2 Chapter

Base Materials
(Fe-Base Alloys And Superalloys)

2.1 BASE MATERIALS – INTRODUCTION

Materials which are very commonly employed in engineering applications are iron, iron base alloys, steels alloy, titanium alloys, nickel and cobalt base alloys. The alloying elements that are very often used to increase the properties of these base materials are manganese, silicon, molybdenum, chromium, cobalt, and other rare elements like tantalum, niobium, hafnium etc. In the following important metallurgical properties of iron base alloys and Ni-base alloys are presented. For detailed information, it is advised to refer to standard books on physical metallurgy, and heat treatment.

2.2 Fe-BASE ALLOYS

The service conditions of many of the machines and structural parts will severely affect the material surface and, so a proper protection must be provided to the surface of the working machine parts, so that its life can be extended. It is very important to understand the chemical composition and metallurgical structure of the material and this will help to select the proper surface treatment, specially, in hardfacing of machine parts.

Phase Diagram of Carbon Steel

Many of the surface hardening treatments, such as, flame hardening, induction hardening, laser hardening, or electron beam hardening, heat the surface of the steel to a high temperature and allow the temperature to rapidly decrease by quenching methods. The surface hardening mechanism actually depends on the phase transformation that takes place during heating and then sudden quenching of the part. To understand the process, it is very essential to have thorough knowledge of phase transformation in hardenable steels and their alloys and the phase diagram will help to achieve this goal.

Figure 2.1 shows the phase diagram of plain carbon steel.

The iron-carbon diagram shows the relation between carbon content and temperature, indicating the different phases of the steel. Iron containing C = 0.8% (wt) is known as eutectic steel and carbon less than 0.8% hypo-eutectic and C greater than 0.8% is known as hyper-eutectic steel. Hypo-eutectic steel will have pearlite and ferrite phases and hyper-eutectic steel will have pearlite and cementite phases as indicated in the figure.
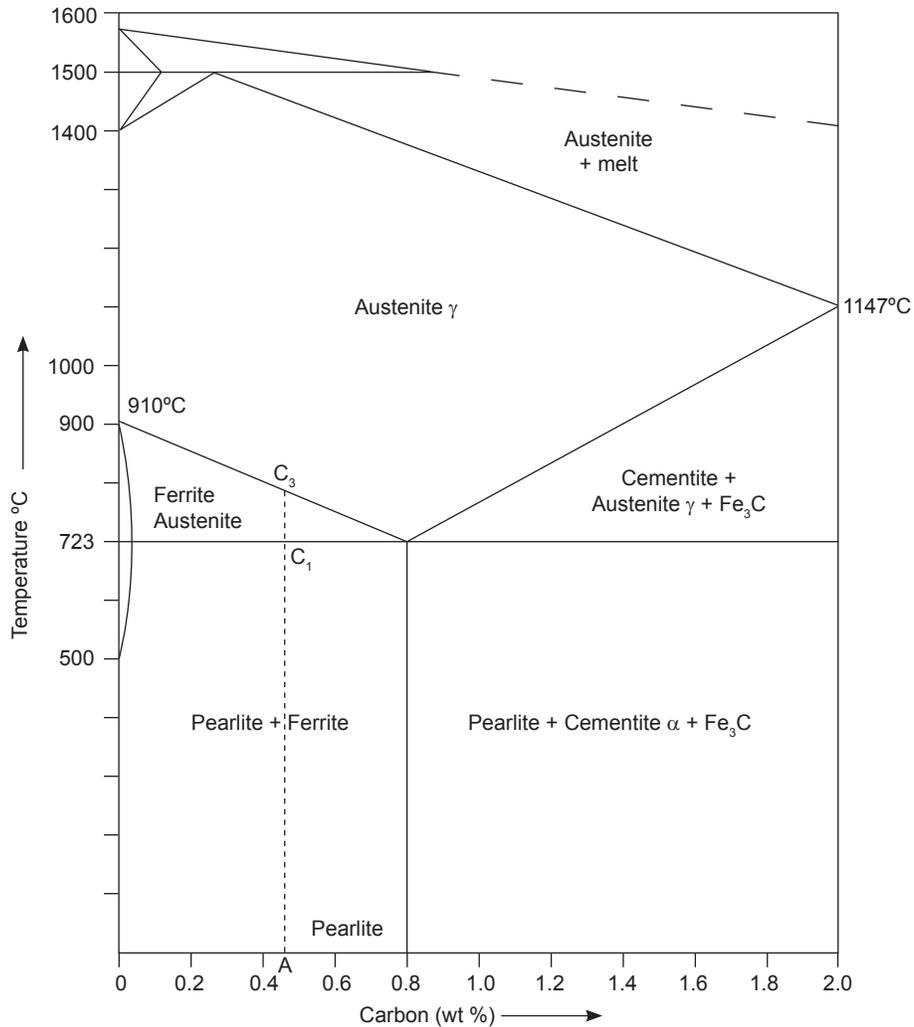
Fig. 2.1 Iron-carbon equilibrium diagram

