

CHAPTER 2

LITERATURE SURVEY

2.1 GENERAL

In recent decades, the role of surface engineering is becoming a widely recognized area for ensuring improved material performance particularly in severe environments (Bhuvaneshwaran et al 2003) and also because of the growing commercial maturity of a wide range of cost-effective surface technologies (Bell 1992). Surfaces of engineering components are subjected to higher stress and greater fatigue, abrasion, and corrosive damages than the interior. Therefore, more than 90% of the service failures of engineering components initiate at or near the surface (Gopalakrishnan et al 2002). The basic requirement is to develop a hard, wear resistant metal surface backed up by a tougher, more shock resistant core to withstand the impact loading and misalignment in service.

The success of surface engineering is demonstrated by the application of surface technologies such as thermochemical treatments and coatings to a variety of engineering components. The properties of the steel surface layers can be enhanced by changing the chemical composition of the steel surface by thermochemical processes such as carburizing, nitriding, boriding (Wahl 1996) or by hard coatings on the surface, induction hardening, and ion-impregnation on the surface (Kamat 1995). These processes play an important role in modern manufacturing technologies. They exist in many varieties depending on the type of diffusing element used and the respective

process procedure. Case hardening is one of the important heat treatment process used in industries. (Winfried Grafen and Bernd Edenhofer 2005).

There are many ways of treating the metal surfaces to enhance their tribological properties

- i) Modifying the surface without altering the substrate's chemical constitution - transformation hardening, machining and peening.
- ii) Changing the surface layers by altering the alloy chemistry by chemical/thermochemical diffusion treatments - carburizing, nitriding, boriding, ion implantation.
- iii) Adding layers of material to the surface - weld overlays, PVD, CVD, electroplating, metal spraying.

When metallic coatings are subjected to a high temperature, an alloy layer is formed which is known as diffusion coating. The diffusing species may be a non-metallic element such as C, N, B or Si or a metal such as Al, Zn or Cr (Castle and Gabe 1999). The outstanding characteristic feature is the metallurgical bond produced between the coating and the substrate by diffusion. If intermetallic compounds are formed within the diffusion layer, they may produce diffusion barriers or create brittle effects. The application of diffusion coatings has become an established metallurgical tool for the protection and upgradation of a diverse range of metals.

Boriding or boronizing is a process of diffusion of boron into the surface in the range of 973 K-1273 K for 1-12 h (Sinha 1991). Diffusion of boron into the surface results in the formation of metallic borides, which provide extremely hard, wear and erosion resistant surfaces. The interlocking structure of borides with the base metal provides excellent layer adhesion.

Thermochemical boronizing of iron alloys depends on the composition of the base metal. Alloying elements greatly influence the deposition and properties of iron borides in the thermally grown surface layers. The formation of iron boride layers on ferrous substrate has a wide range of applications.

Boronizing can be performed in numerous ways, including gas boronizing, molten salt boronizing, with and without electrolysis and pack boronizing (Ugur Sen et al 2004). Solid boronizing produces stable profile qualities with the advantage of processing at relatively low temperatures for short durations (Yang and Peng 2003 and Song et al 2001). In liquid boriding, in an induction salt bath, a reinforced type boride structure is formed. Such borided parts possess increased resistance to crack formation, which finds application in dies, tools and measuring instruments (Simonenko et al 1982). Boronized steel possess high hardness values of 1400-2000 Hv_{0.1} and good wear-resistance, but is brittle.

Chromizing is a surface treatment, where Cr is diffused into the steel to provide high temperature surface protection, corrosion and wear resistance (Jyh Wei Lee et al 2002). In soft chromizing, Cr is diffused into the steel containing < 0.1% C. In hard chromizing, Cr is diffused into the steel containing $\geq 0.3\%$ C. During the process, the C in the base metal combines with the Cr to form chromium carbide on the surface of the steel with hardness varying from 1800-2200 Hv_{0.1}. This layer, which is around 10-30 μm thick, provides the resistance against wear, corrosion and temperature. Core hardening after chromizing is also possible (Jongbloed 1994).

2.2 ALUMINIZING

Aluminizing is a thermo chemical diffusion treatment where in the surface layer of the material is impregnated with aluminium. It is primarily

used on steels, but also on nickel and cobalt based alloys to obtain greater creep resistance, hardness and corrosion resistance.

