predominantly with in grain.

2 .5 Inconel MA754:

In 1980, Weber prepared a large amount mechanically alloyed (MA) ODS Superalloy (INCONEL MA 754) [11]. It is essentially a Ni-20% Cr alloy strengthened by about 1 vol% Y_2O_3. The Ni-Cr and Y_2O_3 powders were welded until a homogeneous Ni-20% Cr alloy was formed in which the Y_2O_3 particles were uniformly distributed. The fabricated alloy powder was then consolidated by hot extrusion which was followed by hot rolling. A recrystallisation step, often directional followed consolidation that resulted in elongated high aspect ratios grains that were very stable owing to the inert oxide pinning. After the directional crystallization the grains are had typical dimensions of ~500 to 700 μm parallel to the working direction and ~ 15 μm perpendicular to this direction [3]. The typical BFI of the fabricated MA 754 is displayed in Fig 2.1.

Benjimen *et al.* have suggested that fine particles are a uniform dispersion of stable yttrium aluminates formed by the reaction between the added Y_2O_3, excess oxygen in the powder, and the aluminium added to getter oxygen. In Fig 2.1. the larger particles are Titanium carbonitrides. The dispersoids are typically 14nm in diameter with an averaging spacing of 0.2μm. The 10930C stress rupture properties of INCONEL MA 754 are compared to those of other alloys in Fig. 2.2. The MA 754 alloy, like other ODS materials, has a fine, flat, log stress-log rupture life slope compared to conventional alloys. The strength of MA 754 alloy, about 100 MPa for 100hrs life, is some what higher than both of the other ODS alloys and several times than conventional materials. Thus, while MA 754 alloy incomparable to TD (Thoria dispersed) NiCr, it has a non-radioactive dispersoid and high strength, so it is suitable for applications such as gas turbine blades [12]. Table 2.8 shows the nominal composition of the INCONEL MA754 alloy.

Table 2.8 Nominal composition of INCONEL MA754 [13]

Alloying Element	Ni	Cr	Fe	C	Al	Ti	Y_2O_3
Content (wt%)	78	20	1.0	0.05	0.3	0.5	0.6

Melting point (Approximate solidus)	1400^0C
Density	8.3 g/cm^3

High strength, especially at elevated temperature, is the outstanding characteristic of MA754 due to which it is a attractive material for gas turbine components (Vanes).It can also be used in furnace fixtures and skid rails, fasteners and other applications where high temperature creep and corrosion resistance are required.

2.6. Properties:

Mechanical Properties

The prime reason for the existence of the entire stable of superalloys compositions is their outstanding strength over the temperature ranges in which gas turbine components operate. The close-packed face-centered-cubic (FCC) lattice of these compositions has great capability to maintain good tensile, good rupture and good creep properties because of several factors including the excellent modulus and diffusitivity of the FCC lattice for secondary elements. Superalloys have good ductility, outstanding impact resistance and good resistance to high-cycle and low cycle mechanical fatigue as well as thermal fatigue. Fig 2.4 shows the rupture strengths of several candidate alloys. Table 2.9 shows the tensile properties of INCONEL MA754.

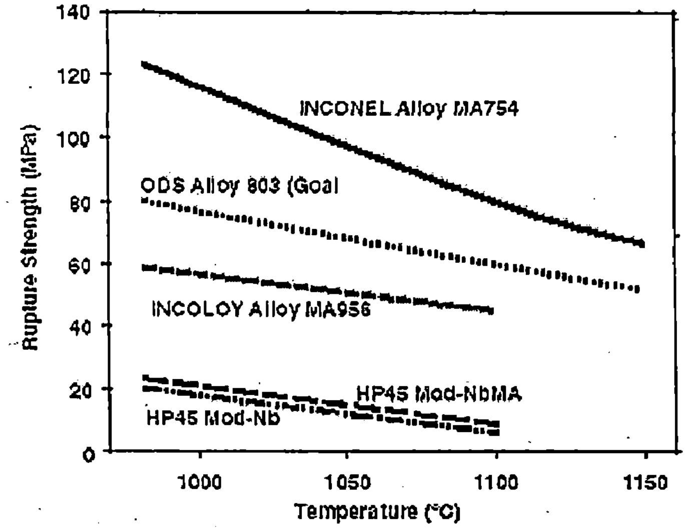

Figure 2.4 Creep ruptures strengths of several candidate alloys at 10,000 hour [14]

Surface stability

The surface stability of superalloys can be estimated by the oxidation and hot corrosion characteristics. In gas turbine engine, the high-velocity hot gas stream produced by compression and combustion has a great capacity to degrade hot stage parts by oxidation and hot corrosion. Good oxidation resistance is achieved by formation of a light continuous surface scale that acts as a diffusion barrier and does not spell off during thermal cycling. Chromium is added to superalloys to control the oxidation rate.

Ni-Cr alloys with high aluminum content, are considered to have excellent resistance to oxidation due to this ability to form the protective oxides Cr_2O_3 and Al_2O_3.Yttria particles stops the oxygen to penetrate into the grain boundary area.

With in the gas turbine industry, hot corrosion refers to a particularly aggressive attack resulting from the combined effects of normal oxidation plus reaction with sulfur and other contaminants injected with inlet air and contained in fuel.

Table 2.9 : Longitudinal tensile properties of MA754 at different temperatures[15]

Temperature (^{0}C)	U.T.S (MPa)	Y.S (0.2% offset) (MPa)	Elongation (%)
21	965	586	21.0
427	869	538	16.0
649	600	476	25.0
760	345	276	34.0
871	248	214	31.0
982	190	169	18.0
1093	148	134	12.5

Oxidation Resistance:

Resistance to Oxidizing environment at high temperatures is a requisite for superalloys whether used coated or uncoated. [16]. Small additions of rare-earth elements and oxygen-active elements have been found to alter the oxidation resistance of Cr_2O_3 forming alloys. The effect of these additions usually include (1) formation of continuous Cr_2O_3 scales at lower alloy chromium concentrations, (2) reduction in the rate of Cr_2O_3 growth, (3) improved scale adhesion, (4) change in the primary growth mechanism of the oxide from outward cation migration to inward anion migration, and (5) a reduction of the grain size in the Cr_2O_3 scale. Similar effects have also been observed when the oxygen-active elements are present as a fine oxide dispersion in the alloy prior to the oxidation [17-21]

In addition to Chromium, aluminum plays a critical role in the oxidation of γ'-strengthened superalloys. This element also provides the basis of oxidation-resistant NiAl diffusion aluminide and MCrAlY overlay coatings. Ni (Co, Fe) base alloys with both chromium and aluminum additions benefit from a remarkable synergistic effect of these elements amounting to great technological importance [16].

