

DEVELOPMENT AND CHARACTERIZATION OF Fe-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

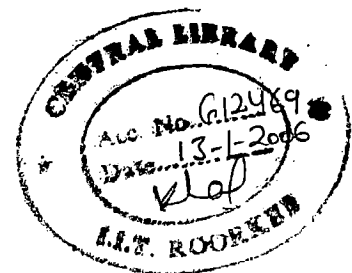
in

METALLURGICAL AND MATERIALS ENGINEERING

(With Specialization in Physical Metallurgy)

By

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JUNE, 2005

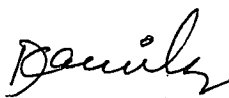
CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this dissertation entitled "Development and Characterisation of Fe-Based ODS Superalloy for High Temperature Application", in partial fulfillment of the award of the degree of Master of Technology in Metallurgy and Materials Engineering with specialization in "Physical Metallurgy", submitted in the department of **METALLURGICAL AND MATERIALS ENGINEERING, INDIAN INSTITUTE OF TECHNOLOGY, ROORKEE**, is an authentic record of my own work carried out during the period from July, 2004 to June 2005 under the most valuable guidance of **Dr. P. S. Mishra**, professor, MMED, IIT Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree of this institute or any other institute.

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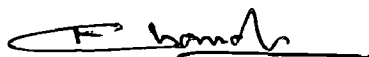
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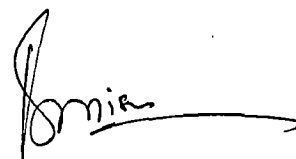


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ACKNOWLEDGEMENT

Gratitude is the memory of the heart and in carrying out this academic project, persistent inspiration, unflinching support and encouragement of countless persons has served as the driving force.

I am deeply indebted to my guide **Dr. P.S. Mishra**, Professor, Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee, without whom his this concept of working in the area of the “Development and Characterisation of Fe-Based ODS superalloy for High temperature applications”, would not have taken birth in my mind. I would like to sincerely acknowledge his valuable guidance, relentless support, discerning thoughts and lots of inspiration that led me forward to delve deeper in to the issue.

I am highly thankful to Dr. V. K. Tiwari, Professor, MMED, IIT Roorkee, for providing me all necessary facilities in the department to complete this work.

I am thankful to OC'S & laboratory staff of different laboratories of the department & particularly to S/Sri

- R. K. Sharma.
- Giri Ji.
- A.K. Ahuja.
- Ashish Kumar.
- M. Pandey.
- Samsher Singh.
- S. K. Seth.
- S. S. Gupta.

I am thankful to my friends Somanath Behera, Sunayan Thakur, Akhilesh Kumar, K. Harikrishnan, and others for their love, support and constant motivation.

Above all I would like to acknowledge that the greatest role has been of my parents and other family members for their encouragement and support which gave me courage and confidence to materialize my dreams.

Place: Roorkee.

Date: June 7, 2005


Daitari Kamila

ABSTRACT

Super alloys are metallic materials which exhibit high heat resistance even at temperatures of up to 90% of their absolute melting point. This is normally achieved by the combined hardening effect of carbides & rare earth oxides (mainly) in Iron (Fe) based super alloys. Oxide Dispersion Strengthened (ODS) alloys are manufactured by mechanical alloying (MA) techniques. This results in alloy powders of extremely fine grained structure, in which the dispersion fine particles are responsible for boosting the strength of materials in high temperature applications like jet turbine, aircraft turbine, furnace heating elements, etc. The alloying elements themselves are distributed very uniformly & homogeneously.

The main advantage of powder forging process is the use of cost effective indigenously available raw materials, like iron instead of extrusion process where high purity powders atomized with argon gas, which is used in many leading ODS manufactures, like M/s INCO ALLOYS, USA. The aim of the present work is to develop ferritic ODS alloys through powder forging route economically & to compare its oxidation at 1100⁰C & corrosion behavior in 40% Na₂SO₄+60% V₂O₅ at 900⁰C with MA 956, superfer 800H alloys. The alloy composition of the present work is

Cr -22 % (In the form of Ferrochrome)

Al -5.5%

Y₂O₃ -0.5 % (In the form of Yttrium oxalate)

Fe -72 % (Balance)

?? Is Y-stable
at higher
temp

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A super alloy is defined as an alloy whose composition is based on Nickel, Iron, Cobalt or Nickel plus Iron that has been developed for high temperature performance applications involving relatively high stresses & temperature generally above 700⁰C, where resistance against oxidation & environmental attack is required. The oxidation resistance & good creep performance of mechanically alloyed Fe-based Oxide Dispersion Strengthened (ODS) alloy makes them prime candidate for the heat exchangers, turbine applications, heating elements, aircraft gas turbines, etc. M/s INCO ALLOY Co, USA & leading manufacturer of ODS use powder extrusion route, where strain rate is slow & controllable. But for extrusion of powder high purity powder atomized with argon gas is required which makes these alloys costlier. In our present process for the development of alloys we adopted powder forging technique, where the indigenously available powder was compacted after reduction of powder by hydrogen gas which was made in our laboratory itself (using H₂-generating plant).here the high strain rate is controlled by applying post homogenizing treatment to the forged slab. So due to low cost of this process it is more likely to be adopted.

This process aims at developing materials (alloys) for high temperature application through powder forging technique & by taking commercially available metal/alloy powders without bothering about the oxygen contents. The properties of the alloy developed is well comparable with other super alloys like MA 956, Superfer 800H. The objective of the present work is to estimate the cyclic oxidation behavior at 1100⁰C, & corrosion behavior at 900⁰C in 40% Na₂SO₄+60% V₂O₅ atmosphere.

Since early 1940's, super alloys development has been paced by the increasing demands of advanced gas turbines technology. However in addition to aircraft, marine, industrial & vehicular gas turbines, super alloys are now used in space vehicles, rocket engines, experimental aircraft, nuclear reactors, sub-marines, steam power plants, petrochemical equipments, furnace heating elements & other high temperature application.

2.1 HISTORY OF SUPER ALLOYS:

Super alloys are those materials used at elevated temperature & at that elevated temperature they sustain their mechanical, chemical stability. Earlier austenitic stainless steel was the best material for high temperature application, but above 700°C temperature it loses its stability. Further development for high temperature stability leads to development of super alloys which are categorized as

- (1) Fe-based super alloys
- (2) Ni-based super alloys
- (3) Co-based super alloys
- (4) Ni-Fe-based super alloys

Table 2.1 Density of Fe, Co, Ni

Elements	Density (g/cc)
Fe	7.85
Co	8.85
Ni	8.90

The above table shows about the densities of various elements used as main constituents in super alloys. In case of rotating components low density is important to minimize centrifugal stresses. So the density of most super alloys lies within the range of 7.76 to 9.28 g/cc [1]. Hence as a class, Fe-based alloys enjoy the advantage of lowest density among them.

2.2 TYPES OF SUPERALLOYS:

2.2.1 Fe-BASED SUPER ALLOYS:

The utilization of Fe-based super alloys dates back to 1940's with the development of 16-25-6(Cr-Ni-Mo). Here solid solution strengthening plays the major role for stability. But now minimum of 20% Cr is used along with rare earth metals & their oxides for better oxidation & corrosion resistance at temperature above 1100°C. The table given below gives composition of some Fe-based super alloys [1].

Table 2.2 Compositions and applications of Fe- Based superalloys

Alloy Common name	Main alloying elements (wt %)							Application
	Cr	Ni	Mo	Ti	Al	Y ₂ O ₃	Fe	
INCOLLOY 956	20	----	----	0.5	4.5	0.5	Bal	Gas turbine engine, Combustion chamber
LAPELLOY 619	11-12	0.5 max	2.5-3	----	----	----	Bal	Turbine shaft, Compressor wheels, Bucket, Bolts, Blades
DISCALLOY	14	26	2.7	----	----	----	54	Turbine Disc

2.2.2 Ni-BASED SUPER ALLOYS:

These super alloys on the basis of chemical composition are fairly complex alloys. Various alloying elements are added for various purposes in these cases. Al & Ti are added for γ (Gamma prime) phase. These elements give solid solution strengthening as well as precipitation hardening by combining with NI, Ta etc. Also carbide forming elements like Cr, Mo, W, V, Nb, Ta, and Ti are added for the formation of various types of carbides, which imparts hardening. The main types of carbides are:

MC - Carbides

M₂₃C₆ - Carbides

Cr₇C₃ - Carbides

M₆C - Carbides

Examples of some Ni-based super alloys, their composition & application are bellow [1]

Table 2.3 composition and application of Ni-Based superalloys

Alloy designation	Main alloying elements (wt %)								Application
	C	Cr	Co	Mo	Fe	Ti	Al	Ni	
NIMONIC 942	0.03	12.5	1.0	6.0	26.7	3.7	.6	49.5	Gas turbine disc, Blades
INCONEL MA 754	----	20	----	----	0.6 Y ₂ O ₃	----	----	Bal	Gas turbine starter, Vanes, Shroud bands
INCONEL MA 6000	----	15.0	----	2	1.1 Y ₂ O ₃	2.5	4.4	Bal	Gas turbine, Rotor blades

2.2.3 Co-BASED SUPER ALLOYS:

Cobalt based super alloys have played a very important role in early stages of super alloy development. These alloys exhibit better oxidation, corrosion resistance in comparisons to Fe-based, & Ni-based super alloys but only at low stress level. This makes them attractive for non-rotating application.

Typical composition & application of some Co-based super alloys are given below [1]

Table 2.4 Composition and application of Co-Based superalloys

Alloy name/designation	Main alloying elements (wt %)							Application
	Ni	Fe	W	Ti+Zr+Cb+Ta+Al+Mo+Mn	Cr	C	Co	
UMCO-50	----	20	--	2	27-29	0.05-0.12	50	Heat treating facilities, glass making, furnace equipments, Load carrying parts
HAYENS ALLOY NO. 150	3 max	20	--	2.5	27.5	0.08	46.3	In the field of High temperature corrosion
S-816, AISI 617	20	5	--	1.5	20	0.3-0.45	42	Parts of combustion chamber & gas turbines

2.3 DEVELOPMENT OF SUPER ALLOYS:

Super alloys are utilized at a high fraction of their melting point than any other class of broadly commercial metallurgical materials. Super alloys are the materials which have made much of our very-high-temperature engineering technology possible. They are the material leading edge of Jet engines. Methods of Casting, Hot extrusion, were earlier used for development of super alloys, but the powder forging through mechanical alloying method now proved to be cheaper than the earlier.

This history is an attempt to tell their story. However it is not intended to be simply a logical recording of the events that have transpired to create them, but is intended to be a technical & scientifically useful analysis through chronological treatment, based upon consideration of the human factors & other external forces which have generated these unusual & now essential materials.

Though Nichrome (80Ni-20Cr) [5] is the most widely used super alloy in present their development was taken place in 1930's & the first set of heat resistant alloy was produced in 1940. However the first super alloy used in British whittle engine [5]. The first Ni-based super alloy Nimonic-75 was developed from Nichrome-v by the addition of 0.3% Ti & 0.1C. In Britain a number of Nimonic alloys [6] were developed in rapid succession. Increase in Ti content led to the development of Nicrome-80, where as Al addition to the Ni-based alloys resulted in the first 'γ'-hardened Nicromic-30A alloys. In an effort to raise the temperature stability further Co & Mo were added to produce Nicromic-90 & Nicromic-100 respectively. Inconel-X was the first Ni-based super alloy to be developed in the USA. This was modification of Inconel (15 Cr-7 Fe-78 Ni), through controlled addition of Al, Ti, Nb & C. Further modifications in this system led to the development of WASPALOY. [7].

Vacuum melting treatment for production of super alloys replaces the decreases the amount of impurities & to increase the first alloy produced was IN100 in 1965. But the prolonged use of these alloy show poor resistance to hot corrosion. For this purpose "Cr" content is increased above 18%. This develops [5] the alloys. IN-738 & IN-939. Additions of W, Ta cause the delaying of $Cr_{23}C_6$ formation & hence enhance the corrosions resistance by the formation of Cr_2O_3 .