When an hypo-eutectic steel is heated slowly, the phases will start to change to austenite phase at temperature AC_1 (= 720°C), and the transformation to austenite will be completed at temperature AC_3 which will depend on the carbon content. Above the AC_3 temperature the entire material will be in the austenite phase (FCC). Phase transformation in the reverse order will take place when the steel is cooled slowly from the austenitic phase to original phases of steel at room temperature.

When an hyper-eutectic steel is heated slowly, the cementite and pearlite phases will start to transform to austenite at a temperature 723°C and complete at a temperature depending on the carbon percentage. Again the reverse transformation will occur when the steel is cooled down to room temperature slowly.

However, when the cooling rate is changed, as in rapid quenching or if the steel is cooled rapidly and held at an intermediate temperature for a long time, different phases will form, as indicated in the TTT diagram shown in Figure 2.2. Thus different phases can be obtained by controlling the cooling rate. The boundary of different phases will get shifted depending on the alloy content.

Thus, the phase diagram and the Time Temperature Transformation (TTT) diagram will be very useful in understanding the phases formed and in deciding the type of surface treatment to be given to a particular steel component.
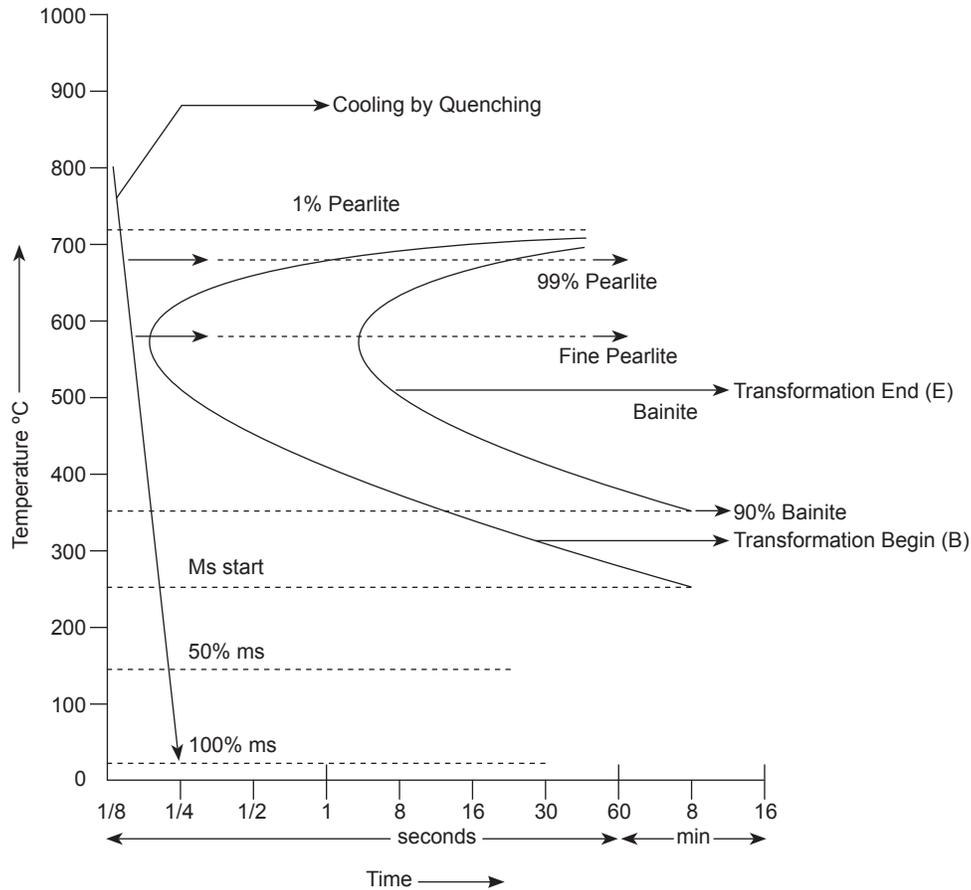