INCONEL alloy MA754 has excellent oxidation resistance. It may be used in high-temperature oxidizing environments without the need for expensive special coatings usually required for conventional high-temperature alloys. This alloy shows parabolic oxidation behavior.

Parabolic law:

The weight gain per unit area is directly proportional to the square root of time of exposure. It follows the mathematical relation:

$$W^2 = At + B$$

where A and B are constants.

It is a diffusion-controlled mechanism. Here the thickness of oxide increases at a decreasing rate. The scale grows mainly at oxide-oxygen interface, i.e., diffusion of metal-cations occurs.

2.7 Role of alloying elements

Nickel

Nickel is a malleable, faintly yellowish-white lustrous metallic element, with a density 8.9 g,.cm^3 and melting point of 1455^{0}C and a FCC structure. Ni combines with Al and forms Ni_3Al which is gamma prime precipitate. Ni is a FCC structure so its formability characteristics are good. Ni has a greater tolerance for alloying additions with out the formation of detrimental phases. The general physical characteristics of Ni are given in table 2.10..

Chromium

Chromium is always a major alloying element contributing oxidation resistance to the systems. chromium is a brilliant bluish–white metal of 7.19 gm/cm^3 density with a melting point of 1850^{0}C. Cr forms solid solution with Ni and contribute solid-solution strengthening. In the presence of carbon, a number of alloy carbides are formed such as cementite $(FeCr)_3C$ (in which chromium may be as high as 20%), $(Cr_2Fe)_3C_2$, $(Cr_2Fe)_7C_3$ and $(CrFe)_4C$. Higher or alloys are susceptible to ebmrittlement, when slowly cooled, through the temperature range of 550-450^{0}C due to '475^{0}C embrittlement mechanism(s). Cr produces an extremely thin, dense, adherent and protective oxide film which protects the metal/matrix from oxidation/corrosion. The chromium oxide layer rapidly grows to a thickness of about 8 microns at temperatures higher than 1000^{0}C and then stabilize and stop growing. The oxide layer is self-healing because damage is rapidly repaired by γ^1 natural oxidation at elevated temperature. In INCONEL MA754, the Cr content is 20%.

Table 2.10 The physical properties of elemental Cobalt, Nickel. Iron and Chromium

	Crystal Structure	M.P. (°F)	Density Lb/in^3	Expansion co-efficient@ RT X 10^6 /°C	Thermal Conductivity @RT BTU/ft^2/hr/°F/in	Phase Stability (alloying tolerance)
Co	HCP	2723	0.32	7.0	464	2
Ni	FCC	2697	0.32	7.4	610	1 (most-stable)
Fe	BCC	2798	0.28	6.7	493	4 (least stable)
Cr	BCC	3407	0.26	3.6	464	3

Aluminium

Aluminium is a principal gamma prime former. Al forms hard precipitate γ^{I}, $Ni_3(Al,Ti)$, the strength of γ^{I} increases as temperature increases. It is useful in imparting oxidation resistance up to 1200^0C due to the formation of a protective oxide film,Al_2O_3. This adherent and protective oxide film resists corrosion. In INCONEL MA754 the Al content is 0.3%.

Yttrium oxide

Its contents vary from 0.6% to 0.7%.Its an hard and inert oxide. It is finely dispersed in the Ni-Cr matrix by mechanical alloying process. It inhibits the motion of dislocations and thus increasing the high temp. strength [1]. It can make oxygen not to penetrate into the grain boundary area and thus prevents the oxidation.

2.8 Mechanical Alloying

Mechanical alloying is a powder metallurgy processing technique involving cold welding, fracturing and re-welding of powder particles in a high-energy ball mill. MA had its origin at the International Nickel Company (INCO), in 1966, where Benjamin and coworkers [7, 8] used MA to prepare nickel–based oxide–dispersion strengthened alloy powders. MA starts with a mixture of powders which are blended together in a ball mill. During MA the powder particles are trapped, heavily plastically deformed and cold welded.

In MA the ball velocities of the order of meters per second. To prepare small quantities of powder, researchers use attritors in which the necessary ball energy is provided through a rotating impeller.

One of the greatest advantages of MA is in the synthesis of novel alloys, e.g., alloying elements, which is not possible by any other technique. Extended solid solubilities have been achieved by mechanical alloying. MA is completely solid-state processing technique and therefore limitations imposed by phase diagrams do not apply here.

Calculations show that the maximum departure from equilibrium is 30kJ/mol in MA suggesting that it is possible to achieve greater departure from equilibrium(or "more metastable effects)during MA. The balls used in MA having a diameter generally anywhere in the range of 4 to 12 mm.

Mechanism of alloying

Whenever two steel balls collide, some amount of powder is trapped between them. Typically, around 1000 particles with an aggregate wt of 0.2 mg are trapped during each collision. The force of the impact plastically deforms the powder particles, creates new surfaces and enables the particles to weld together, which leads to an increase in particle size. In the early stages of milling, the particles are soft and their tendency to weld together and form large particles is high. A broad range of particles size develops, with some as large as three times bigger than the starting particles. The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents with continued deformation, the particles become work hardened and fracture by a fatigue failure mechanism and/or by the fragmentation of fragile flakes. Fragments generated by this mechanism can continue to reduce in size in the absence of strong agglomerating forces. At this stage, the tendency to fracture predominates over cold welding.