2.4 DEVELOPMENT OF ODS SUPER ALLOY:

Oxide dispersion strengthened (ODS) alloys are produced from powders by mechanical alloying usually rare earth oxides are used for dispersion strengthening of these super alloys. The spherical Y_2O_3 nano-dispersoids, with a size of 10 to 40 nm, are homogeneously distributed within the alloy. These dispersoids in combination with a gives our ODS alloys excellent creep strength, oxidations & corrosion resistance up to temperature very near to the melting point. In addition the low content of yttrium oxide (0.5% Y_2O_3) improves the corrosion resistance of ODS alloys against hot process gases & hot air. Basically the oxidation & corrosion resistance is given by the high content of Cr (22%) & Al (5.5%). The creep resistance can be enhanced if an alloy has precipitates, which are insoluble in the matrix & so cannot coarsen at elevated temperature for this purpose Al, Ti, are added to Ni & Fe-based super alloys.

2.5 ADVANTAGES WHEN USING ODS SUPER ALLOYS [55]

- (i) Significantly higher creep strength than normal Ni, Fe base materials & HT-steels.
- (ii) High hot strength.
- (iii) Excellent oxidations & corrosion resistance.
- (iv) Resistance against sulfidation & carburization.
- (v) Longer lifetime of components.
- (vi) Distortion free use
- (vii) Lighter component (p/m route materials)
- (viii) Higher process temperature, hence higher efficiency, higher quantities
- (ix) Good mechinability.

2.6 MECHANISM OF STRENGTHENING IN ODS SUPER ALLOYS:[56]

For the oxide dispersion strengthened (ODS) alloys dislocation- particles interactions is generally believed to be repulsive since the elastic constants of the oxides dispersoids are believed to be greater than those of the matrix. High temperature strengthening is thought of in terms of a dislocation climb modified Orowan type bowing mechanism between the particles. Dislocation escape occurs when the stress is sufficient to cause the dislocation to bow to a critical configuration. Contrary to this general belief, through detailed TEM microscopy study of crept & hot tensile tested INCONEL MA 754, it's found that the interactions between dislocation & oxide dispersoids is in fact attractive, with the high temperature properties of ODS alloys stemming from this unexpected attractive interaction. It's proposed that the finding of attractive interaction opens new avenues for the alloy design of ODS alloys, including the pinning of dislocations next to the dispersoids by additional elements & the purposeful introduction of non-adherent interfaces between dispersoids & matrix.

2.7 MICRO STRUCTURAL ASPECTS OF Fe- BASED SUPER ALLOY:

The micro constituent observed by optical microscope in Fe-Ni & Ni-base superalloy is almost identical with few exceptions. All the alloys have an austenite (γ -phase) matrix that is strengthened by solid solution strengthened in & by carbide precipitation. Most of the phase discussed below have some degree of solubility for other elements. Therefore, their true composition will vary from alloy to alloy and may be altered by heat treatment & thermal

exposure. Not all phases permit substitution; however, Eta phase (Ni_3Ti) has no significant solubility for other elements.

(i) Gamma Prime (γ'):

This phase has an ordered FCC $L1_2$ crystal structure and is $\text{Ni}_3(\text{Al Ti})$, although considerable elementary substitution occurs. For example Co & Cr will replace some of Ni & Ti will replace a part of Al. Fe can replace Ni or Al. The lattice parameter of γ and γ' are similar resulting in coherency, which accounts for the value of γ' as the principal strengthening agent in Iron- Nickel & Ni-based superalloys. Gamma prime γ' is spherical in Fe-Ni base & in some of Ni-base alloys such as Nicrome-80A and Waspaloy. Experiments have shown that variations in molybdenum content & in Al/Ti ration can change the morphology of γ [γ']. When the γ/γ' lattice mismatch is high extended exposure above 700°C causes undesirable Eta-phase (Ni_3Ti) or Delta-phase (Ni_3Nb) phase to form. The volume fraction size & distribution for control of properties, the volume fraction of γ' increases with the addition of Al and Ti. Gamma prime content above approximately 45% render the alloy difficult to deform by hot or cold working. In the Fe- Ni base alloy γ' phase is less than 0.2% and it is usually spherical. Optimum strength results when γ' is in the size range of 0.01 to 0.05 μm . Aging precipitates γ' uniformly throughout the matrix and precipitates M_{23}C_6 carbides at grain and twin boundaries. Alloys with γ' content of approximately 30% are solution treated then given two aging treatments. Alloys with 40 to 45% γ' are solution treated, then given three aging treatments. [6]

(ii) Gamma double prime (γ''):

Gamma double prime has an ordered ...crystal-structure with a Ni_3Nb composition & is found in Fe- Ni base alloys containing Niobium. It gained prominence as the strengthening phase with the introduction of Inconel 718. Gamma double prime has a disc-shaped morphology and precipitates with a well defined relationship to the austenitic matrix. Although γ'' and γ' are present in INCONEL 718 after aging, the amount of γ' is much less and γ'' is the primary strengthening agent. Because γ'' is not a stable phase. Application of alloy such as INCONEL 718 is restricted to below 700°C . Above this temperature, extended exposure produces a loss of strength due to rapid coarsening of γ'' . Electron diffraction study reveals the presence of γ'' as lines.

(iii) Eta phase (η):

Eta phase has a hexagonal crystal structure with Ni_3Ti composition. This phase is present in Fe- Ni, Ni or Co based alloys especially in grade with high Ti/ Al ratio that had extended high temperature exposure. Eta-phase precipitates slowly but grows rapidly and has no solubility for other elements. Coarse Eta can be observed under optical microscope.

(iv) Borides:

Boron is added in small amount to may super alloy to improve stress rapture and creep properties or to retard the formation of Eta-phase; which impairs creep strength. Boron reduces the solubility of carbon in austenite, M_{23}C_6 & M_6C carbides. If boron addition is higher than detrimental borides will precipitate at grain boundaries.

(v) Laves phase:

Laves phase, a TCP phase, has an MgZn_2 hexagonal crystal structure with a composition of AB_2 type. Typical example includes Fe_2Ti , Fe_2Nb & FeMo . They are most commonly observed in the Fe- Ni based alloys as coarsen inter granular particles. Si & Nb promotes formation of Laves phase in INCONEL 718. Excessive amounts will impair room temperature tensile ductility but creep properties are not significantly affects.

(vi) Sigma Phase (σ):

Sigma phase is tetragonal intermetallic TCP phase that forms with a wide range of compositions. Various morphologies may be encountered, some of which are quite detrimental to properties. Sigma in the form of .on as a grain boundary film is detrimental, but globular intra-granular precipitation can improve creep properties. Sigma phase can be preferentially attacked on stained by a no of reagents. However, because of the wide range of alloy composition that may contain sigma-phase & the variable nature of composition, positive identification by etching is not always possible. So X- ray diffraction study is am ore reliable technique for its identification.

(vii) Mu Phase (μ):

Mu phase is a rhombohedral (trigonal) TCP phase with W_6Fe_7 structure. In general it has little influence on properties. Mu precipitates as coarsen, irregularly shaped platelets in a widmanstatten pattern. A general formula for Mu is $(\text{Fe}, \text{Co})_7(\text{Mo}, \text{W})_6$. Nickel can substituted for part of the iron or cobalt

(viii) Nitrides:

Nitrides are commonly observed in superalloys containing Nb on Ti as Niobium nitride or Titanium nitride. Nitrides are not influenced by heat treatment & are insoluble to the melting point. Nitrides are quite hard & will appear in relief after polishing. The usual amounts present in superalloys generally have little influence on properties.

(ix) Carbides:

These are important constituent & are present in all the heat treatment superalloys. Four basic types of carbides encountered are

- (a) MC e.g. Titanium Carbides
- (b) $M_{23}C_6$ e.g. Cr, Ni, Co, Fe, Mo, W—Carbides
- (c) M_6C e.g. Mo, W-Carbides

Carbides in super alloys serve three principal functions:

- (1) Carbides formed along grain boundaries strengthen the grain boundaries prevent grain boundary sliding & permits stress relaxation.
- (2) Carbides precipitation in the matrix
- (3) Carbides can tie up contain elements that would otherwise promote phase instability during services.

Aging for Fe-Ni, on Ni-base superalloys cause $M_{23}C_6$ to form at the grain boundaries. This increases creep rapture life. But continues carbides film along grain boundaries has a negative effect on creep properties. M_6C carbides are observed in as cast Ni-Base alloys & are randomly distributed through the matrix. M_7C_3 carbides are not widely observed in superalloys, but it appears in some of Co-base superalloys in Nicrome-80A when heated above $1800^{\circ}C$. Additives of Co, Mo, and Nb to Ni- base alloys prevent the formation of M_7C_3 .

(x) Other phase:

A few other phases are frequently observed in wrought heat resistant alloys. For example a few Co-based alloys have Co_3Al , Co_3Mo , Co_3Ti inter-metallic compounds, along grain boundaries. These have detrimental effect on stress rapture life. However in the Ni-based alloys Titanium sulfides may be observed. Oxides such as Al_2O_3 on magnesia may also be present. These oxides & sulfides are observed at the surface of components due to environmental effects.

2.8 POWER METALLURGY BASED SUPER ALLOYS:

In 1960's ODS alloys are invented where the oxides are insoluble to the matrix & shows latter properties. In 1970's MA 574, MA 956 & MA 6000 were developed. Tables given below gives about these alloys

Stages of development of ODS superalloys

Year of Invention	Alloy	Processing Route
1910	Ductile tungsten	Conventional P/M(press + sinter + wire drawing)
1930	Cu, Ag, & Be- Alloy	Internal oxidation
1958	TD- Nickel	Fine P/M , Mechanical alloying
1970	IN853	Mechanical alloying

Table No: 2.5 Compositions of MA-ODS Alloys:--

Alloy	Fe	Ni	Cr	Al	Ti	C	Y ₂ O ₃
MA956	Bal.	---	22	5.5	0.5	<0.1	0.5
MA957	Bal.	---	14	0.03	1.0	0.03	0.025
MA754	1.0	78	20	0.3	0.5	0.05	0.6
MA6000	----	69	15	4.5	2.5	0.05	1.1
PM2000	Bal.	----	20	5.5	0.5	----	0.5

MA 956:

INCOLOY MA 956 is mechanically alloyed FE-Cr-Al alloy strengthened by refractory oxides Y₂O₃. It's an ODS ferrite (BCC) alloy produced by MA. The dispersed oxides Y₂O₃ remain stable at temperature up to melting point of the material. The alloy combinations strength at high temperature with excellent resistance to oxidation, carburization & corrosion, High temperature strength of this alloy is enhanced by controlled thermal processing.

MA957:

MA 957 is oxide dispersion strength (ODS) ferrite steel [11], produced by mechanical alloying. MA 957 received international consideration for fuel cladding applications in liquid metal fast breeder reaction [12]. The alloy shows excellent long term microstructure stability in irradiation environment [13]. The microstructure consists of a metal matrix of the order of 5mm...in diameter [13]. It also contains a highly elongated sub grain structure which is introduced by thermal mechanical processing.

R.A.F.M ODS steel:

Raising the operating temperature of fusion reactor is one of the keys to reduce activation. Ferrite, martensitic (RAFM) steel allows operations at temperatures less than about 550°C. The use of RAFM ODS steel offers the potential of temperatures up to 650°C and 750°C. No ODS steels with reduced activation are commercially available. In the frame of the European fusion programme, material studies have been undertaken to demonstrate the benefits of RAFM ODS steels for blanket design. During the development of RAFM ODS steel, often ODS powders, produced by MA are consolidated by HIP at 1020°C under 1000 bar during 2 hours and then furnace cooled.

Inconel MA 574:

INCONEL alloys MA 754 is basically Ni-20% Cr strengthened by about 1 Volume percent of Ytria. Y_2O_3 as dispersoids imparts resistance to the alloy [11]. Optimum high temperature strength is developed in MA 754 by controlled stable recrystallized grain structure that is coarse and highly elongated in the direction of hot working with grain aspect as high as 10:1.

INCONEL MA 6000:

It's a Ni-base super alloy produced by mechanical alloying & is strengthened & precipitation hardened for creep & rupture properties at 1095°C as well as 760°C. It was developed as a blade material for gas turbines. MA 6000 is thermo-mechanically processed & given high temperature annealing to develop a coarse, highly elongated grain structure. Its coarse grain structure gives better creep properties.