Fig. 2.2 Time-Temperature-Transformation diagram for 1% carbon steel

The plain carbon steels are iron-carbon alloys containing a maximum of 2.0% carbon. Carbon content decides the type of steel.

Low carbon steel	C less than 0.25%,
Medium carbon steel	C = 0.3 to 0.6%
High carbon steel	C = 0.6 to 1.4%

Carbon content influences the structure of the steel. The structure of the slowly cooled carbon steels at room temperature will be

(*a*) up to 0.025% C ……... Ferrite

(*b*) 0.025 to 0.8% C …….. Ferrite and pearlite

(*c*) 0.8 to 2.06% C ……… Pearlite and carbides

(*d*) 2.06 to 4.2% C ……… Pearlite and graphite

Carbon is the principal hardening element in steel. It combines with iron to form cementite (Fe_3C) which is hard. The hardness increases with carbon content. As the carbon content increases the heat conductivity of steel decreases.

At room temperature the stable phase of iron is BCC ferrite which transforms to FCC austenite on heating above 723ºC. Austenite transforms to ferrite and cementite on slow cooling and to martensite during rapid cooling. At intermediate cooling rates, bainite is formed. The needle shaped martensite matrix has the highest hardness of 60 HRC and upper bainite matrix has hardness of 40 – 45 HRC.

The high temperature phase, austenite can be stabilized at room temperature by the additions of nickel, manganese, and nitrogen. The strength and hardness of steels are increased by solid solution hardening of the matrix by interstitials (C, N) and substitutional (Si, Mn) elements or by precipitation of hard phases (WC, NbC or MoC).

In many applications of steel, microstructure forms the basis for selection of the material. The much used rail steel has the eutectoid composition (0.8% C) with a fully pearlitic structure. Dry sliding wear rates of the pearlitic steels are found to be lower than those of martensitic or bainitic steels. The dry sliding wear properties of 0.5 Mo-B bainitic steels are similar to those of fully pearlitic steels.

Plain carbon steels 1025 to 1050 can be easily flame hardened. Steels 1010 – 1020 and 1108 – 1120 grades are carburized grades of plain steels.

Effect of Alloying Elements

Carbon Equivalent

Alloying elements are added to carbon steel to alter the mechanical, physical, wear and corrosion properties. Some of the alloying elements like Mn, Si, Cr, Mo, Ni, Cu and V will have the similar effect on the hardenability as carbon, though their contributions may be of different weightage. To evaluate the hardenability carbon equivalent (CE) has been proposed and, given in the form

CE = C + (Mn+Si)/6 + (Ni+Cu)/15 + (Cr+Mo+V)/5

If the carbon equivalent of alloy steel is less than 0.15%, weld overlay can be easily carried out. Figure 2.3 shows the relation between carbon and carbon equivalent (C vs C.E.) indicating the different zones of hardfacing of steel. The carbon equivalent will help to know whether the substrate has to be pre-heated or not, and whether cracking may result during overlay. Carbon and carbon equivalent are different and with the same carbon equivalent, carbon content in two steels may differ and influence the properties of the steels.