The characteristic feature of this process is a two-stage formation of strong bonds between atoms of the materials. In the first stage, a physical contact is established i.e. the materials being bonded are brought close to allow interaction between atoms. In the second stage, the chemical interaction, the formation of a strong bond is completed. The atoms come together as a result of the wetting process and thermal activity on the surface of the solid material. A definite time is allowed to form a bond depending on the physical contact process and the chemical interaction of the phases. (Ryabov 1985). Wetting and nucleation are relatively fast processes and take 1-3 seconds to complete (Yeremenko et al 1981). The interface morphology is controlled by the nucleation rate of the aluminide grains at the initial surface of contact and the intermetallic diffusion (Denner and Jones 1976, Kwon and Lee 1981).

2.2.1 Fe-Al Binary System

Fe-Al phase diagram shown in Figure. 2.1. (Kattner and Massalski 1990) consists of five types of intermetallic compounds (Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_3 phases). FeAl_2 , Fe_2Al_5 and FeAl_3 compounds with a high aluminum composition, have limited application due to their brittleness (Lee et al 1992) and reduced oxidation resistance (Soliman et al 1997). Conversely, high iron composition compounds Fe_3Al and FeAl may be used as structural materials because of their good wear resistance, oxidation resistance, corrosion resistance and specific strength properties (Stoloff 1998). Therefore, the preferential growth of Fe_3Al and FeAl layers can improve the fracture toughness, oxidation resistance and interface strength of aluminized steel.

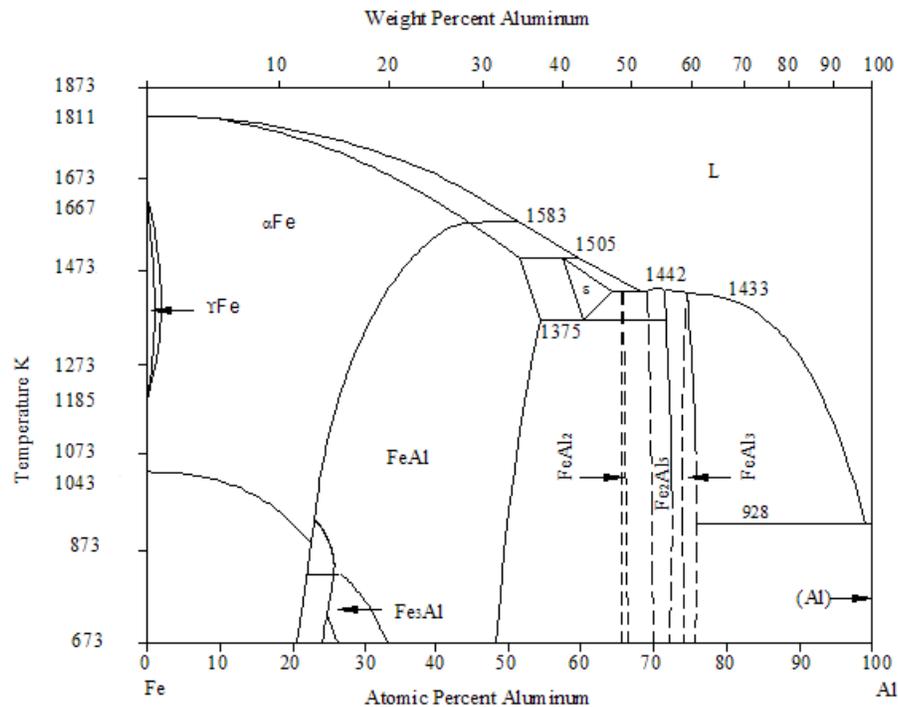


Figure 2.1 Phase diagram of Fe-Al (Kattner and Massalski 1990)

The formation and growth of intermetallic compound layers during dissimilar metal contact at high temperatures is a common phenomenon (Hickel et al 1975 and Bhagat 1988). The control of intermetallic layers is important for improving interfacial strength in processing techniques concerned with the interfacial reaction between steel and aluminum such as welding, diffusion bonding and hot dip coating (Yeremenko et al 1981). It is established that the growth of the intermediate phases can be governed by chemical reactions at the interfaces (linear kinetics) and by interdiffusion of the reacting species through the different phases (parabolic kinetics).

The preferential growth of Fe-Al intermetallic compound layers with high aluminum composition is dependent on diffusion coefficients between the steel substrate and the molten aluminum. The diffusion

coefficient of iron into aluminum, which is $53 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ (793 - 922 K) (Neumann 1990), is larger than that of aluminum into iron, which is $1.8 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ (1003 - 1673K) (Le Claire 1990). The temperature range of the Fe into Al is lower than that of the Al into Fe. Moreover, the growth rate of the intermetallic compound layers decreases with increasing carbon content in the steel substrate, and is inhibited by silicon atoms (Koda et al 1962 and Akdeniz et al 1998).