2.9 MA ODS ALLOYS & SUPERFER 800H[58] ALLOY & THEIR APPLICATIONS:

Mechanical alloying, a new technique was developed by Benjamin[14,15] in around 1966 to develop an alloy combining oxide dispersion strengthening (ODS) with ' γ ' precipitations on ferritic matrix in case of Fe-based or Fe-Ni based superalloys intended for gas turbine applications.

The fundamental process in mechanical alloying to produce metal process with controlled microstructure, uniform & homogeneous distribution of powders is the repeated welding, fracturing & rewelding of powder mixture in a dry, high energy ball charge [16,19] in a high energy attritor mill. In an attritor the central shaft carries paddles which when collision between the steel balls of the charge & allow mechanical alloy to take place. [Diagram of attritor mill Fig. 2.1, 2.2, 2.3]. Mill atmosphere temperature must be carefully controlled in sequence which is often unique to a particular alloy. Milling time is also very important parameter for better charge preparation & it's usually lies in between 2-3 hrs.

The very homogeneous distribution of alloying elements during MA gives both the solid solution strengthened & precipitation hardened alloys, more stability at elevated temperature & overall improvement in properties.

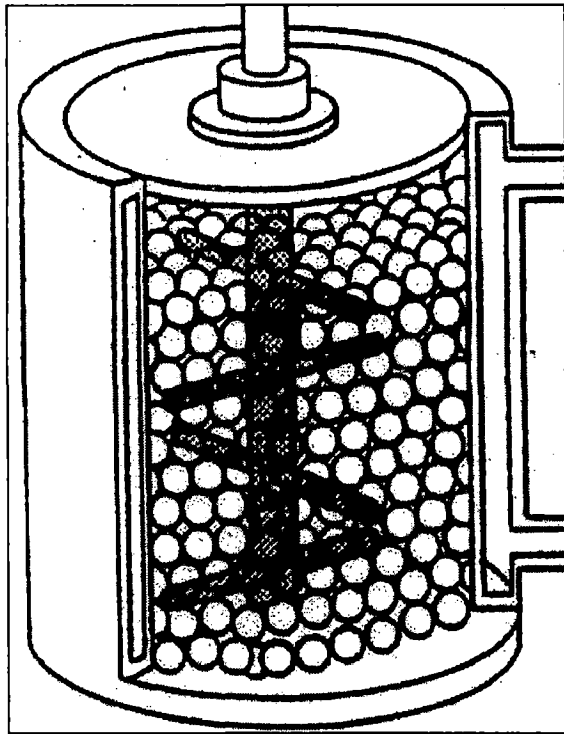


Fig 2.1 Schematic Diagram of High Energy Attritor Mill.

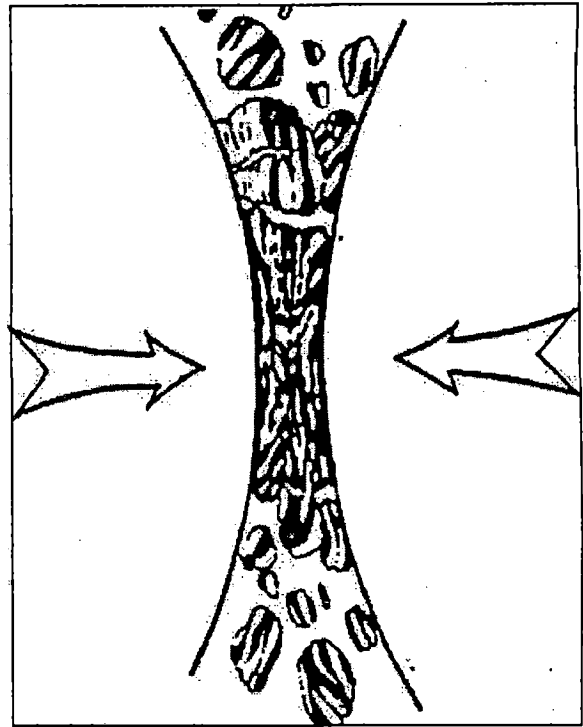


Fig 2.2 Schematic Diagram showing Powder fracturing, rewelding in attritor.



Fig 2.3 Photograph of Attritor used in Laboratory.

Table 2.5 Typical composition & applications MA-ODS alloys & Superfer 800H

Alloy	Composition (wt %)									Typical applications
	Fe	Ni	Cr	Al	Ti	Mo	W	Ta	Y ₂ O ₃	
MA956	Bal.	----	20	4.5	.05	---	---	---	0.5	Steam boilers, furnace Vacuum furnace muffles, baskets & in glass - processing Industry.
MA957	Bal.	----	14	----	1.0	0.3	---	---	0.25	Fuel cladding for fast neutron, fast breeder reactor, heat exchanger tubes.
MA745	----	Bal.	202	0.3	0.5	----	---	---	0.6	Vanes & bands for aircraft gas turbines engine.
MA6000	----	Bal.	15	4.5	0.5	2.0	4.0	2.0	1.1	Gas turbines blows and vanes.
Superfer 800H (Incoloy 800H)	Bal.	32	21.0	0.3	0.3	---	---	---	---	Furnace equipment, heat exchanger piping in chemical industry, baffles, tubes plates in fertilizer plant.

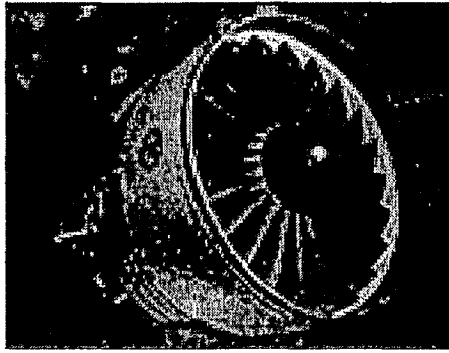


Fig 2.4 Superalloys in Turbine

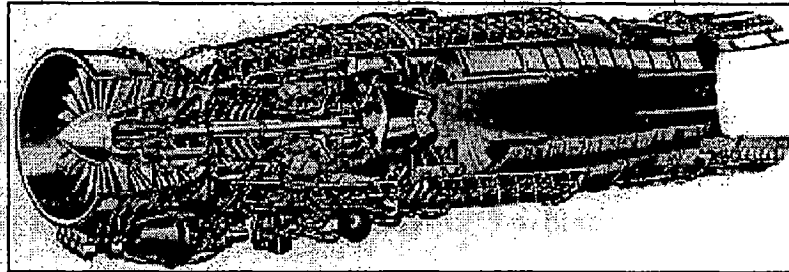
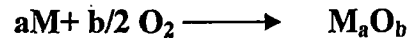


Fig 2.5 Superalloys in Jet Engine

2.10 HIGH TEMPERATURE OXIDATION OF METALS & SUPERALLOYS:

Metals and alloys get oxidized when they are heated to elevated temperature in air on highly oxidized environments, such as a combustion gas with excess of air on oxygen. Considering the chemical equation for the reaction between a metal and oxygen gas to form the metal oxide.



The initial step in the metal oxygen reaction involves the absorption of gas on the metal surface. As the reaction proceeds, oxygen may dissolve in the metal, resulting in the formation of oxide on the surface either as a film or as separate oxide nuclei. Both the absorption & the initial oxide formation are functions of surface orientation, crystal defects at the surface, surface preparation & impurities in both the metal & the gas thermodynamically, an oxide is likely to form on a metal surface when the oxygen potential in the environment is greater than the oxygen partial pressure in the equilibrium with the oxide. [52] The surface oxide then separates the metal & the gas. When a compact film covers the surface, the reaction may proceed only through a solid state diffusion of the reactants through the film. For thin film the driving force for this transport of reactants may be due to the electric field in or porous oxide scales which as such do not serve as a solid-state diffusion barrier between the reactants. In such case the reaction may be limited by process occurring at phase boundaries. Further, at high temperature, the oxide may also be liquid or volatile [52]

It has been described that [53] the phenomenon for Ni-20 Cr alloy oxidation here approximately 80% of the surface gets covered with NiO phase & 20% by the Cr₂O₃ phase during initial stage of oxidation (neglecting the formation of NiCr₂O₄). The rate of oxidation is controlled by transport for much slower process that across the initially formed NiO rich layer. Because Cr₂O₃ is much more stable oxide than NiO.

There are various empirical rate laws observed during oxidation upon the service condition

Linear Law:

The amount of oxidation increases linearly mathematically

$$\Delta W = kt, \quad \text{Where } \Delta W = \text{increase in weight of the specimen}$$

$$t = \text{time of exposure to environment}$$

$$k = \text{constant}$$

The oxides that grow according to this law are non-protective due to the formation of porous or cracked scale.

Parabolic law:

Here the rate of oxidation of is directly proportional to the square root of time

Mathematically

$$(\Delta W)^2 = k t$$

This law is valid for the oxidation for protective oxide. Al, Cu, Fe oxidation follow the law of oxidation.

Cubic law:

Here the rate of oxidation is directly proportional to the cube root of time

$$\text{i.e. } (\Delta W)^3 = k t$$

Usually such behaviour is restricted to short exposure periods. For oxidation of Zr an apparent cubic law is followed. It results from a combination of diffusion-limited scale formation & oxygen dissolution into the metal.

Linear oxidation rate is least desirable, because weight gain increases at constant rate with time. Parabolic & logarithmic oxidation rates are preferred in materials oxidations e.g. Al oxidizes in air at ambient temperature according to the logarithmic rate law as a consequence the film growth essentially stops after some days to exposures. [3]

2.11 OXIDATION OF SUPER ALLOY:

The super alloys have been developed to achieve oxidation resistance by utilizing the concept of selective oxidation. The selective oxidation approached to obtain oxidation resistance in super alloys consists of oxidizing essentially only one element oxide for protection. For effective protections it's anticipated that the oxide should over the whole surface of the alloy & it must be a n oxide through which the diffusion of the reactants takes place at comparatively slow rate. Usually in Ni, Fe- Ni base super alloy, Al & Cr are chosen for selective oxidation for this purpose. The selective oxidation [54] process is affected by

- (i) Alloy composition
- (ii) Surface condition
- (iii) Environment
- (iv) Cracking of oxide scale

During isothermal oxidation of Ni-base super alloy Cr_2O_3 & Al_2O_3 scales are expected to be formed, where as under cyclic condition depletion of Cr, Al results eventually in formation of

NiO scale. The time over which Ni- base super alloy can maintain protective, external scales of Al_2O_3 & Cr_2O_3 is affected by temperature, gas environment & alloy composition. Generally the super alloys remain Al_2O_3 or Cr_2O_3 formers for longer times as the Al or Cr concentration are increases other elements such as Yttrium Or Cerium can extend this time as these elements improves the oxide scale adherence. Further the alloys which are in alumina formers generally have better oxidation resistance than the chromium formers, since diffusions through the alumina scales is generally slower than through chromia.

So far as the Co & Fe based super alloy are concerned, they usually cannot be made to obtain enough Al to permit them to be Al_2O_3 formers as it will have detrimental effects on their mechanical properties. That is why these super alloys have to rely on the Cr_2O_3 scale for oxidation resistance. Further more, even when considering the Ni- based super alloys that are Cr_2O_3 formers, as degradation begins, i.e. Cr_2O_3 scales are damaged the less protective oxides formers on the Ni-based alloys contain significant amount of NiO as compared to Co & Fe oxides on Co & Fe-based super alloys respectively. Since Ni- oxides are more protective than Fe & Co-oxides the oxidation resistance drop-off is more abrupt in the case of Fe & Co-based super alloys. Further the oxidation resistance of Co & Fe- based super alloy usually increase with the Cr concentrations & the oxidation resistance of the alloys with the oxidation resistance of the alloys with less than about 20% Cr is comparatively poor. [54]

2.12 HOT CORROSION OF SUPERALLOYS IN 40% Na_2SO_4 & 60 % V_2O_5 ATMOSPHERE:

Metals and alloys sometimes experiences accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas (air) at elevated temperature [55]. This's known as hot corrosion where a porous non-protective oxide scale is formed at the surfaces & sulphides in the substrate [44]. If concentration of sulphate exceeds the saturation vapour pressure at the operating metal temperature for turbine blades, vanes & energy generation components at 700-1000 °C [45], then Na_2SO_4 will deposit on the surface of these components. At higher temperature these deposits of Na_2SO_4 are molten (MP 884 °C) [46] & [47] can cause accelerated attack of Ni- & Co-based super alloys. Further the accelerated corrosion can also be caused by other salts, such as vanadates on sulphate-Vanadates mixtures [48] and in the presence of solid on gaseous salts such as chlorides. The sources of the salts may be

- (i) The direct contact of sea salt in a marine environment
- (ii) Due to fuel combustion (Na_2SO_4).