In low alloy or plain carbon steels, the strength and hardness increase with carbon content and alloying elements up to a carbon or carbon equivalent of 0.5 to 0.6%, beyond which there is not much further increase in hardness.

Mn, Si, S and P are common elements present in any steel. Though manganese will increase hardness and toughness of steel, it should not be more than 1.2%. Sulphur and phosphorous must below 0.05%. Manganese reduces the critical rate of cooling, thereby increasing the hardenability of the steel. Manganese also increases the resistance to abrasion. The ratio Mn/S should at least be 10:1 to avoid cooling cracks. Chromium steel with carbon less than 0.18%, can be easily cladded. If carbon exceeds a limit (greater than 0.2%), the hardness of steel will increase and pre-heating becomes essential before surface treatment.
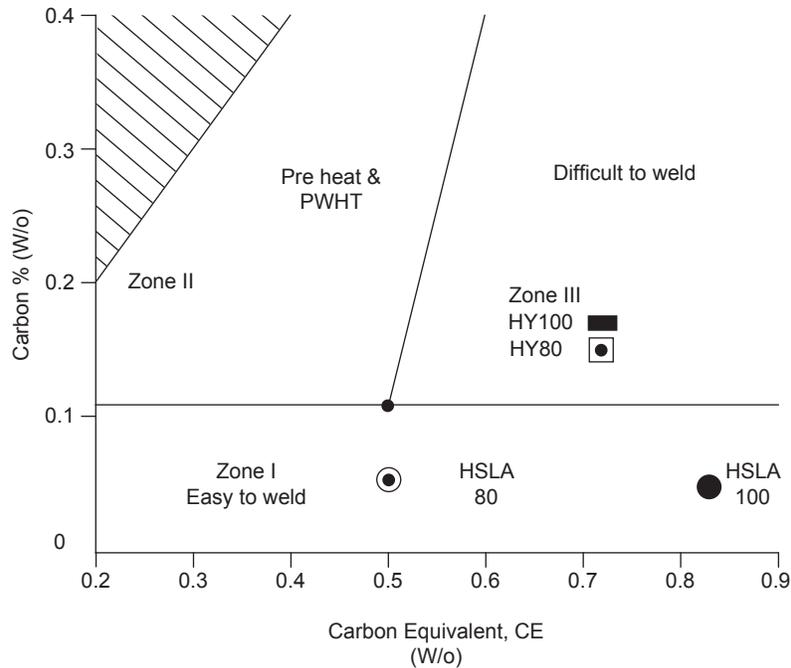
Fig. 2.3 Carbon-Carbon equivalent diagram

Silicon is commonly present in steel. Silicon develops hardness and elasticity in steel. However, tensile strength and ductility may be reduced. With hardening and tempering treatment, silicon steels may develop high strength, ductility and impact resistance. Silicon steels are used in springs, and in acid resistant components.

Chromium in steel forms several carbides, depending on the treatment and the amount of chromium present. Chromium increases the hardenability of steel. Toughness, and resistance to corrosion and abrasion are also increased by chromium addition to steel.

Nickel increases the strength and toughness of steel. With sufficient amount present in steel, will make it austenitic even at room temperature. Nickel does not form any carbide, but improves corrosion resistance even at elevated temperatures.

Nickel forms a complete series of solid solution with gamma iron with which it has a common FCC structure. With BCC iron it has only a limited solubility. With chromium = 18%, a nickel content of around 10% will fully retain the austenitic structure. Increase in nickel content may lead to the formation of brittle sigma phase.

Molybdenum reduces the critical cooling rate and, increases the depth of hardening. Toughness and creep strength are also increased by molybdenum in steel. It forms carbides and improves the resistance to wear. Moly-alloyed steels are used in tools and machine parts. However, high molybdenum content, higher than 3.5%, will promote sigma phase formation in austenitic and ferritic steels.