After milling for a certain length of time, steady state equilibrium is attained when a balance is achieved between the rate of welding, which tends to increase the average particles size and the rate of fracturing, which tends to decrease the average composite particle size. At this stage, each particle contains substantially all of the starting ingredients in the proportion they were mixed together and the particles reach saturation hardness due to the accumulation of strain energy. The particles size distribution at this stage is narrow, because particles larger than average are reduced in size at the same rate that fragments smaller than average grow through agglomeration of smaller particles. The average particle size obtained at this stage depends on the relative case with which agglomerates can be formed by welding, fatigue and fracture strength of composite particles and resistance of particles to deformation.

During MA, heavy deformation is introduced into the particles. This is manifested by the presence of variety of crystal defects, such as dislocations, vacancies, stacking faults and increased number of grain boundaries. The presence of this defect structure increases the diffusivity of solute elements into the matrix. Further, the refined microstructural features decrease the diffusion distances. Additionally, the slight rise in the temperature during milling further aids the diffusion behaviour and consequently, the alloying takes place among the constituent elements. While this alloying generally takes place nominally at room temperature.

2.9 Processing Routes:

Hot Isostatic Pressing

In Hot Isostatic Pressing (HIP) the containerized powder is heated to an elevated temperature (either above or below the gamma prime solvus depending on the desired grain size of the product) under a high external gas pressure (approximately 15,000 psi). The combination of temperature and pressure on the container is transferred to the powder mass and affects densification.

The general structural goal of HIP consolidation is to have a fully dense product without retention of prior precipitation boundaries (PPBs). The conditions for successful HIP consolidation require sufficient time, temperature, and deformation during the cycle. Varying HIP cycle parameters can influence whether plastic deformation or creep is the predominant densification mode, which can in turn influence the PPB retention in the microstructure.

Hot compaction and Extrusion

The other commercial consolidation process is sub-solvus hot compaction followed by extrusion. In this process containerized powder is hot compacted. The consolidated powder (>95% dense) is subsequently extruded at a ratio of about 6:1 to fully dense billet.

Chapter 3

FORMULATION OF THE PROBLEM

A review on literature on ODS alloys reveals that the ODS alloys are ordinarily strain rate sensitive alloys; and therefore high speed deformation associated with processes like forging is not suitable for the manufacture and M/s. INCO alloy and similar other companies preferred extrusion (where strain rate is slow and controllable)to manufacture these alloys out of high quality argon atomized low oxygen(<100 ppm) alloy powders. The extrusion process offers high density in the alloys, which unnecessarily gives weight to the product.

Here we practiced the powder forging technique but strain rate sensitivity of these alloys has been carefully avoided. The present technique practiced instead of starting with high quality powders as mentioned in previous point, one can start with elemental powders, not bothering about oxygen levels. These elemental powders are not allowed to form alloy till the forging is complete. It is only after forging that alloy formation is attempted by way of high temperature homogenization treatment and it is at this state that alloy is strain rate sensitive and free from deleterious oxygen content.

The powder forging technique was evolved in this department for the first time in the year 1991 for the production of ferritic base ODS alloy mainly MA956 and was patented under Indian patent no. 184576/92. This technique could successfully produce this alloy to near density and the properties obtained were of high quality in comparison to MA956 alloy produced by costly extrusion process by M/s. INCO alloy company.

This way one affects by choosing forging route great economy in processing these alloys and greater flexibility in manufacture of precision components of various shapes and sizes through this technique. In this present investigation, this forging technique has been applied to Ni-base ODS alloy equivalent MA754 of M/s. INCO alloy company. The Y_2O_3 dispersoid employed is in the form of precipitates in some micron range (<1 micron). The powders used for this investigation are varying in size.

In this research work done in 1991, many of other parameters of the process was optimized to yield fully dense product. However no effort was made to assess the response of the formation on microstructure particularly porosity on the final properties of the product.

Porosity and finer defects in the matrix are extremely sensitive parameters which influence the final properties in great way.[ONE OF THE IMPORTANT OBJECTIVE OF THE PRESENT INVESTIGATION IS TO ESTIMATE THE INFLUNCE OF DEFORMATION POROSITY ON THE FINAL PRODUCT PROPERTIES NAMELY ITS OXIDATION RESISTANCE].

It is expected that porosity and its mobility under the influence of deformed matrix at high temperature [associated with oxidation studies] will lead to different oxidation patterns. The present investigation is going to concentrate in this aspect. So that scatter of oxidation behaviour may be evolved for future possible application of these alloys when they are relatively lighter in comparison to fully dense alloys.

The oxidation data so obtained would then be compared and evaluated with that of fully dense alloys. The overall emphasis is lies on the estimation of flexibility on processing parameters, vis-à-vis the overall product properties. The present report restricts itself to oxidation studies only, owing to limited period of time , however other properties could also be similarly evaluated.

Chapter 4

EXPERIMENTAL PROCEDURE

4.1 Alloy preparation

The MA754 alloy was prepared by mechanical alloying. The size taken for Ni powder is 200mesh. The size range taken for chromium powder is given in table 4.1. The composition of the alloy is given in table 4.2. Before placing the powder in attritor the powder particles were mixed in a Pestol mortar. The elemental powders are mixed in an attritor for 8 hours. The balls used the size (diameter) of 5-6 mm, and its quantity for mixing should be four times the weight of the powder mix. While mixing, the powder particles should not be heated, so water cooling facility has provided to extract from attritor. The speed of the impeller is around 1400 rpm.

Table 4.1 The Chromium powder particles size distribution

Weight proportionality (%)	**Particle size (micron)**
76.13	250
21.05	180
2.40	150
.30	75

Table 4.2 Chemical composition of powder mix

Alloying Element	Ni	Cr	Al	Y_2O_3
Content (wt%)	79	20	0.3	0.7

4.2 Powder Forging

The mechanically prepared alloy was encapsulated in mild steel cans of length 12 cm and dia. of 4 cm. The cans have a facility to passage for hydrogen gas. The encapsulated cans were heated in tube furnace at 1050^0C-1100^0C for 1 hour. While heating, the hydrogen gas was supplied to the powder to avoid oxidation. After 1 hour the powder mass in heated condition forged under friction screw press of 100 tons capacity to make the product in to the slab of size 12cm X 6cm X 2cm. after cooling the mild steel can was removed by machining.

4.3 Homogenization

The forged slab homogenized for 6 hours at 1300^0C to get uniform distribution of the alloying elements. The muffle furnace was used for homogenization treatment.