Hot corrosion degradation process of the superalloys usually consists of two stages, namely an initiation stage & propagation stage [54]. It's a fact that all corrosion resistant alloys degrade via these two stages & it's the result of using selective oxidation to develop oxidation on corrosion resistance. Petit & Meier further elaborated that the condition causing hot corrosion therefore so nothing more than shortening the time for which superalloys can form protective Al_2O_3 on Cr_2O_3 scales via selective oxidation.

Harris et al. [48] in their study on the scaling resistance in moving air of some typical gas turbine alloys with & without creating of Vanadium pentoxides through their useful temperature range upto 1100°C in 70 hrs cycles found that in all cases Vanadium pentoxide coating have a deleterious effect. It's more pronounced for Fe-based alloys at temperature above 750°C . Sachs [49] studies accelerated high temperature corrosion of steels & stainless steels in V_2O_5 environment. They reported that oxidation of pure Cr in V_2O_5 occurs with a very rapid diffusion rate & so only the initial stages of the curve were supposed to be more important. Later slowing down of the oxidation rate was attributed mainly to the effect of scale thickening loose & spongy appearance of the scale was observed by them at the beginning of the process. V_2O_5 was present in excess & did dissolve the products of oxidation. According to them at the same point the liquid was saturated with the oxide which subsequently could get precipitated. The presence of various Phases in a thin layer of scale would impose such severe strain on the film that cracking & exfoliation could be expected. This would permit liquid phase to reach form a spongy scale were seen to prevail. This mechanism would apply only to prevail. This mechanism would apply only to Fe- base alloys which are susceptible to catastrophic corrosion

Fairman [50] has studied some metal specimen in an ash mixture ($\text{V}_2\text{O}_5 + 10\% \text{Na}_2\text{SO}_4$) environment in air. The results showed that the corrosion was most severe at the ash/air or ash/ atmosphere interface. He has observed that the attack was greatest where the concentration of oxygen & V_2O_5 are greatest suggesting the transfer of oxygen atoms or ions by the V_2O_5 to the metal surface. According to him accelerated oxidation is a diffusion controlled process. Accelerated attack by the sluggish action of low melting point oxides constantly exposed fresh metal to the atmosphere. However, if this mechanism is valid, V_2O_5 can only have any affect

when the ash is molten. The mechanism of accelerated attack thus has been most satisfactorily explained by the catalytic action of V_2O_5 operating with an increase in the defect concentration of the scale.

Thilkan [51] studied hot corrosion of Ni free austenite stainless steel Cr-Ni stainless steel & INCONEL in oxygen atmosphere at different temperature with Vanadium-Sodium slag of varying compositions. They justified the use of saturated solution of Na_2SO_4 as the liquid medium because of its low gas solubility, vapour pressure & viscosity. Threshold temperature was found to lie between $700^\circ C$ to $800^\circ C$. Above this temperature the extent of attack initially increased but with increases in temperature either it becomes constant [as observed for Inconel]. Increase in the amount of Na_2SO_4 increase the rate of oxidation first & then decreases at $850^\circ C$ - $870^\circ C$ temperature. At $950^\circ C$ temperature all Na_2SO_4 additions decreased the corrosive effects of V_2O_5 . They observed that fluidity of slag was important in allowing diffusion of oxygen.

CHAPTER-3 DEVELOPMENT OF THE POWDER FORGING PROCESS AND FURMULATION OF PROBLEMS

ODS alloys are ordinarily strain rate sensitive alloys & therefore high speed deformation associated with process like powder forging was not suitable for their manufacturing. Moreover M/S INCO alloys Co. , USA & similar other companies leading ODA manufacturers, preferred costly extrusion process where strain rate is slow & controllable but for manufacturing ODS alloy through this extrusion technique high quality pure powder atomized using argon was required with very low oxygen constant ($< 100\text{ppm}$) , which made these cloys costly.

In our work development & characterization of ODS alloys we produced alloy by using powder forging technique to minimize the cost of powder was reduced by hydrogen which was made in our lab. It self by using H_2 - generating plant.

Before forging into slab. So we need not bother about impurity(oxygen) level in the powder & used indigenously available raw materials & the characterization of our alloys showed a well comparative & some how a better high temperature oxidation & corrosion behaviour.

Failure reports:

In our present work failure occurred in carious stages for the sample preparation. These failures were due to some inconvenience in our working procedure. We made around 10 forgings out of which 3 were in a condition for further experimental work. The alloy composition was

Cr (in the form of ferrochrome) - 22%

Al - 5.5%

Y_2O_3 (in the form of oxalate) - 0.5%

Fe - 72%

Various failures occurs in forging were discussion below

Forging No. 1 & 2:

Failure in these samples occurs due to closing of hydrogen flow valve before forging. As a result of the reduces powder again got oxidized hence the samples have no proper compaction, which was seen after removal of the skin from the sample. It shows dark colour instead of shining metallic colour.

Forging No. 3 & 4:

In this case also due to the switching off the hydrogen valve before forging back pressure was created which results in the explosion at the samples.

Forging No. 5 & 6:

Failure in these samples occurred in hot pressing of samples after homogenization treatment. Due to sudden heat loss while pressing if caused cracking of the samples, hence very small pieces were found.

Forging No. 7 & 8:

Here the failure was due to the exposure of samples to high temperature of samples to high temperature which results in the melting in some points & others are remained in inhomogeneous in compositions.

Forging No. 9 & 10:

Failure occurs here due the forging strokes after the samples lost its high temperature, resulting in the cracking on small pieces of the finally samples.

So to avoid the failure & to get good sample pieces the following precautions should be taken

- (i) Attrition time should not be too large otherwise very fine particles will form which will create problem in permeability good flow of hydrogen.
- (ii) Hydrogen gas flow should not be stopped before forging after one stroke it will automatically switch off on switch off after first stroke.
- (iii) Forging stroke should be applied only in red hot condition, otherwise sample will crack.
- (iv) Homogenization temperature should be $\leq 1300^{\circ}\text{C}$, otherwise melting will take place, causing the compositional inhomogeneity.
- (v) Hot pressing should be done only in red hot corrosion, otherwise sample will crack.

Selection of the work:

Commercially Fe-based ODS super alloys e.g. MA 956 have a composition that is selected for better creep properties, high temperature oxidation & corrosion resistance these alloys have homogeneously distributed rare earth oxides i.e. Y_2O_3 (10-40nm particles size). Ferrite ODS alloys take their corrosion resistance at elevated temperature from at least 20% Cr & 5 % Al. The present work consists of the following steps:

- (i) Powder preparation, H_2 gas filling in cylinder
- (ii) Powder mixing
- (iii) Capsulating the powder
- (iv) Reducing of powder by using Hydrogen at 1100 °C temperature.
- (v) Hot forging of the capsule of 1100 °C immediately after the reduction of powder mixture.
- (vi) Homogenization of the forged slab at 1300 °C for 5 hrs
- (vii) Hot pressing at 1100 °C
- (viii) Removal of skin from the homogenized forged capsule by using shaper to produce the final design product.

Based on the above points, aiming to develop ferrite ODS alloy economically with the properties in comparison to MA956 alloy through powder forging technique & by taking commercially available metal/ alloy powders not bothering about oxygen level,

Development & characterization of Fe-based ODS super alloy for high temperature applications has been selected as a dissertation work

In the present technique powder forging has been employed but strain rate sensitivity of these alloys has been carefully avoided, so that in the high quality alloy powder we stated with elemental powders not bothering about oxygen levels. Various parameters for our works were:

- (i) Composition of mixture.
- (ii) Time & temperature of reduction.
- (iii) Forging force
- (iv) Homogenizing temperature

By altering these parameters the properties can be varied.

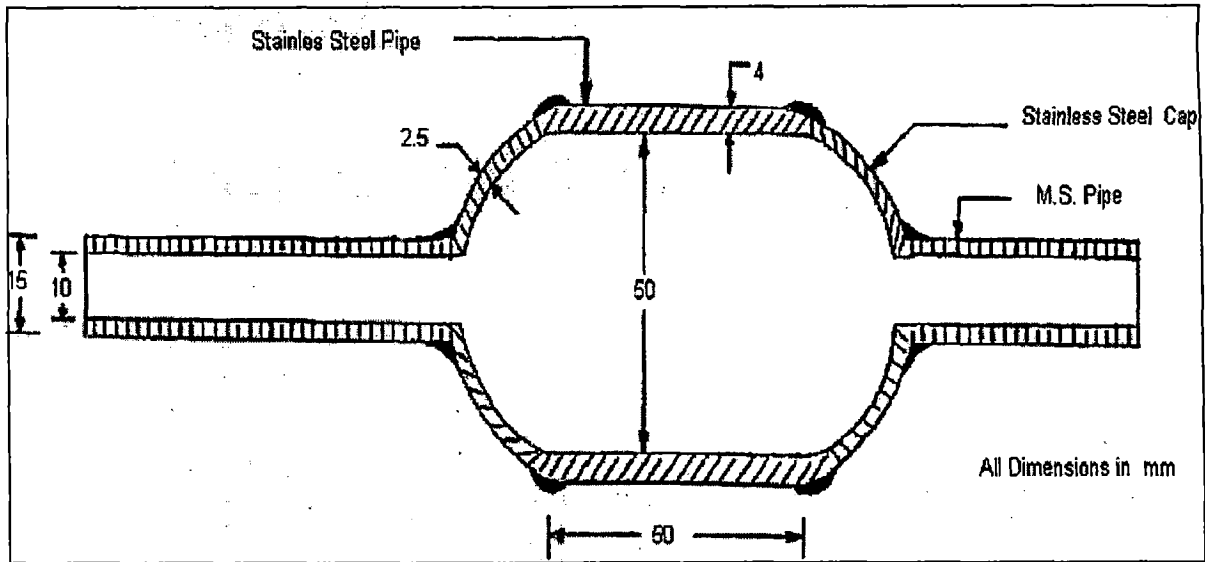


Fig 4.1 Capsule For Hot Powder Forging.

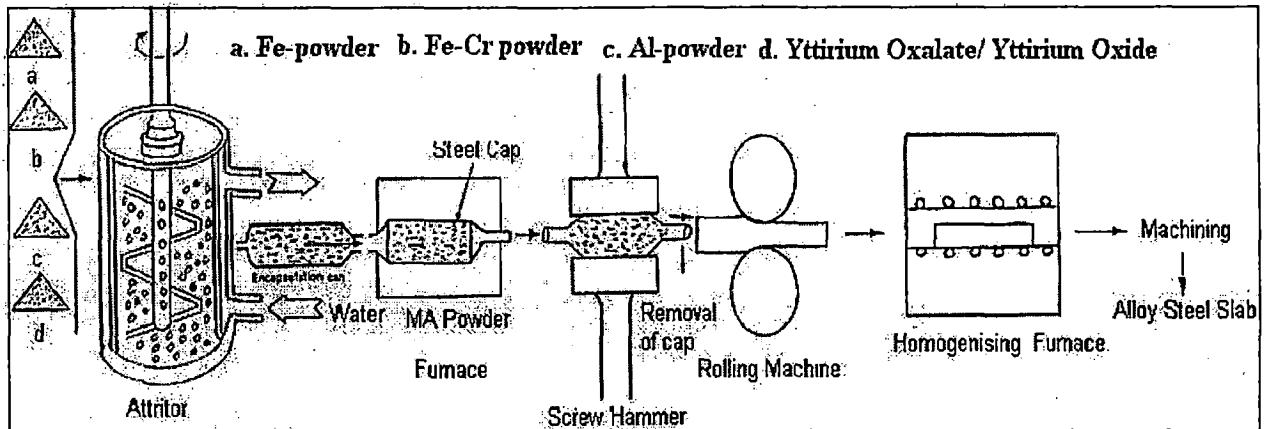


Fig 4.2 Schematic Diagram of Powder Forging.