Tungsten forms complex carbides. It imparts high cutting hardness and resistance to abrasion wear. It reduces the grain growth and gives high temperature strength. Tungsten alloyed steels are used in high speed steels, hot working steels, magnets and valve parts.

Vanadium increases the yield and ultimate strength of steel. It is a strong carbide former and its carbides are very stable. It is used in tool steels and dies and punches.

Stainless steels can be classified as:

(*a*) austenitic stainless steel, AISI 300 series, austenitic with nickel as the primary austenite stabilizer,

(*b*) ferritic stainless steel, AISI 200 series, austenitic with "manganese and nitrogen" as nickel substitutes,

(*c*) martensitic stainless steel, AISI series, ferritic and martensitic with little or nil nickel,

(*d*) precipitation hardening stainless steels have compositions with a potential for hardening by martensitic or other transformations by thermal and mechanical treatments, and

(*e*) duplex stainless steel, containing 28% (wt) chromium equivalent and 6% nickel equivalent to produce structures with equal proportions of austenite and ferrite.

Heat conduction in stainless steels is less than that in low carbon steels by 50%, and so, low heat input will be sufficient for welding purposes. However, thermal expansion in stainless steel is much higher than in low carbon steels. Further, hardening and tempering of ferritic and austenitic stainless steels are not possible. Sigma phase may form in austenitic stainless steels in the temperature range of 450 – 900ºC. This must be avoided, as otherwise intergranular corrosion may occur. To avoid weld decay, stainless must be heated to 1025 – 1100ºC and then quenched in water. Stainless steel containing nitrogen will be completely austenitic and so post weld heat treatment can be easily carried out.

Austenitic stainless steels of AISI 300 series are extensively used to resist corrosion, heat, and cavitation erosion. Its normal compositions are 18% Cr and 8% Ni and any treatment leading to the formation of chromium carbide precipitates at the grain boundaries will make the material susceptible to intergranular corrosion. Stabilized grades with titanium (AISI 321) niobium (AISI 347) are used in the most severe corrosive conditions with high service temperatures. Molybdenum containing grades such as AISI 316 have excellent pitting resistance.

Martensitic stainless steels (AISI 431 and AISI 400C) have good corrosion resistance properties and are used for metal forming tools and dies. Reduced carbon content in AISI 400 reduces the risk of weld decay. Ferritic/martensitic stainless steels exhibit excellent galling, heat-erosion-cavitation resistance. They are used for engine valves for galling problems and hydro turbine components for cavitation problems. Duplex stainless steels have very good resistance to chloride-induced stress corrosion.

Because of their high hardness and resistance to wear, tool steels and high speed steels are used for hardfacing; however, due to their poor weldability an intermediate or buffer layer of nickel-base alloy (80Ni-20Cr) is used on the surface to be hardfaced, before overlaying the tool steel overlay.

Applications

Medium carbon or low alloy steels are used in manufacturing gears and shafts. Surface hardening of gear teeth or shafts, made from steels with good hardenability, is carried out by induction, flame or laser heating process. For low hardenability steels, a suitable case depth of high hardness is formed by carburizing, nitriding or carbo-nitriding the parts. Low alloy heat resistant steels, such as Cr-Ni-Mo steels, are extensively used for rebuilding worn out forging dies by welding.

Alloy steels that can be carburized are 4615 – 4620 and 8615 – 8620. Cast irons (ASTM class) for flame hardening are Class 30, Class 40, Class 45010, 50007, 53004 and Class 80002.

Austenitic manganese steels are extensively used for heavy repetitive impact wear applications, such as impact crushers, shovel lips and mining equipments. Because of the work hardening nature of these steels, the wear rate, after initial set-in period, is very negligible.

Hadfield manganese (Mn) steels with a basic composition of 12-14% Mn and 0.4-0.6% carbon will contain around 10% Cr. Addition of 3.5% Ti will reduce abrasive wear considerably. Weld overlays of austenitic manganese steels must be rapidly cooled to produce a purely austenitic microstructure with no carbide precipitations at the grain boundaries. Hydro turbine blades are resurfaced with high chromium manganese steels.