4.4 Thermo-Mechanical Treatment

The slab was hot rolled to nearly 27% of reduction. The hot rolling was done at 1100^0C. The general aim of thermo-mechanical processing (TMP) is to achieve coarse grain morphologies by means of secondary recrystallisation and is to increase the availability of the necessary product forms.

4.5 Oxidation Testing

It is the preliminary step to asses the quality of the product. The oxidation test was conducted for as-forged and as-rolled samples for six hours at temperatures 1050^0C, 1150^0C, 1200^0C, 1250^0C. The oxidation rate was measured in terms of weight gain per square meter.

4.6 Cyclic Oxidation Testing

The cyclic oxidation test conducted at 20 hours duration cycle at 1100^{0}C. The test was conducted till the stabilized weight gain occurred. This test was conducted as-rolled and as-forged samples.

4.7 Metallographic Study

The three samples as-forged, oxidized; as-rolled, oxidized; and as-rolled, un-oxidized were observed under metallographic study. The specimens were prepared by polishing on emery papers up to 4/0. Then after the samples were disc polished using fine alumina powder. The features of microstructural porosity were studied under microscope.

4.8 Hardness measurement

For three samples as-forged, oxidized; as-rolled, oxidized; and as-rolled, un-oxidized, the hardness was measured. The tests were conducted on Vickers hardness tester under 10kg load.

4.9. Equipment used

Attritor:

Attritor is an instrument used for mixing the powder particles. It consists of a drum in which the powder particles are mixed thoroughly by an impeller. The impeller is rotated by motor. The impeller speed is around 1400 rpm. The drum has water facility around it, for cooling purpose while attritor is in operation. In drum, the powder mass and balls are charged before starting mixing. The balls used are **Cr** steel balls, whose having diameter of 4mm. In attritor the powder mass is mixed for a specified time to get complete mixing. Figure.4.1 shows the schematic diagram of the attritor.

Friction screw press:

Friction screw press is used for forging the powder mass. It is an energy restricted machine, and they use energy stored in a flywheel to provide the force for forging. The rotating energy or inertia of the flywheel is converted to linear motion by a threaded screw attached to the flywheel on one end and to the ram on the other hand. The screw press uses a friction to accelerate the flywheel and the screw assembly, and it converts the angular kinetic energy into the linear energy of the slide or ram. Fig 4.2. shows the schematic diagram of the friction screw press. The total process was schematically shown in the figure 4.3. as a process flow sheet.

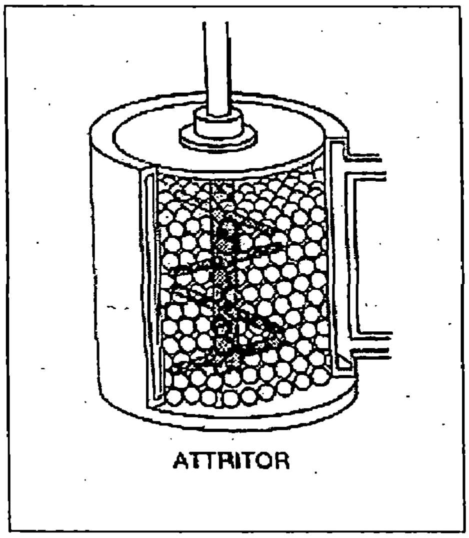

Figure 4.1: Schematic diagram of the attritor

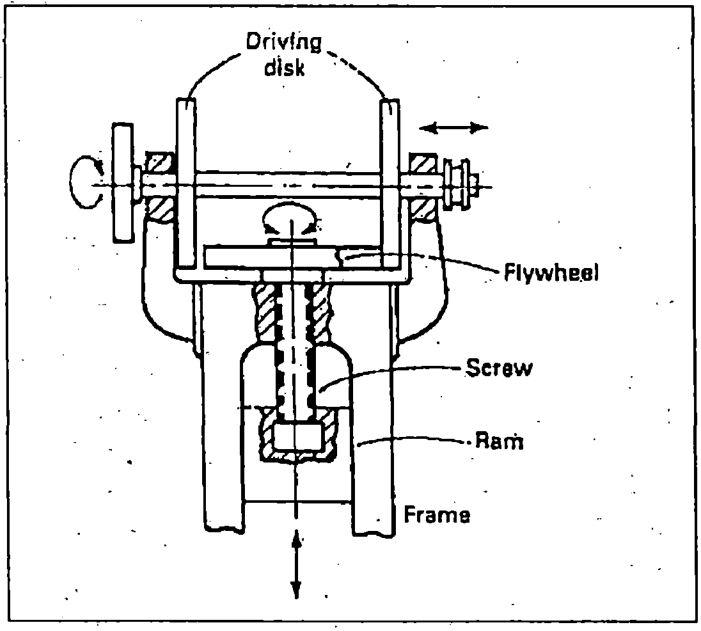

Figure 4.2.: Schematic diagram of the friction screw press.