The alloy to be made has the following composition.

Table 5.1: composition of the alloy developed by us.

Cr (wt in %)	Al (wt in %)	Y ₂ O ₃ (wt in %)	Fe (wt in %)
22	5.5	0.5	72

The purity of elements is as follows

- 'Cr' is the form of Ferrochrome 70% has < 0.1% carbon
- 'Al' powder has 99.7% purity
- Y₂O₃ is 99.9% pure
- Fe is 99.4% pure
- H₂ used for reduction is 99.99% pure.

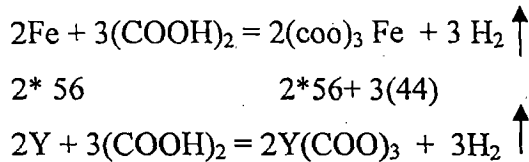
Powder conditioning:-

Usually all the elements used for mechanical alloying are less than 100 mesh size. For homogeneous distribution of Y₂O₃ in the powder mixture, it's added in the form of Yttrium-Oxalate which has particle size in the range of 4-10 nm.

Nearly pure hydrogen is produced by electrolysis of distilled water in hydrogen plant.

Yttrium oxalate preparation:

Same quantity of Fe-powder & "Yttrium" were taken. Then these two powders dissolved separately in dilute 50% Nitric Acid & after complete dissolution these two solutions were mixed in a large beaker. This solution had P^H value of 2.5, but since the precipitation of oxalate required a slightly higher P^H, the above solution was made ammoniacal by using 25% NH₃. Finally addition of oxalic acid crystal or concentrated Oxalic acid solution was done to cause the precipitation of Yttrium-oxalate & Fe- Oxalate. The solution after precipitation of oxalate was again added with 25% NH₃ & then oxalic acid to check whether all the traces of precipitation has come out or not. After complete precipitation the solution becomes colour less. The precipitation was then dried in an oven at 110°C for 2 hrs for complete removal of moisture.

Equation & Calculation:

From these equation we can calculate the total amount of oxalate (theoretically) & from the experiment amount of oxalate we can calculate the yield percentage which lies between 95-105%. From this we can also calculate the amount of oxalate required for 0.5% Y₂O₃ in the mixture. Fe- is then balanced.

Mechanical alloying of the powder:

Here the proper composition of powder mixture of changed in a high energy attritor mill in a ration of 5:1 to 6:1 call to powder ratio for 2 hrs to produced microscopically homogeneous chemical composition .

Table 5.2 Details of attrition for mechanical alloying

Attritor mill speed	250 rpm
Diameter Attritor mill	280 mm
Height Attritor mill	310 mm
Weight of steel ball	2.5 kg
Diameter of steel ball	3 mm
charge powder	500 gm
time of attrition	2 hrs

Encapsulation of powder mixture:

Here the powder mixture after attrition is filled in mild steel tube of 8 cm diameter, 1.5 cm thick & 10 cm length capsule & a protective hydrogen atmosphere was created by connecting one (longer) end of the capsule, with the H₂- cylinder at 90 psi.

Heating the powder mass:

After encapsulation of the powder the capsule is inserted in a tube furnace at temperature of 1100 °C for 1 to 2 hrs for effective reduction & to prevent oxidation of the capsule into the furnace at a constant follow of hydrogen.

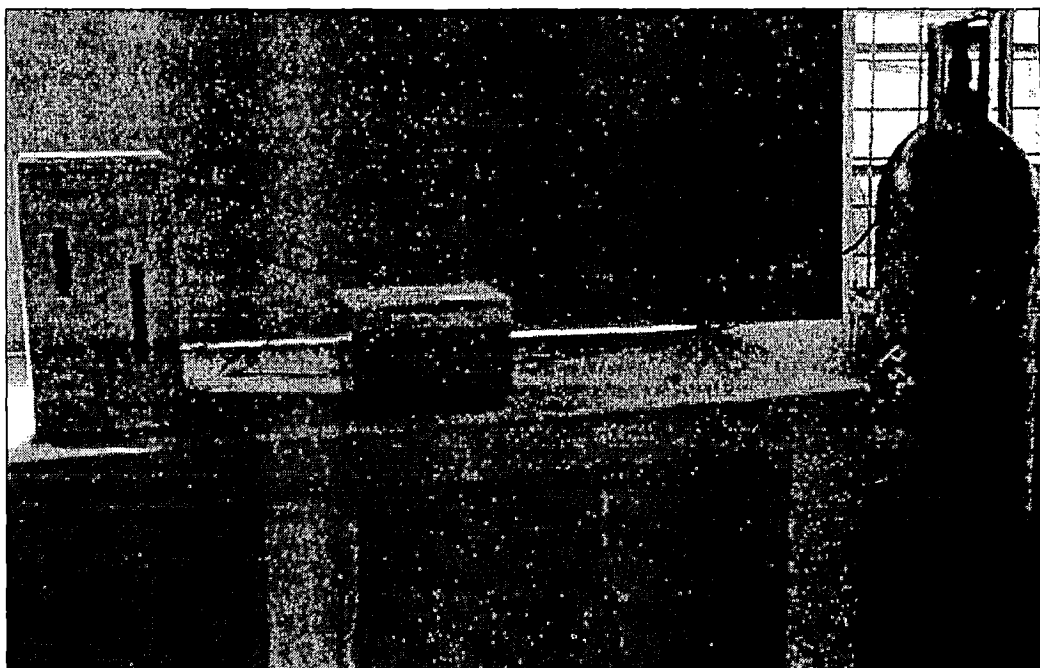


Fig 5.1 Photograph of H₂- Plant Assembly in Laboratory.



Fig 5.2 Photograph of Tube Furnace used in Laboratory.

Forging of the powder mass:

The tube containing powder was subjected to forging in a high capacity forging press under the flow of hydrogen till the first blow of forging hammer followed by subsequent hammering only in red hot condition. The powder gets consolidated inside the forged tube to 90-100% of its theoretical density.

Homogenization:

The forged product was homogenised in a muffle furnace starting from 1100 °C to 6 hrs at 1300°C. This gives microstructurally homogeneous product & eliminates the precipitation of Fe₃Al. Here diffusion of individual constituents across the particle surfaces leads to alloy formation.

After the homogenization the mild steel capsule cover is removed by using shapers, grinder, & subjected to hot pressing at 1100°C to form the slab samples.

These samples are taken for further study. These samples are then subjected to Density measurement, Vickers's hardness testing (VHN) & micro structural study before high temperature oxidation & corrosion testing.

Table 5.3 Densities and Vicker's hardness of various samples

Samples	Density of samples (g/cc)	VHN
Melted	7.4	519
Partially melted (coarse grained)	6.63	478
Not melted	4.34	276
Pure Fe-before hot rolling	4.95	92
Pure Fe- after hot rolling	6.74	126

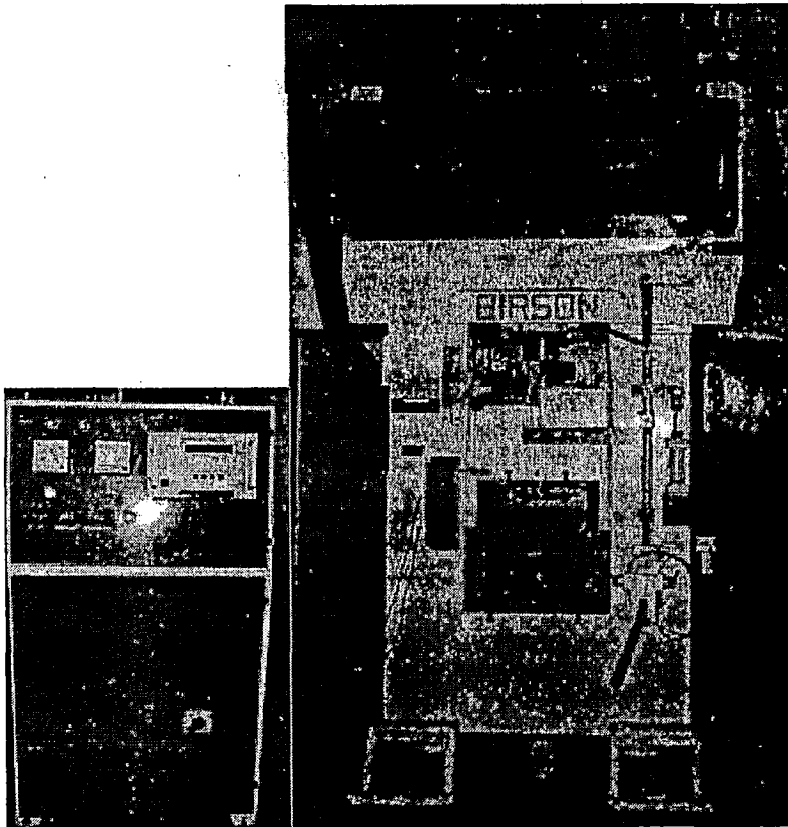


Fig 5.3 Photograph of High Energy Power Press.

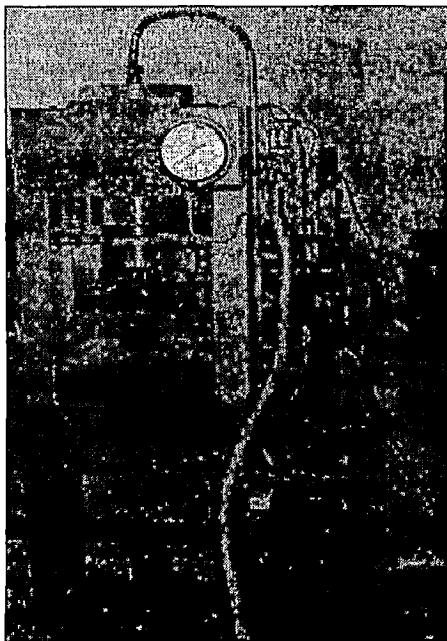


Fig 5.4.a Photograph of Pressing Machine.

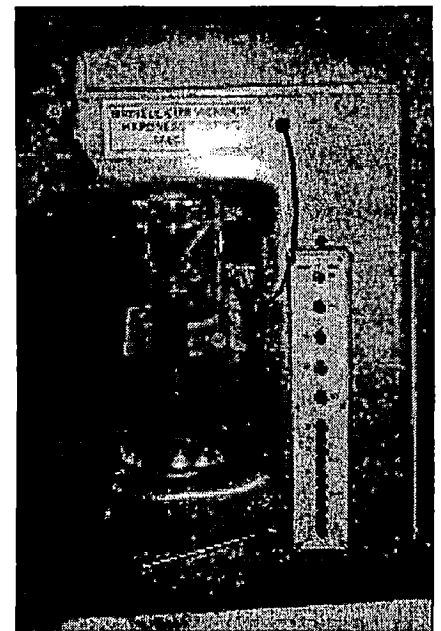


Fig 5.4.b Vicker's Hardness Testing Machine.

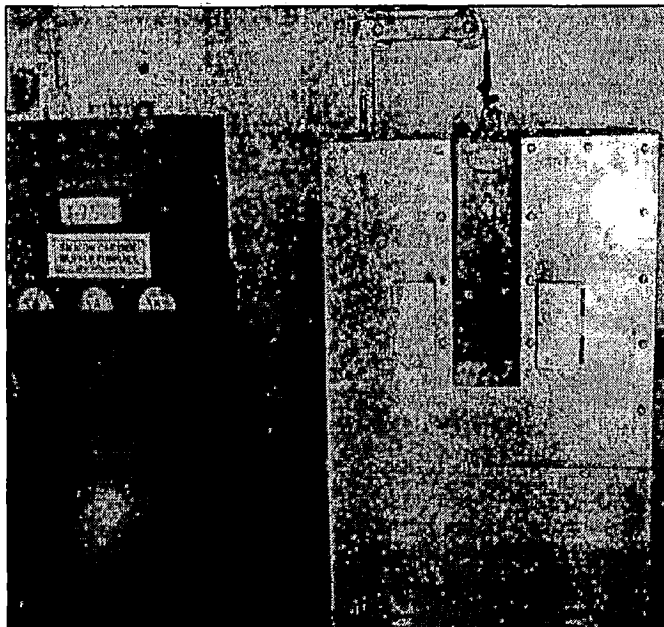


Fig 5.5.a Photograph of Silicon-Carbide Muffle Furnace used for Homogenisation.