For high abrasion resistance as in mineral processing equipments, high nickel or high chromium white cast irons are used. Fine carbide particles offer great resistance to wear. Mixed carbide welding overlays are developed to resist abrasive and erosive wear at elevated temperature. The materials are available in both flux-coated and flux-cored electrodes.

Tungsten carbide composites are used for rock drills, oil drills, sand mixer blades, and oil well fishing tools. Sintered tungsten carbide rods are used as welding electrodes in MMAW and FCAW welding modes of overlay purposes. Chromium carbide powders mixed within a nickel-chromium matrix are extensively used as thermal spray coatings on boiler tubes for corrosion and erosion resistance.

Copper base alloys contain tin or zinc such as tin-bronze or brass and possess medium hardness and good ductility. For wear and corrosion resistance aluminium bronze, silicon bronze and nickel silver are used in marine pumps, bearings, bushes, propellers, piston rings, and valve guides. These alloys can be used to form thermal spray deposits.

Super Alloys

For high temperature applications in boiler super heaters, turbine blades and other components, super alloys based on nickel-cobalt and iron have been developed with many additions of alloying elements and processing. These components are subjected to high temperature oxidation, hot corrosion, and erosion. The surface chemistry and structure change together with thermal, fatigue, and creep properties. The surface material of these components must be properly coated with suitable layers of hardfacing overlays. In the following, the properties of superalloys and the protection of the surfaces of the components from the degrading factors are discussed.

2.3 Ni-BASE ALLOYS

General Metallurgical Aspects

Nickel has an FCC lattice and its thermal and electrical conductivities are quite high. It is ferro-magnetic but less stronger than iron. It has a melting temperature of 1453ºC and it retains significant strength at elevated temperature. It is tough and ductile. Nickel forms extensive solid solutions in binary systems with other passivating metals like copper, chromium, iron, molybdenum and cobalt. Most Ni-base super alloys are multi component formulations and contain additional components selected from aluminium, titanium, tantalum, niobium and carbon that may be added to increase resistance to corrosion or oxidation or improve mechanical properties.

Nickel base alloys can be grouped into two categories:
  1. Alloys for corrosion resistance in aggressive chemical environments including marine

conditions. These are mainly solid solutions with simple structures designed to passivate in the given media.

2. Alloys for blades and other associated components operating at elevated temperatures in gas turbines for aircrafts. These are complex alloys containing as many as ten alloying elements. The microstructures will be designed and controlled to maintain mechanical stability and metallurgical integrity at the working environments.

Wear and corrosion resistant nickel base alloys belong to the following groups:

1. Nickel copper alloys (Monel)
2. Nickel chromium alloys (Inconel)
3. Nickel-iron-chromium alloys (Incoloy)
4. Nickel-chromium-molybdenum alloys (Hastelloy)
5. Nickel-chromium-molybdenum-titanium-aluminium alloys (Nimonic)

Nickel-copper alloys are collectively known as Monels. Monel 400 alloy contains 31% Cu has very good resistance to seawater, hydrofluoric, sulfuric acids and alkalis. The alloy is widely used in chemical industry equipments such as pumps, valves and also in marine applications. The combined nobility and passivation qualities of copper and nickel impart the corrosion resistance properties of monel.

Monels exhibit negligible corrosion and erosion corrosion in hard and soft waters at all temperatures. Monel is best suited for valves controlling the flow of water to turbines.

Nichrome and inconel are chromium alloyed nickel base, promoted to give excellent oxidation resistance at high temperature. Alloys in general use, include the binary alloy nichrome and the ternary nickel-chromium–iron inconel 600. Chromium forms an extensive solid solution in nickel but, with the iron-chromium system, the chromium content must be restricted to 20% to avoid embrittlement by sigma phase precipitation. Inconel 600 with 76% Ni, 15.5% Cr, and 7.5% Fe has good resistance to corrosion in reducing conditions characteristic of nickel with passivation in oxidizing conditions characteristic of chromium and iron.