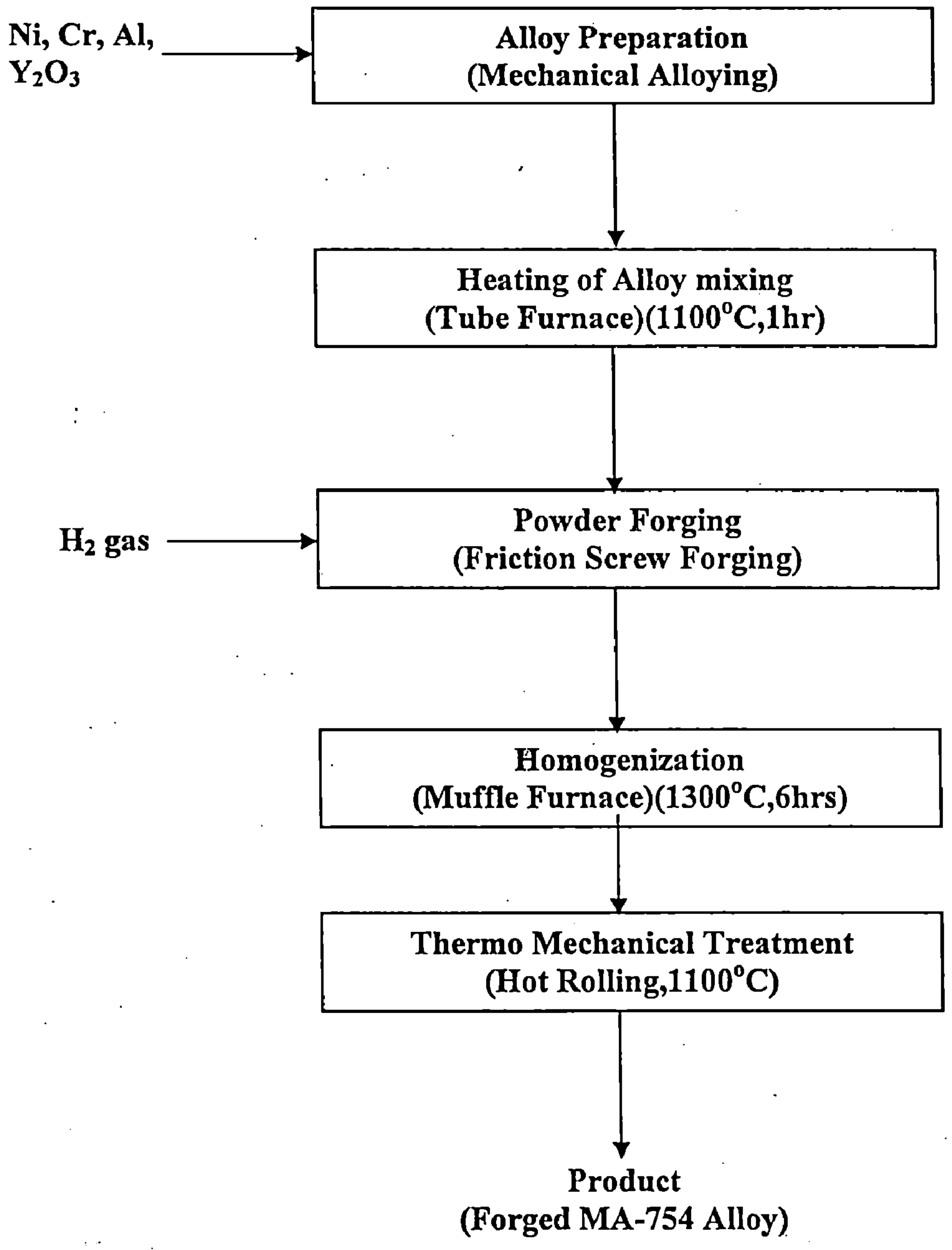

Fig 4.3 Flow Sheet of the Process

It consists of two large energy-storing driving disks are mounted on a horizontal shaft and rotated continuously by an electric motor. For a down stroke, one of the driving disks is pressed against the flywheel by a servomotor. The flywheel, which is connected to the screw either positively or by a friction-slip clutch, is accelerated by this driving disk through friction. The flywheel energy and the ram speed continue to increase until the ram hits the work piece. Thus, the load necessary for forming is built up and transmitted through the slide, the screw, and the bed to the press frame. flywheel, the screw, and the bed to the press frame. The flywheel, the screw, and the slide stop when the entire energy in the flywheel is used in deforming the work piece and elastically deflecting the press. At this moment, the servomotor activates the horizontal shaft and presses the upstroke-driving disk wheel against the flywheel. Thus, the flywheel and the screw are accelerated in the reverse direction, and the slide is lifted to its top position.

Chapter 5

RESULTS AND DISCUSSIONS

5.1 Rolling response

The product obtained form modified powder forging process has a density nearly 7.2 gms/m^2, which is of 87.64% of Inconel MA754 material. The developed material has less density compared with other material of same composition developed by different processing routes. The material has porous structure. The product was rolled to deform from slab to plate. The deformation obtained is nearly 27%.

5.2 High Temperature Oxidation Behaviour

The oxidation testing data so obtained of this material by exposing 6 hours at different temperatures 1050^{0}C,1150^{0}C,1200^{0}C,1250^{0}C. This material shows parabolic oxidation behavior. The oxidation testing data of the as-forged, as-rolled specimens for 6 hrs given in table 5.1.

Table 5.1: the oxidation testing data of the as-forged, as-rolled material by exposing for 6 hours (the stabilized weight gain)

Temperature(^{0}C)	Weight gain (gm/m^2)	
	As-forged	As-rolled
1050	13.806	6.896
1150	12.44	10.51
1200	6.391	7.119
1250	8.654	7.334

The as–forged sample after exposing for 6 hours at 1050^{0}C gets uniform oxide layer. The two odd patches were observed in the corners of the specimen. The as-rolled specimen gets uniform oxide layer around it, the appearance is blackish grey colour. The weight gain by the as-forged sample is more compared with as-rolled sample. The as-rolled product has less porous structure, so it gets oxidized less in quantity.

At 1150^{0}C, the oxidation data reveals that the as-forged and as-rolled structures given weight gain with similar in quantity. One odd patch was noticed on the as-forged sample. The as-rolled sample gets uniform oxide layer. The weight gain obtained is more compared with samples oxidized at 1050^{0}C. After exposing for 6 hours at high temperatures 1050^{0}C, the pores gets closed and after exposing at further temperatures, the weight gain of this specimen is in low value and similar to the as-rolled product.

At 1200^{0}C, the as-forged specimen gets uniform oxide layer. The as-rolled specimen also gets uniform oxide layer. At 1250^{0}C, the specimens gets more weight gain, but the values for as-forged and as-rolled samples are close. It s due to the as-forged sample when exposed to higher temperatures, the pores gets closed. So after exposing at higher temperatures, the weight gain values are less compared with previous exposure temperatures.