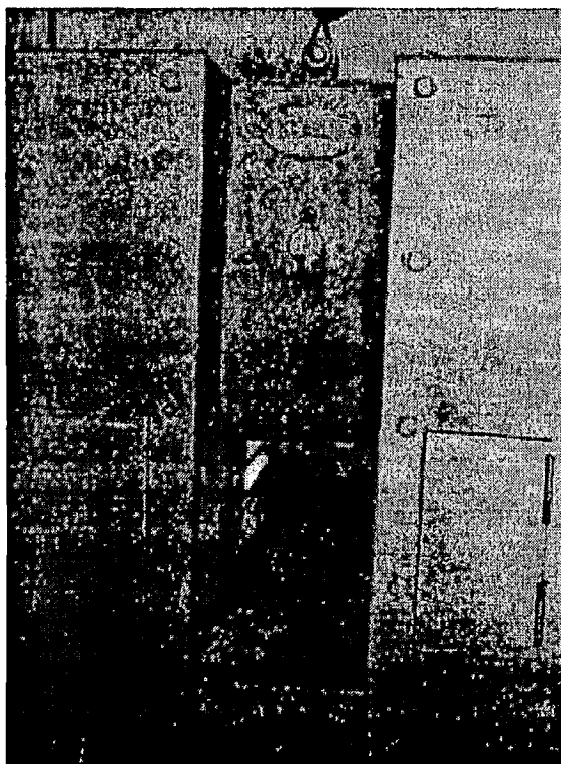
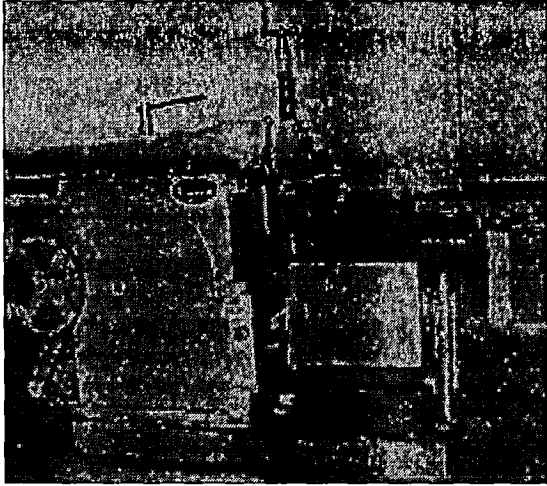
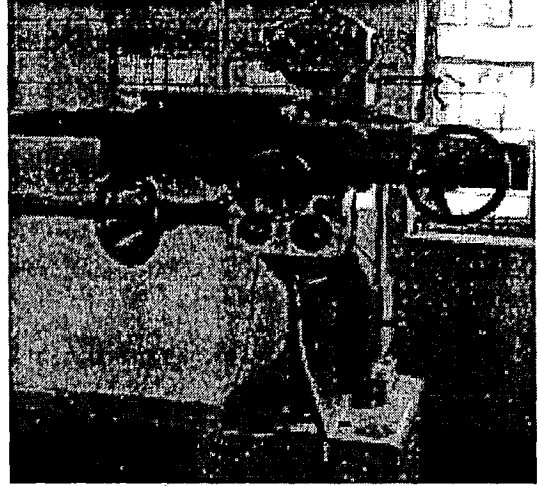


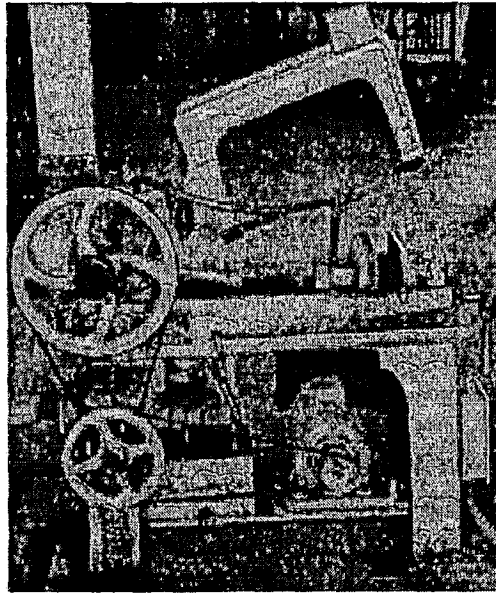
Fig 5.5.b Photograph of Interior of Muffle Furnace.



(a)



(b)



(c)

Fig 5.6 Photograph of (a) Shaper, (b) Grinder, (c) Cutter used for Skin Removal.

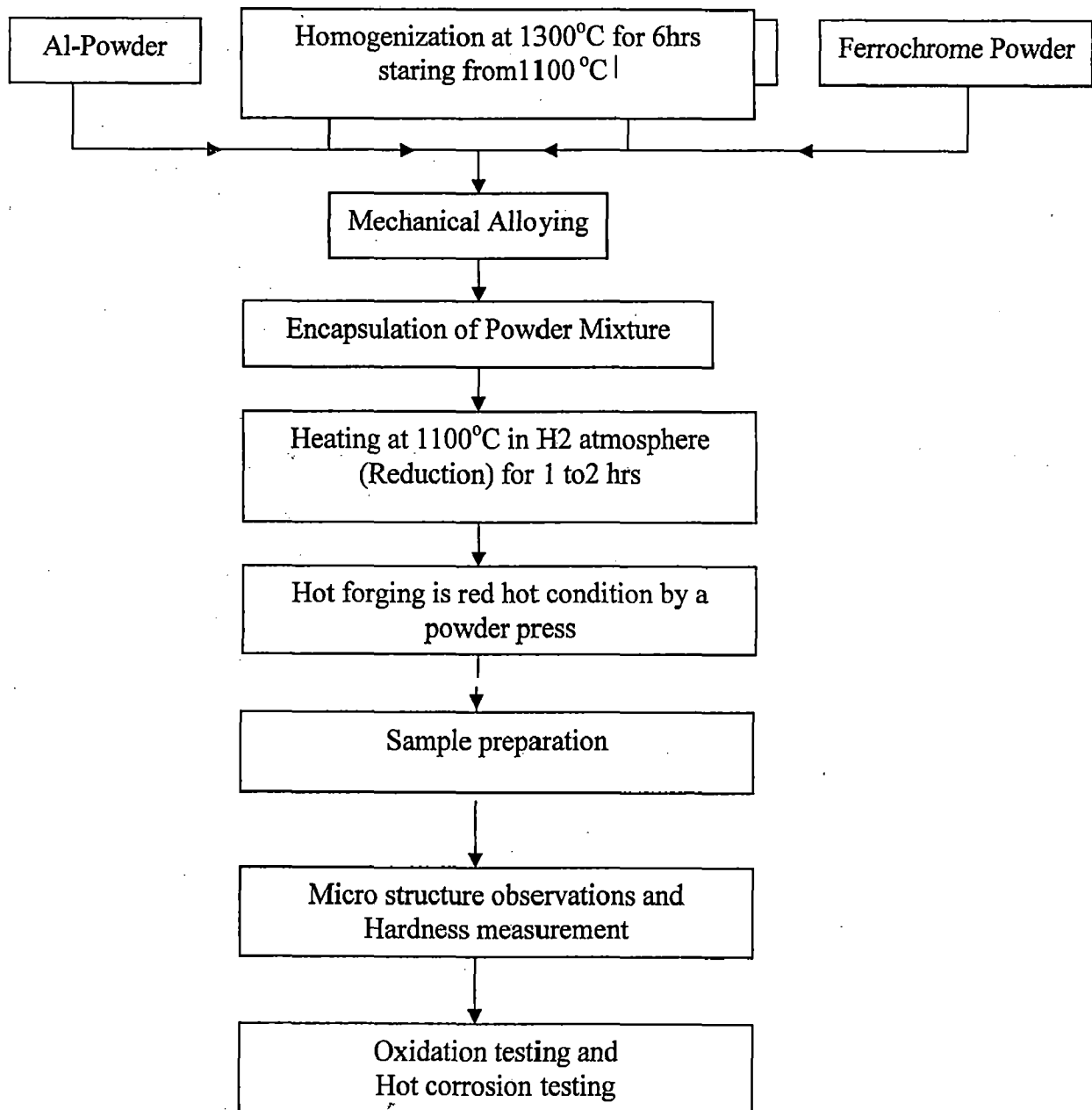
Study of oxidation behaviour (Cyclic Oxidation Testing):

In cyclic oxidation testing the specimens were subjected to expose at temperature 1100 °C for 20hrs & then these were cooled to room temperature for 10mins. Before the test the surface area & weights of the specimen were then suspended inside the surface by using platinum wire & selumnide refractory arrangement. Each cycle consists of 20 hrs heating & 10 mins. The number of cycles is repeated till the constantly is weight change is maintained.

Hot corrosion studies:

Here after the cycle oxidation testing specimen areas & weight were calculated again without removing the oxide layers formed on the specimen. Then ceramic boats used were kept in oven at temperature of 200 °C for two hrs for complete removal of moisture in boat. The coating consists of 40% Na₂ SO₄ + 60 % V₂O₅. The amount of salt coating should be between 3 to 5 mg/cm² is applied to the warm specimen kept at 100 °C for 2 hrs. Then the initial weights of the specimens were calculated. These specimens were then subjected to the tube furnace kept at a temperature of 900 °C for 5 hrs & then cooled to room temperature in air for 20 minutes each cycle consist of 5 hrs heating & 20 minutes cooling. This way experiment was conducted till the consistency in weight was observed.

FLOW SHEET FOR EXPERIMENTAL PROCEDURE



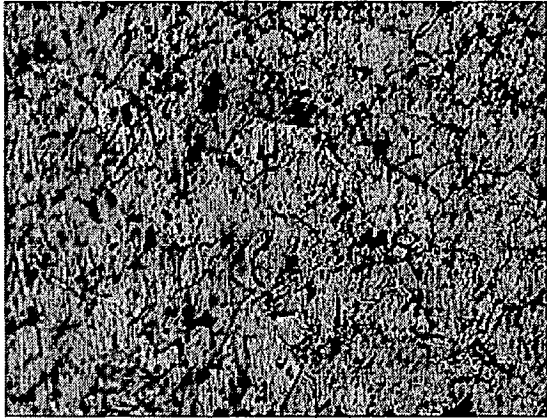


Fig 5.7.a Fe-Sample Before Rolling(100X).