Nickel alloys containing molybdenum, Hastelloy C276 can be used for equipments exposed to severe conditions prevailing in chemical, petrochemical and other industrial operations that are too aggressive for other engineering metals. They include concentrated sulfuric acid, hydrochloric acid, and phosphoric acid and solutions of sulfur dioxide. The stability of gamma phase depends on the balance of nickel, iron and chromium contents. Increase in molybdenum may lead to the formation of harmful sigma phase, but it will reduce vulnerability to stress corrosion cracking and pitting introduced by chlorides.

Gas Turbine Components

Nickel base superalloys have been developed for gas turbine components including blades and discs and combustion chambers. Resistance to creep and high temperature accelerated oxidation, hot corrosion are the important properties required for such applications.

Representative Nickel base alloys developed for gas turbine engines are:

(*a*) Mar M002,   (*b*) IN 738,   (*c*) IN 939,   (*d*) IN 718,
(*e*) Waspalloy,   (*f*) Astralloy,   (*g*) C 246, and   (*h*) SRR 99.

They have chromium, titanium, aluminium, molybdenum, cobalt and carbon as main alloying elements.

Designing the alloy content of nickel base superalloy is very important in the sense that the alloying elements must be in the proper proportion. Aluminium and titanium are added to nickel base alloys but their proportions must properly controlled. Figure 2.4 shows the relation between aluminium and titanium in nickel base alloys indicating two zones, one free from any defects and the other with possibility of strain age cracking.
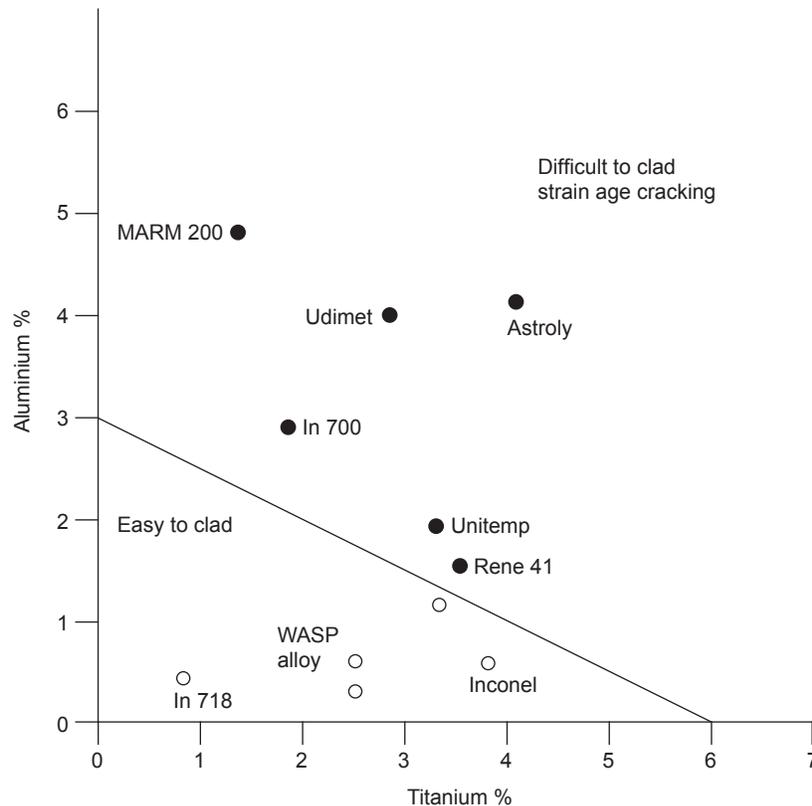

Fig. 2.4 Effect of (Al + Ti) on cladding of Ni-base Alloy

The main precipitation in Ni-base alloys is gamma prime, Ni_3Al, as fine dispersed particle in gamma matrix, that confers strength by hindering the dislocation motion. Because both gamma and gamma prime have FCC structures with similar lattice parameters, the precipitates are coherent with the matrix and have low interfacial energy and good long term stability at elevated temperatures.