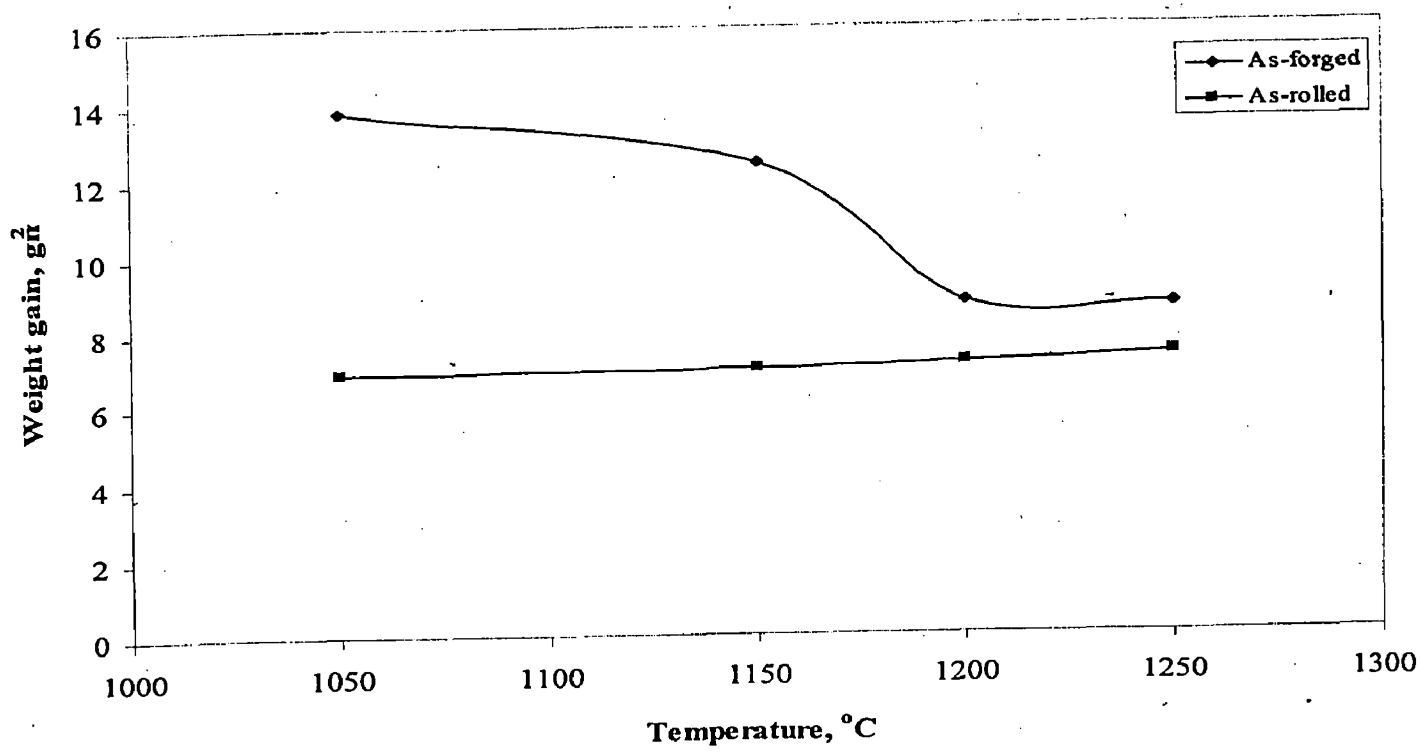

Figure 5.1: oxidation behaviour for 6 hours of as-forged, as-rolled samples.

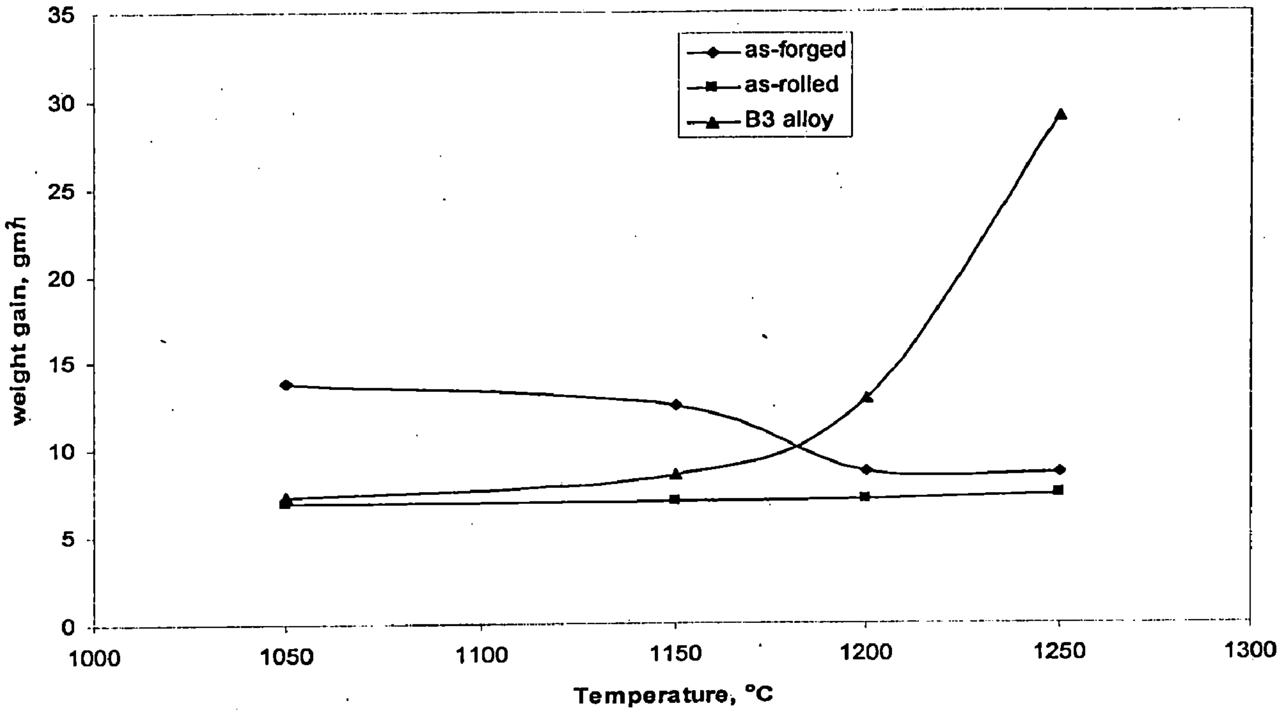

Figure 5.2: oxidation behaviour for 6 hours of as-forged, as-rolled and B3 alloy samples

The stabilized weight gain of as-forged, as-rolled samples can be comparable to that of B3 alloy (fig 5.2). The Ni- based ODS alloys of types as-forged and as-rolled showed strikingly improved oxidation resistance.