2.2.2 Types of Aluminizing

Various coating methods include the following:

- Spraying, in which aluminium wire is flame melted, atomized and deposited on the steel surface by a gas blast surrounding the flame.
- Electrodeposition from molten salt or organic liquid electrolytes.
- Vacuum deposition from condensation of aluminium vapour formed by evaporation.
- Cladding in which aluminium is rolled, drawn or extruded into the steel surface.
- Hot dip aluminizing in which steel is dipped into molten aluminium.
- Calorizing or cementation from powder mixtures of aluminium and ammonium chloride at high temperatures.
- Special process using combinations of aluminium powder with ball milling, the firing of frits and extrusion.

2.2.3 Selection of Process

The criteria for selecting a particular technique depend primarily on the understanding of the basic principles of operating mechanism, coating or modified surface/substrate interactions and the behaviour between modified surface and its environment during use.

In order to identify a suitable aluminizing method (process of alloying with aluminum), a comparison was made on the relative merits of the different aluminizing methods commonly encountered in the literature (Ryabov 1985). Based on the results of this comparison shown in Table 2.1, hot-dip aluminizing (HDA) was chosen as the method of incorporating the alloying element aluminium into the medium plain carbon steel.

Table 2.1 Comparative data on different aluminizing methods (Ryabov 1985)

Process	Coating thickness (mm)	Relative cost	Absence of intermediate layer	Continuity of coating
Hot-dipping	0.01-0.08	1 ^a	2	2
Cladding	0.01-0.13	2	3	1
Galvanic coating	0.003-0.05	3	1	3
Metallizing	0.05-0.50	4	1	4
Calorizing ^b	0.25-1.10	3	4	-

^a Rating of 1 indicates the best results

^b includes all types of diffusion coatings in solid mixtures.

2.2.4 Effect of Alloying Elements in the Molten Bath

Hughes and Moses (1953) reported that the coating thickness increases with dip temperature and dip time due to growth of the alloy layer. This provides the bonding of the coating to the base metal. The excessive

growth of the alloy layer deteriorates the mechanical properties. Alloying elements like C, Si, Cr, Ni, Mn, Cu in the substrate reduces the thickness of the alloy layers (Niinomi and Ueda 1982). Bath additions of Si, Cu, Be improves the ductility of the coating (Gittings and Rowland 1951, Eggler et al 1986) but decreases the corrosion resistance, electrical conductivity and silver luster (Langenscheid and Klein 1977). The addition of alloying elements like W, Mo and Nb to the aluminium melt also reduces the thickness of the alloy layers.

Silicon is used as the major alloying element to decrease the alloy layer thickness and to make the alloy layer smooth (Li Yajiang 2002). The tendency of Si to increase the spalling rate of the alloy layer (Richards 1994). When Si is maintained between 3-5%, it is observed that the layer formed is least. The addition of 11.6% Si reduces the growth rate of the diffusion layer $FeAl_3$ and Fe_2Al_5 compared to the pure aluminium bath (Stroup and Purdy 1950).

Many researchers have reported that the major effect of Si is to increase the dissolution rate of the alloy layer producing a thinner layer and to inhibit the solid state diffusion on annealing hot dipped aluminized steels (Heumann and Dittrich 1959, Jones and Richards 1988) and aluminium coated, high silicon containing steels (Bedford and Boustead 1974).

2.2.5 Effects of operating variables

During hot dip aluminizing several variables besides the coating alloy composition influence the thickness of the Al and alloy layers in the coating. The effects of some of these variables are:

- i) Bath temperature: When the dip time is kept constant, the aluminum coating thickness decreases as the bath temperature

increases. As the temperature increases the thickness of the alloy layer also increases.

However, the aluminum layer will stop thickening with time at a given temperature, when identical temperature and complete wetting occur between liquid aluminum and the substrate surface. This combination produces losses in coating ductility and corrosion resistance.

- ii) Dip time: The temperature and time during which steel and Al are in contact determine the rate and extent of diffusion between Al and steel. Irrespective of the dip temperature, the thickness of the aluminium coating reduces with increase in dip time.
- iii) Speed: Higher speeds of withdrawal from the coating bath and more rapid cooling after coating also increase the thickness of the Al layer. As temperature increases, a thick interfacial layer is formed. Steels of higher carbon and alloy content produce thinner coatings.

Thus during the hot dip aluminizing method (HDA), the process variables can be identified as the temperature of the coating bath, dip time and withdrawal speed.