Formation of gamma prime precipitates can also occur by alloy additions of titanium, tantalum and niobium with high volume fraction of the particles. The matrix can be further strengthened by adding elements such as tungsten, or molybdenum that enter solid solution, stiffening the matrix and slowing the diffusion of metallic solutes which otherwise may lead to high temperature instability.

The superalloys used in gas turbine components, are specifically designed considering the conflicting demands on alloy content to secure mechanical properties and resistance to hot corrosion at the engine operating temperature. Hot corrosion with sulfidation in the presence of NaCl and Na_2SO_4 and also V_2O_5

derived from sulfur and vanadium compounds in the fuel and the ingested air, may cause corrosion even at temperatures in the range of 600 – 700ºC.

Depending on the alloy composition, protective surface films of chromium and aluminium, namely, chromia Cr_2O_3 and Alumina Al_2O_3, will form and are distinguished by the terms chromia formers and alumina formers. The strongest superalloys have high aluminium–titanium ratios, and high concentrations of other components for solid solution strengthening. The main requirement is that the gamma prime precipitates must be stable and the other alloy components must be retained in solution. So the chromium contents are consequently reduced to below the critical compositions needed to stabilize Cr_2O_3 as the protective film. The role of Cr_2O_3 is taken over by a film of Al_2O_3, which is thermodynamically stable with respect to the alloy bulk composition.

However, the Al_2O_3 is unable to maintain the protection unaided, because the supply of aluminium by relatively slow diffusion from the interior is insufficient to replenish that which is consumed in forming and repairing the film. This can be overcome to some extent by aluminizing the surface by pack aluminizing process. The details of oxidation and hot corrosion are discussed elsewhere.

Properties of Ni-base Alloys

For wear resistance overlays nickel-chromium-boron-silicon alloys, known as self-fluxing alloys are used.

In nickel-chromium superalloys for high temperature applications, addition of chromium improves high temperature oxidation and hot corrosion resistance of the component. Inconel 600 is used as a buffer layer for building up of an austenitic overlay on a ferritic substrate. It is also used as buffer for joining dissimilar metals such as high carbon steels, alloys steels and non ferrous metals.

In nickel base super alloys titanium and aluminium content (Ti/2 + Al) combination must be less than 3. Otherwise "strain ageing" cracking will develop.

Nickel-chromium–molybdenum-niobium alloys can withstand a wide range of severe corrosive environments, including pitting and crevice corrosion. Inconel 718 alloy containing 13% Fe 3% or less Mo is used for gas turbines rocket motors, nuclear reactors, because of good weldability and creep strength.

Hastelloy B2 has good resistance to corrosion by hydrochloric, sulphuric, and reagent grade phosphoric acids and other strongly reducing chemicals. Hastelloy C276 has excellent resistance to general corrosion, pitting, and stress corrosion cracking, (SCC) in chlorine, seawater and brine. It is used for overlay on evaporator plates, forging dies and hammers. It is also used in fuel gas desulphurization plants.

Nimonic alloys have been developed for gas turbine components such as rotors, stator blades, discs, shafts compressor wheels combustion chambers and rings. They are also used in nuclear applications, boiler components in furnaces, and glass working tools. Normally TIG, MIG, or plasma transferred arc (PTA) welding processes are used to make weld overlays of nickel and cobalt base alloys.

Self fluxing nickel base alloys are available over a wide range of compositions and hardness levels. Boron and silicon are added to these alloys as fluxing agents. The formation of hard phase in these alloys is determined by the amount of chromium addition, forming chromium borides. (CrB).

These alloys possess excellent wear, corrosion, galling and oxidation resistance. The self fluxing alloys in powder form are normally sprayed with an oxyacetylene flame and subsequently fused by the same torch or by induction heating.