5.3 Cyclic Oxidation Behaviour:

The cyclic oxidation testing values are given in table 5.2. The weight gains are measured after 20 hours cycle. After 20 hours the samples attained the stabilized weight gain. The further oxidation rate was not possible. The specimens gets uniform oxide layer. The Yttrium oxide acts a major role for effective oxidation resistance.

Table 5.2: The weight gain of as-forged, as-rolled specimens after 20-hours cycle

Exposing time(hrs)	Weight gain (gms/m^2)	
	As-forged	As-rolled
20	2.178	3.750
40	2.178	3.750
60	2.178	3.750

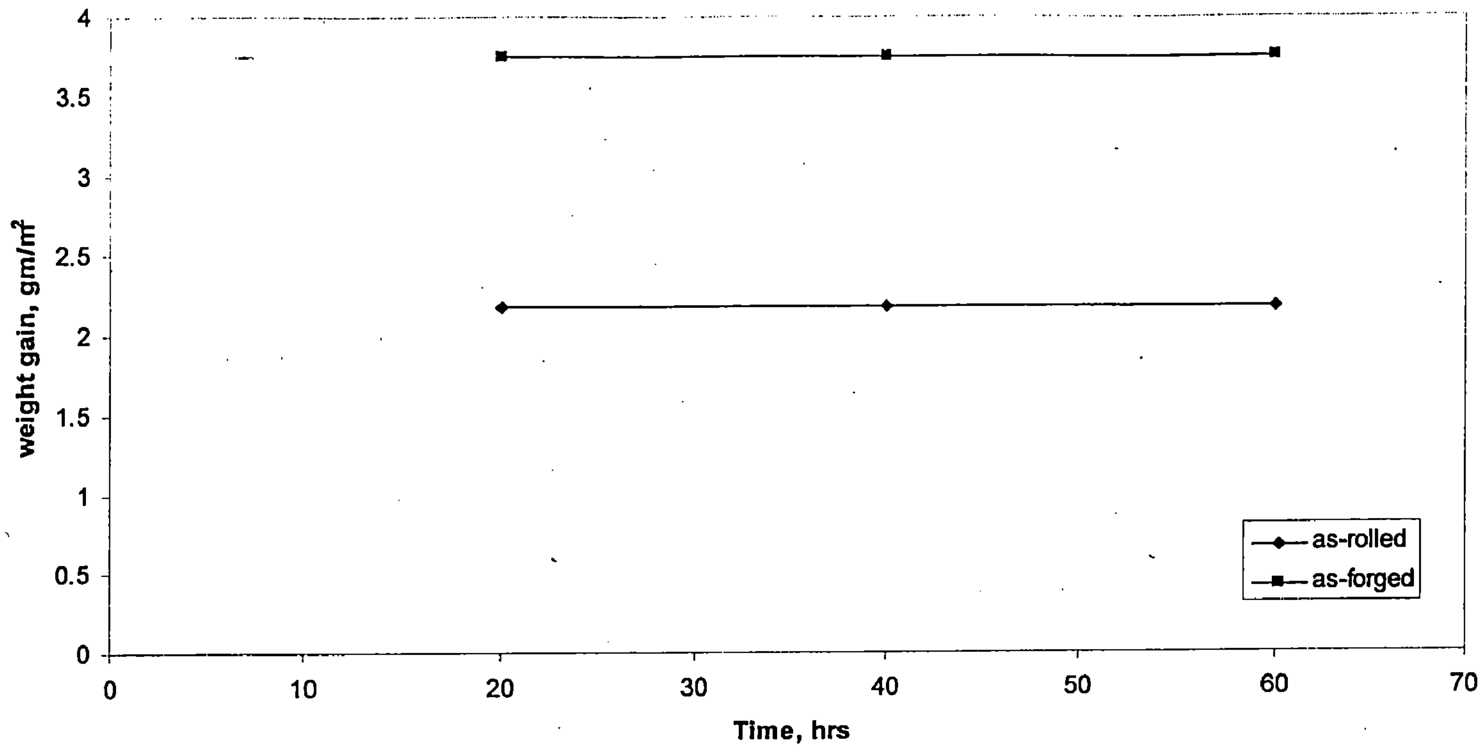

Figure 5.3: cyclic oxidation behavior for as-forged, and as-rolled specimens

5.4 metallographic observations

The three samples as-forged (oxidized), as-rolled (oxidized), as-rolled (un-oxidized) were observed under optical microscope. The microstructures are shown in fig. 5.4, 5.5 and 5.6. The black spots on the microstructure are the porosity. The structures contains lot amount of porosity. In the as-rolled samples the pores size is less compared with forged samples. In as-rolled, un-oxidised samples the porosity is of fine size.

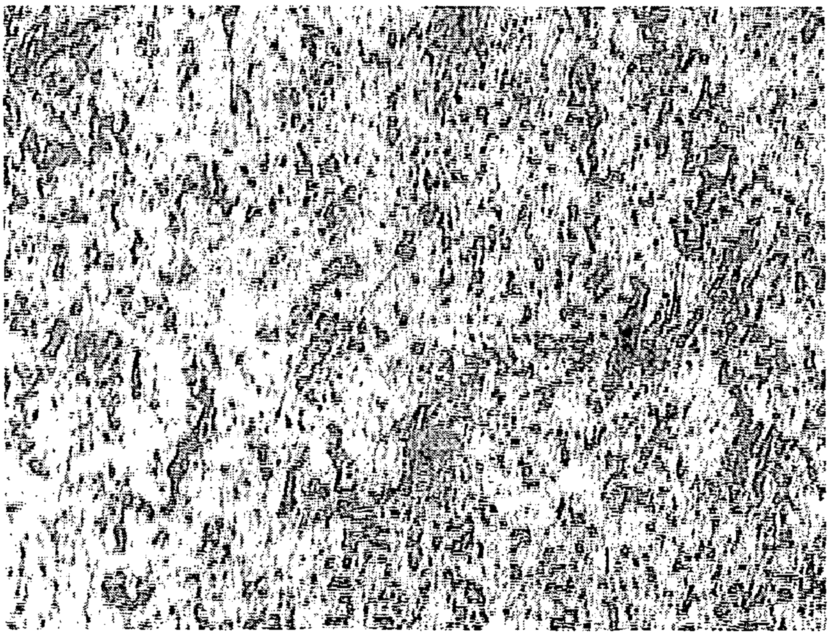

Figure 5.4: as-forged, oxidized specimen, 200X.