2.2.6 Hot dip aluminizing

Hot dip aluminizing is an efficient means of providing corrosion protection to iron and steel at elevated temperatures and in a variety of atmospheric conditions (William C. Patterson and James E.Hall 1970). Hot dipped aluminized steel can even replace stainless steels in some cases, and can be applied to many industries such as petroleum refineries, electric power, transportation, and metallurgy through products like heat exchangers, pipes

on ships, fences on expressways, outdoor billboards, furnace components, and exhaust pipes (Li et al 2001, Wei 1997 and Wu et al 2004).

The alloys containing high Al are difficult to make and handle due to poor workability and mechanical properties. It is therefore, beneficial to provide a diffusion layer on iron and steel with aluminium, coupled with the inherent ductility and toughness of the base steel (Bahadur and Mohanty 1995).

Arora et al (1966) conducted detailed studies on coating by aluminizing process and developed suitable techniques for application in auto-mufflers, furnace hardware, petroleum refinery equipments, jet aircraft parts, telephone and telegraphic wires. Metal-coated steel wires are widely used as supports for telecommunication cables. The erosive wear and corrosion behaviour of zinc and aluminum-coated steels in simulated coastal environment were studied and it was found that the aluminum-coated steel performed 60% better than the zinc coated steel (Horng et al 2003).

Denner and Jones (1975) and Bahadur and Mohanty (1995) conducted studies on adherence of coating in hot dip aluminizing of sheets of low and medium carbon steel. The phases formed in the case of the interaction of pure liquid aluminium (or saturated with iron) with pure solid iron (or a mild steel) are FeAl_3 near aluminium and Fe_2Al_5 near the ferrous substrate (Eggler et al 1986). Li Yajiang et al (1995) reported that FeAl and Fe_3Al intermetallic layers with a low aluminum composition were formed by heat treatment of low-carbon aluminum-coated steel at 1323 K for 15 min.

Previous studies were mainly concerned with hot dip aluminizing of steels and effort was often directed towards adherence. Eggler et al (1986) studied the reactions between low alloyed steels and pure as well as iron saturated aluminium melts. They detected two intermetallic layers, the Fe_2Al_5

phase adhering to the steel substrate by an irregular interface and the FeAl_3 phase adhering to the solidified aluminium. Bouche et al (1998) studied the interaction between solid iron and liquid aluminium. The Fe_2Al_5 and FeAl_3 phases were identified in the temperature range of 973-1173 K and found that their growth is mainly controlled by diffusion.

Mohamed (1999) has investigated the effect of diffusion temperatures of 1223, 1273 and 1323 K and diffusion times of 3, 5 and 7 h on the thickness of aluminized coating layer and also the influence of diffusion annealing on the aluminized surface. The penetration of the coating material into the carbon steel was more pronounced due to annealing and coating thickness increased with increase in the diffusion temperature and time. The abrasive wear resistance of aluminized carbon steel increased with increase in the diffusion temperature. It was found that the specimens treated at 1323 K and 7 h offered minimum wear values.

Shigeaki Kobayashi and Takao Yakou (2002) conducted aluminizing experiments on steel containing 0.45% C at dip temperatures of 973, 1023, 1073 and 1173 K for a dip time of 5 min. Diffusion treatment was carried out at temperatures of 873, 1073, 1273 and 1323 K for 20 min or 1 h in air. It was found that the thickness of the coating layer increases with increasing dip temperature. Fe_2Al_5 was formed at temperatures lower than 1273 K, while FeAl and Fe_3Al were produced at temperatures higher than 1273 K.

Sasaki (2003) carried out experiments to obtain the ductile and corrosive coating by aluminizing treatments using aluminum foil on mild steel surface at diffusion temperature from 973 to 1273 K. The foil aluminized steels at diffusion temperature less than 1073 K, had a thin brittle layer of aluminum rich intermetallic Fe_2Al_5 and that at diffusion temperature greater than 1173 K had thick layers of iron rich intermetallics such as FeAl and

Fe_3Al . It was found that the three body abrasive wear rates of aluminized steels diffused at higher than 1173 K against free SiC grains were smaller than those of the steels diffused at higher than 1073 K.

Wang Deqing et al (2003) studied the coating of pure aluminum on a steel substrate followed by oxidation. The specimens were dipped at different temperatures of 963, 983 and 1003 K and heated in air to a temperature of 823 K for 1 h. X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analysis revealed that the top portion of the steel substrate is composed of a thin layer of $\alpha\text{-Al}_2\text{O}_3$ followed by a thinner layer of FeAl_3 and then a much thicker one of Fe_2Al_5 on the steel base side. In addition, there is a carbon enrichment zone in diffusion front. Controlled corrosion test was conducted in pure aluminum bath at 1023 K for 240 h and 983 K for 120 min. The aluminum oxide formed on the steel substrate after corrosion test in liquid aluminum at 1023 K for 240 h, had good resistance to aluminum melt corrosion.