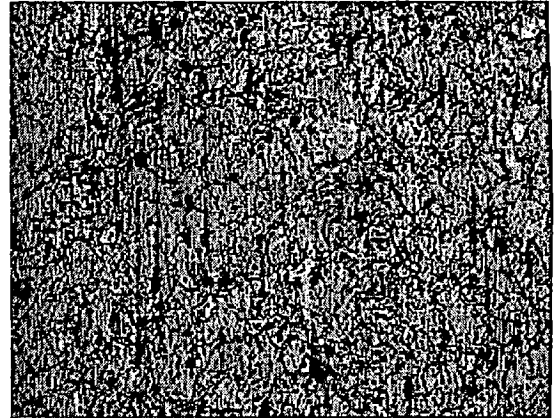
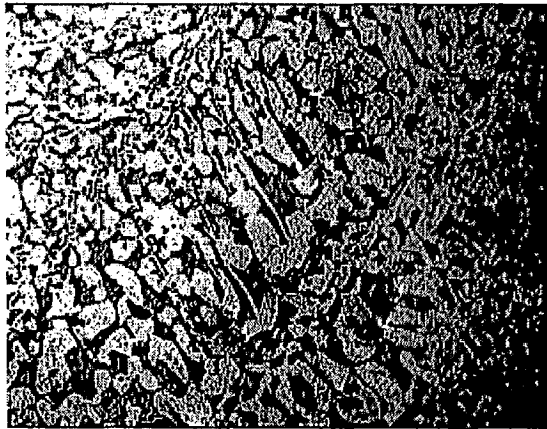
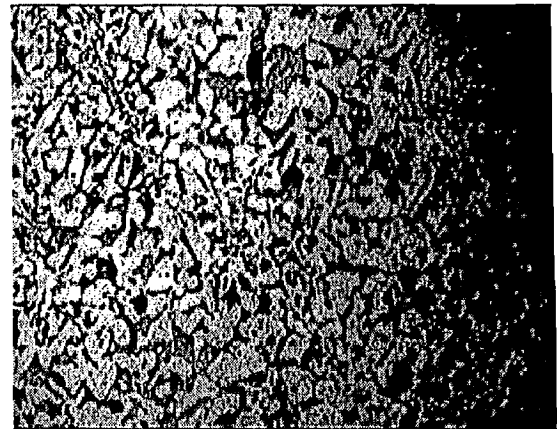


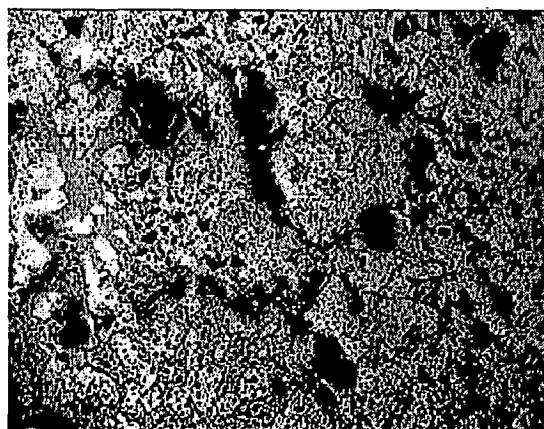
Fig 5.7.b Fe- Sample After Rolling(100X).



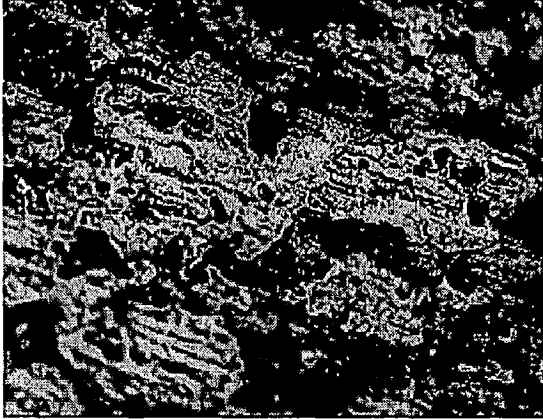
**Fig 5.7.c Melted Sample (200 X)
Before Testing.**



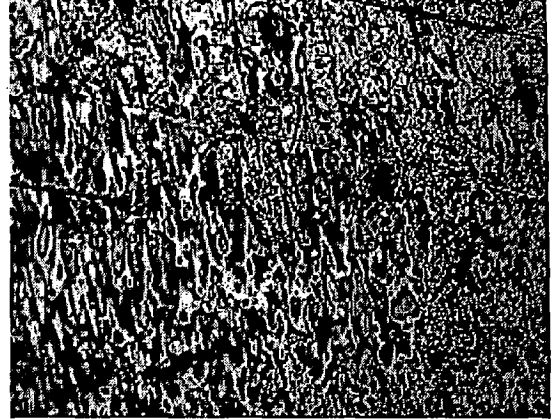
**Fig 5.7.d Coarse Grain Sample (100X).
Before Testing.**



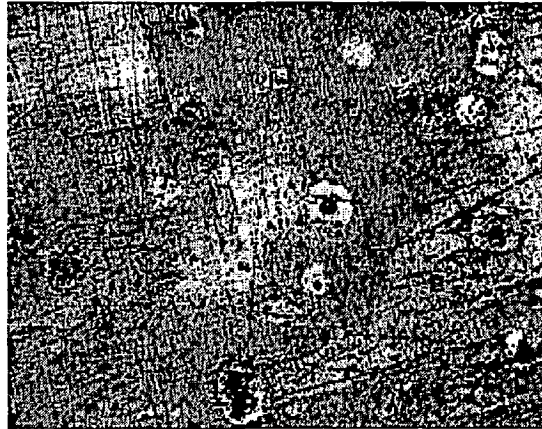
**Fig 5.7.e Low density Sample (100X)
Before Testing.**



**Fig 5.8.a Low Density Sample
after Testing (200X).**



**Fig 5.8.b Melted Sample
after Testing (200X).**



**Fig 5.8.c Coarsened Grain Sample
after Testing (100X).**

All the parameters in the present work was optimized & compared with work done by Amar Singh Sudan ,1992 [3] fully densed alloy-B3 and on MA 956 ODS & Gitanjali [2] 2003,on a fully dense Fe-based ODS i.e. super alloy 800H.

The alloy with which results were compared in discussion has the following composition

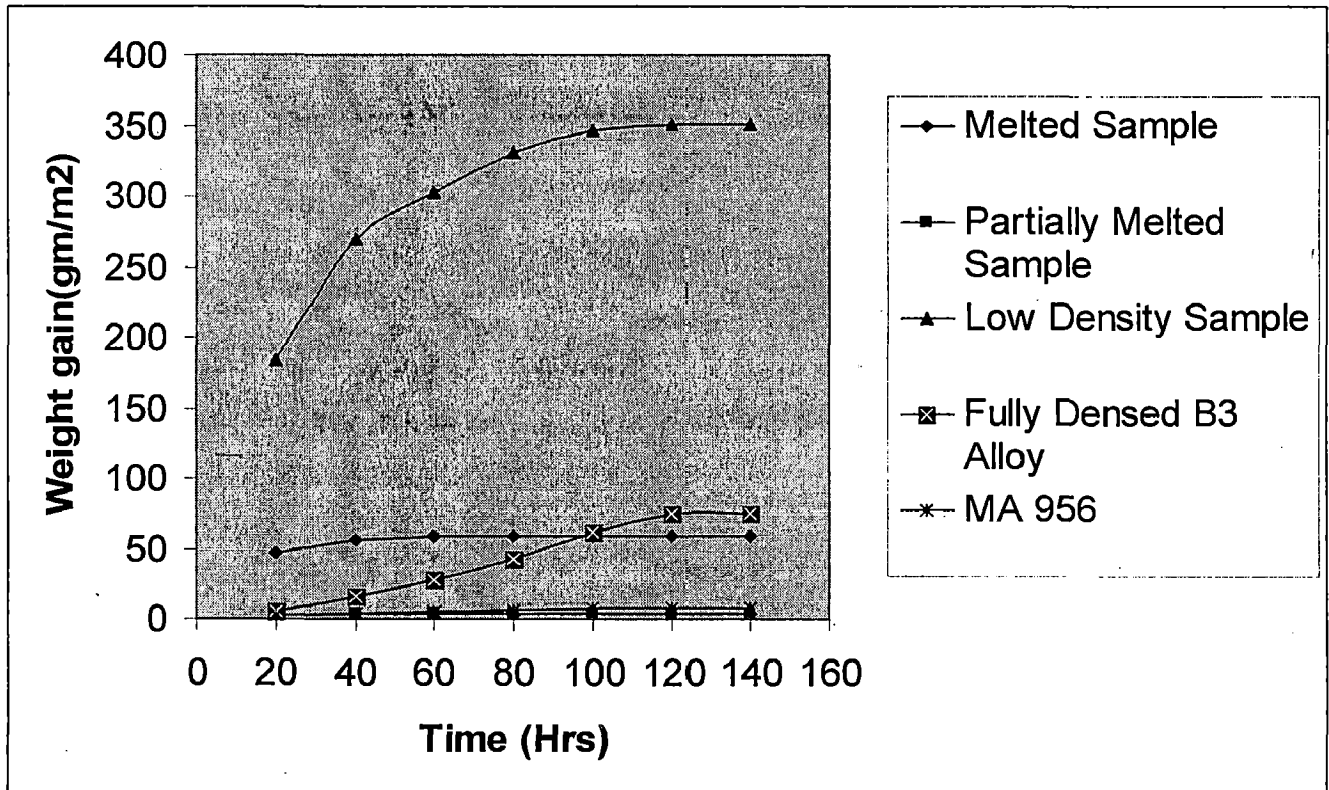
Name of alloys	Percentages of alloying elements (wt %)						
	Cr	Al	Y2O3	Ni	Ti	Mn , Si	Fe
Fully densed alloy B3	17	5.5	0.4	---	---	---	Bal.
Superfer 800H (Incoloy 800H)	21	0.3	---	32	0.3	1 max each	Bal.
Alloy developed by us	22	5.5	0.5	---	---	---	Bal.

Results of cyclic oxidation testing:

Table 6.1 Weight gain data of cyclic oxidation testing at 1100°C temperature

Times in hrs	Weights change (gain) in gm/m ²				
	Melted sample	Partially melted sample	Low density sample	Fully densed B3 alloy	MA 956
20	46.357	3.171	184.01	5.00	3.21
40	56.291	4.438	269.44	15.83	4.52
60	59.30	4.438	302.30	27.49	5.43
80	59.30	4.438	330.77	43.31	6.55
100	59.30	4.438	346.23	61.68	7.40
120	59.30	4.438	351.18	75.00	8.25
140	59.30	4.438	351.18	75.00	8.25

Graph 5.9 Cyclic oxidation behaviour of alloy developed, MA 956 and Fully densed B₃ [3] alloy

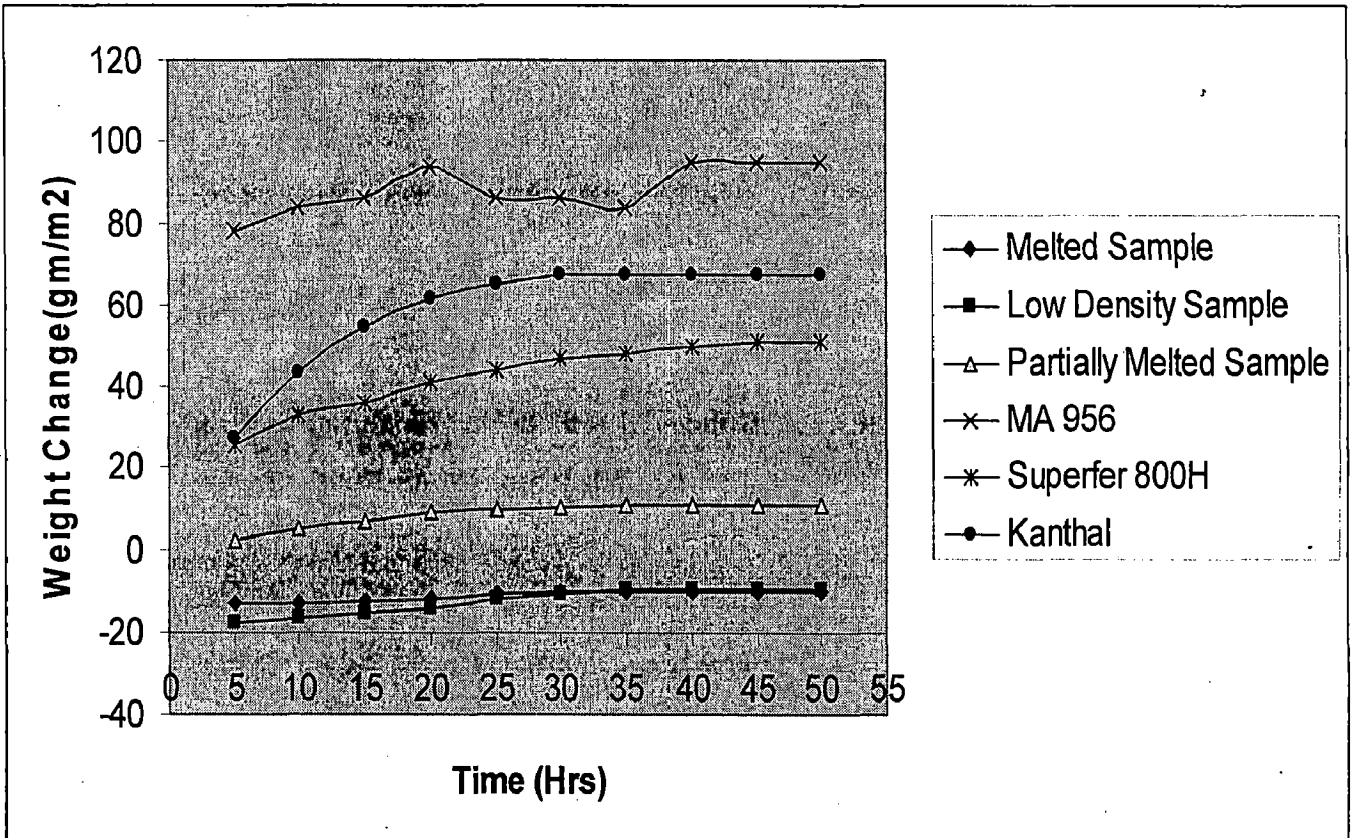


Results of hot corrosion testing:

Table 6.2 Weight change data of hot corrosion testing at 900°C temperature in Na₂SO₄+60% V₂O₅ environment:

Time in hrs	Weight change in gm/cm ²					
	Melted sample	Low density	Partially melted	MA 956 ODS	Superfer 800H	Kanthal
5	-13.16	-17.52	1.902	78	25.25	27.248
10	-12.91	-16.43	5.07	84	33.12	43.597
15	-12.58	-15.43	6.97	86	36.01	54.496
20	-11.92	-14.22	8.87	94	41.33	61.762
25	-10.589	-12.05	9.51	86	44.00	65.395
30	-9.93	-10.95	10.15	86	46.72	67.212
35	-9.93	-9.86	10.78	84	48.20	67.212
40	-9.93	-9.86	10.78	95	50.00	67.212
45	-9.93	-9.86	10.78	95	51.22	67.212
50	-9.93	-9.86	10.78	95	51.22	67.212

Graph 5.10 Hot corrosion behaviour of alloy developed, fully densified B₃ alloy, Superfer 800H and Kanthal sample.



DISCUSSION

In case of cyclic oxidation testing increase in weight in case of the melted sample was large than the partially melting & the weight gain is too maximum in case of low density sample. In case low density sample due to the porosity more surface area was exposed hence has the maximum weight gain. But in case of melted sample as it was melted the distribution of the alloying element (especially Cr_2O_3) was not homogeneous distribution through out the sample. Hence the oxidation resistance is less than that of the partially melted (coarsen grain) sample where the decrease of metallization & coarsen grain structure is adequate for low oxidation. Here the distribution of alloying elements & low grain- boundary area play the domination role for effective oxidation resistance.

In case of high temperature corrosion testing the loss in weight first in case of melted & low density alloy was due to spitting of scale initially. But later the increase in weight shows some accelerated corrosion (oxidation) was taking place. In almost all the samples often around 5 cycles the constancy in weight gain was marked. In a low density initially weight loss was more due to the environment and after 5 cycles due to the layer of Cr_2O_3 formation the further oxidation was prevented. In case of partially melted coarse grained sample due to homogeneously distributed Cr_2O_3 the oxidation & corrosion was the least to be found out.

Thus the initial weight changes is due to the surface & then due to the oxide layer formation the diffusion of ' O_2 ' was decreased & finally ceased which is reflected from the consistency in weight gain after few cycles. The comparison of the alloy developed with the MA ODS 956, superfer 800H & Kanthal is self explaining.

In our work we used Y_2O_3 instead of 'Y' which is used in superfer 800H. Thus the presence of Y_2O_3 and high "Cr" (22%) gives better performance under high temperature testing.

-
- Fe-bases ODS super alloy can be produced economically by P/M forging route by using indigenous raw materials without bothering about starting powder purity & size for the application which requires oxidation/ sulfidation resistance.
 - The present investigation revealed that higher the density better the performance at high temperature proceed the alloying distribution should be homogeneous.
 - The alloys developed should the stabilized weight gain with parabolic law of oxidation.
 - The presence of yttria diepersoids serves many functions, these are
 - (i) Improves high temperature resistance
 - (ii) Reduces porosity
 - (iii) Improves formablity
 - (iv) Reduces electrical resistivity
 - (v) Enhances homogenization of Cr during processing
 - (vi) Increases hardness

The development & characterization of the present alloy should as good comparative properties with MA 956 superfer 800H. So the future scope includes

- Optimization of parameters for the development of this alloy in technique i.e. mechanical alloying composition, forging, homogenization, hot rolling etc.
- Micro structural studies uniform distribution hence in depth micro structural study, TEM, SEM, XRD etc.
- Designing of the alloy changing the alloying elements specially Y_2O_3 up to 1%
- Study of the alloy under molten bath composition of Na_2SO_4 & V_2O_5 .

REFERENCES

1. HAND BOOK OF SUPER ALLOYS, international alloy compositions & Designations series, M.J. Wahll, D.J. Maykuth, and H.J. Hucek, P-2, 22, 36, 80, 82.
2. SUPER ALLOYS 2000, T.M. Pollock, R.D. Kissinger, R.R. Bowman, K.A. Green, M. Mclean, S.L. Olson, J.J. Schirra.
3. Amar Singh Sudan, " Design and Development of Oxide Dispersion Strengthened (ODS) Ferritic Alloys Through the powder Forging Route", PhD. Thesis, REC Hazratbal, Jammu and Kashmir.
4. Gitanjali, " Role of Inhibitor on Hot Corrosion of Super Alloys in Na₂SO₄ V₂O₅ Environment".
5. Geissinger G.H., " Powder Metallurgy of Super Alloys", in introduction part, p.7
6. Betteridge W, and Heslop J(editors), " the Nimonic Alloys", Edward Arnold, London, 1959, P.232.
7. Kessinger G.H and Bomford M.J, International Metals Reviews 19, 1974, P.51
8. Decker R.F., and Bomford M.J., International Metals Reviews 19, 1974, P.7.
9. Benjamin J.S., and Grains R.L., "Elevated Temperature Mechanical Properties of a Dispersion Strengthened Superalloys", H.H. Hausner (Editors), Plenum Press New York, Vol.5, P.47
10. Benjamin J.S., 'Dispersion Strengthened Superalloys by Mechanical Alloying', Metal. Trans, 4 Vol.1, 1970 P 2943-2951.
11. J.J.Fischer, US Patent 4,075,010, 21 February 1978.
12. D.S. Gelles, ISIJ Intl. 30 (1990) 905.
13. D.S. Gelles, DOE/ER-0313 16 (1994) 146.
14. J.S. Benjamin, Sci. Am. 234 (5) (1976) 40-48
15. J.S.Benjamin, Metal Powder Rep. 45 (1990) 122-127
16. BENJAMIN J.S., Met. Trans., 1, Oct., 1-9, (1970)
17. BENJAMIN J.S. and VOLIN T.E., Met. Trans., 5, Aug., 1929-1934, (1974)
18. BENJAMIN J.S., Proc. Conf. Gas Turbines and Fluids Engineering, Pub. ASME, New

Orleans L.A., 1-9, (1976).

19. GILMAN P.S. and BENJAMIN I.S., Ann. Rev. Mater Sci., 13
20. H.Kaltenhauser, MetEngg. Quart., 1972(2),41
21. Cihal, Stahl u. Eisen., 1958, 79, 1944
22. Baumel, ibid., 1965,85, 1462.
23. Picketing, Heat Treatment Aspects of Metal Joining Processes, 1972, Iron and Steel Inst., 84
24. Utting, J. Iron Steel Inst., 1969,207,872.
25. J. Irvine, D.T. Llewellyn and F.B.Pickering, J. Iron Steel Inst, 1961,199,153.
26. Pickering, Metallurgical Achievements, 1965, Pergamon Press, 199.
27. Holmes and D.J Dyson, J. Iron Steel Inst, 1970,208,469.
28. L. Sutton and W. Hume-Rothery, Phil. Mag.,1955,46, 1295.
29. McMullin et al., Trans. A.S.M., 1954,46, 799.
30. Emchysen, A.P.Bond and H.J.Dundas, 'Towards improved ductility and toughness', Climax Molybdenum Co. Symp., Kyoto, 1972, 239.
31. Palmer and G.C.Smith, "Oxide Dispersion Strengthening," p.253, Gordon and Breach Science Publishers, New York (1968)
32. S. Benjamin and M.J. Bomford, Metal. Trans. 8A, 3101 (1977)
33. M. Davidson, "Frontiers of High Temperature Materials II," p.163, Inco Alloys International, Huntington, West Virginia (1983)
34. A. Thompson, "Frontiers of High Temperature Materials I," p.134, Inco Alloys International, Huntington, West Virginia (1981)
35. Grundy, Mat. Science and Tech., 3, 782-790 (1987)
36. Benn, "frontiers of High Temperature Materials II," p.37, Inco Alloys International, Huntington, West Virginia (1983).
37. J. Kelly, Ibid., p.129.
38. Hinze, M.L. Robinson and R.D. Lawson, U.S. Patent 4,402,767.
39. Macdonal, "frontiers of High Temperature Materials II," p.369, Inco Alloys International, Huntington, West Virginia (1983).
40. Nomura, T.Okuda, S.Shikakaura, M.Fujiwara and K.Asabe, "Solid State Powder Processing,"

p.203, Trans. Met Soc., Warrendale, Pennsylvania (1989).

41. Floreen, R.H. Kane, T.J. Kelly and M.L. Robinson, "Frontiers of High Temperature Materials I," p.94, Inco Alloys International, Huntington, West Virginia (1981).
42. Benn and G.M. McColvin, "Superalloys 1988," p.73, The Metallurgical Society, Inc., Warrendale, Pennsylvania (1988)
43. J. Fischer, J.J. deBarbadillo and M.J. Shaw, "Structural Applications of Mechanical Alloying", p.79-85, Proceedings of an ASM International Conference, Myrtle Beach, South Carolina, 27-29 March 1990.
44. app, R.A and Zhang, Y.S., (December, 1994), " Hot Corrosion of Materials: Fundamental Studies," JOM, P.47-55
45. app, R.A., (1990), " Hot Corrosion of Materials," Pure & Appl. Chem., Vol.62, No.1. P.113-22
46. app, R.A., (2002), " Hot Corrosion of Materials: A Fluxing Mechanism," Corros. Sci, Vol.44, No.2, P. 209-21.
47. app, R.A., (1986), " Chemistry and Electrochemistry of the Hot Corrosion of Metals," Corros., Vol. 42. No. 10, P. 568-77.
48. Arris, G.T., Child, H.C. and Kerr, J. A., (1955), "Effect of the composition of Gas Turbine Alloys on Resistance to Scaling and to Vanadium Pentaoxide Attack," Journal of the Iron and Steel Institute, Vol. 179, P. 342-47.
49. Achs, K., (1958), "Accelerated High Temperature Oxidation due to Vanadium Pentaoxide," Metallurgia, Apr., P 167-73.
50. Airman, L., (1962), "Technical Note: Mechanism of Accelerated Oxidation by Vanadium-Containing Fuel Ash," Corros. Sc., Vol. 2, P.293-96.
51. Hilakan, H.R., Lahiri, A.K. and Benerjee, T., (1967)," Studies on Resistance of Alloy Steels against Oil Ash Corrosion-Part-I," NML Technical Journal, May, P.20-25.
52. Kofstad, p. (1966), " Ch.1 : General introduction" In High Temperature Oxidation of Metals, John Wiley & Sons Inc. USA.
53. Scott, F.H.,(1998), " The Roll Of Oxidation In The Wear Of Alloys, Trib. Int., Vol. 31., No. 1-3, PP.61-71.

54. Pettit , F.S & Meier, G.H. (1985), “ Oxidation & Hot corrosion Of Super Alloys”, Super Alloys 85, EDS Gell, M. Kantovich, C.S. Bricknel, R. H. Kent, W.B. Rodovich, J.F.; Met. Soc. Of AIME Warrendale, Pennsylvania, PP (615-687).
55. Rapp, R.A & Zhang, Y.S (1994), “ Hot Corrosion Of Materials: Fundamental Studies,” JOM, Vol. 46, No. 12, PP. 47-55.
56. WWW.SCIENCEDIRECT.COM.
57. WWW.GOOGLE.COM.
58. Sidharth Singh.PhD Scholar.