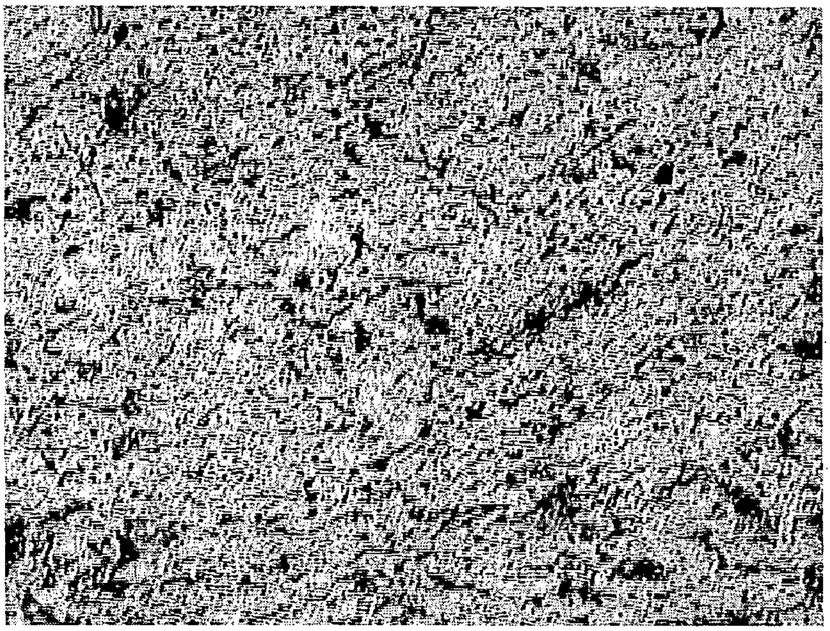

Figure 5.5: as-forged, as-rolled, oxidized specimen, 200X.

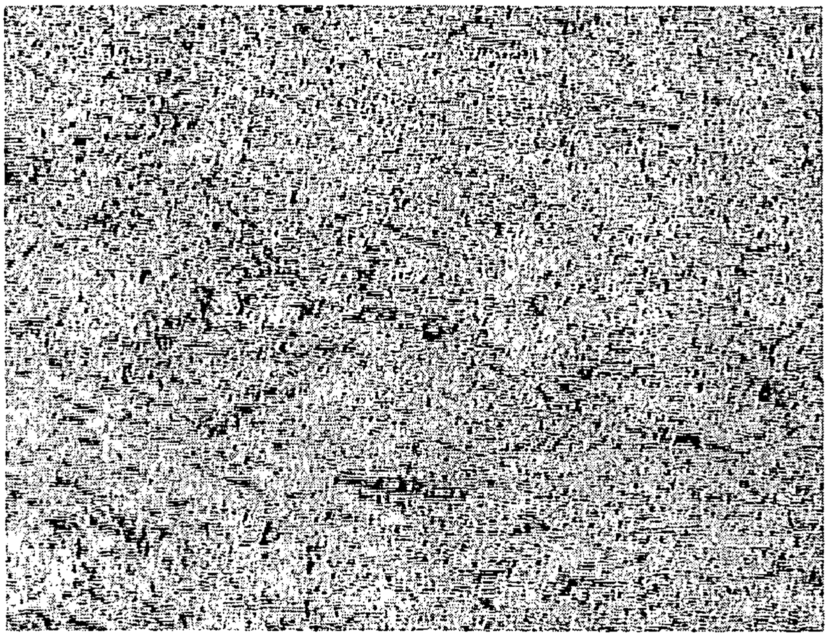

Figure 5.6: as-rolled, un-oxidized, 200X

5.5 Hardness results:

The Vickers hardness values of as-forged, oxidized; as-rolled, oxidized; as-rolled, un-oxidized samples are given in table 5.3. Compared with as-rolled samples, the as-forged specimens hardness values are less. This is due to the less density of the as-forged samples. The as-rolled, un-oxidized got more hardness than other two samples. Due to oxidation, the rolled sample has attained softness than un-oxidized specimen..

Table 5.3 The hardness values of as-forged, oxidized; as-rolled, oxidized; as-rolled, un-oxidized

Sample type	Vickers hardness number
As-forged, oxidized	153±8
As-rolled, oxidized	180±5
As-rolled, un-oxidized	213±10

Chapter 6

CONCLUSIONS

1. The Ni-based ODS superalloys has been developed successfully through powder forging route.
2. This alloy exhibits good rolling characteristics with 27% reduction in Hot Rolling.
3. The produced specimens has characterized with High Temperature Oxidation, Hardness and Microstructural study. The oxidation data so obtained has been comparable to the fully dense alloys.
4. Oxidation and Cyclic Oxidation Test results revealed that produced sample has been showing competent results as INCONEL MA754 by M/s INCO alloy company.
5. This alloy has possesses good response to oxidation resistance even though it is porous.
6. Variation in particle size and not fully cleaned atmosphere has not shown any effect on good oxidation resistance.
7. Oxidation Test results revealed that as rolled sample showing better oxidation resistance compared to as forged component.
8. The as-forged sample weight gain decrease when temperature increases.
9. The as-forged, as-rolled samples attain stabilized weight gain when they are exposed for time 20 hours.
10. The as-rolled, un-oxidised sample given high hardness values compared with as-forged, oxidized; as-rolled, oxidized.

FUTURE WORK

1. The properties like high temperature tensile strength, stress-rupture properties could be evaluated.
2. The intricate shapes could be produced and characterized.
3. The processing parameters can be varied like milling time, forging load.
4. Thermo-mechanical treatment parameters could be varied, hence the rolling characterstics can be improved.

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