Xinmin Luo et al (2005) have carried out studies on aluminizing of plain carbon steel. The specimen was dipped in an aluminium bath at 993-1013 K for 10-30 min followed by diffusion treatment at 1203 K for 5 h. The microhardness of 780-820 $\text{Hv}_{0.1}$ along the aluminized layer was achieved, which gradually reduced to the hardness of the matrix (135-160 $\text{Hv}_{0.1}$).

Chaur-Jeng Wang and Shih-Ming Chen (2006) conducted aluminizing studies by dipping low carbon steel into a molten bath containing Al-10 wt. % Si. The high-temperature oxidation behaviour of the specimen was studied at 1023, 1123 and 1223 K for 72 h in air. After hot dip aluminizing, the coating layer has three phases Al, FeAl_3 , and Fe_2Al_5 . The Fe_2Al_5 formed during dipping, got completely transformed to FeAl_2 , FeAl and

α -Fe (Al) phases because of the composition gradient and the chemical diffusion by oxidation.

Kee-Hyun Kim et al (2007) have carried out studies on aluminizing of mild steel with dip time of 3 s at 933 K (10 % Si). He has reported that a thin Fe_2SiAl_8 alloy is formed adjacent to the interface and Si content of at least 5-6 at. % in concentration is required in the melt.

2.2.7 Wear Studies

Efforts are being made mainly on process, development and enhancement of room-temperature ductility together with the characterization of physical properties such as mechanical properties, oxidation and corrosion (McKamey et al 1991). However, there have been only a few works reported regarding the wear characteristics of the aluminide, one of the most important material properties of the ordered intermetallic alloy. Moreover, the reported works on wear dealt with only abrasive and erosive wear of the alloy (Maupin et al 1992).

Yong-Suk Kim and Yong-Hwan Kim (1998) have investigated room temperature dry sliding wear behaviour of iron-aluminides containing 25, 28 and 30 at. % aluminum using a pin-on-disk wear tester. Wear resistance of the aluminides decreased with the increase in aluminum contents. SEM observations of worn surfaces of the aluminides showed ductile material's wear behaviour associated with plastic deformation.

Garima Sharma et al (2004) have investigated room temperature dry-sliding wear behaviour of iron aluminides (Fe-28 at. % Al-3 at. % Cr) using a ball on plate wear tester. SEM observation of the worn surface showed that microploughing, microcutting and surface delamination were the

dominant sliding wear mechanisms. Wear mechanism of the iron aluminides was plastic deformation dependent.

Though sliding wear and friction of the aluminide have not yet been extensively reported, some researchers have investigated the sliding wear behaviour of Ni-Al intermetallic compounds (Marquardt et al 1985, Blau and DeVore 1988, Johnson et al 1996).

2.2.8 Corrosion Studies

Aluminized coatings provide excellent protection to steel in marine, industrial and rural environments. Though more anodic than iron, aluminium has only a very limited ability to protect steel cathodically. Corrosion tests conducted on aluminized steel by various researchers (Hughes 1953) indicate that aluminized coatings are highly resistant to atmospheric corrosion and are suitable in the humid and sulphurous atmospheres in which zinc is liable to greatly increased attack

From the studies that have been conducted, it appears that in both industrial and rural environments hot dip aluminized steels offer markedly superior corrosion resistance than galvanized or zinc-aluminium coated steels (Kweichen and Pasiak 1987, Tierra and Molera 1985 and Nicholls 1960). Dunbar (1982) reported that the aluminized steel has a slightly greater tendency to pitting corrosion, red rust staining and coating darkening on atmospheric exposure. These imperfections are said to occur from a galvanic effect between the silicon rich inclusions in, and the aluminium matrix of, the outer coating. The unavoidable presence of solute iron in the outer coating has also been shown to exert galvanic effect, which can reduce its corrosion resistance (Schmitt and Rigo 1966, Aksenova et al 1982).

Dovey and Waluski (1963) have also reported premature darkening of aluminized coatings on atmospheric exposure but this does not reduce corrosion resistance. Rigo (1961) found that similar bluish darkening and / or red rust staining often associated with a surface effect. In saline and marine environments, disruption of the surface alumina film on aluminized steels has been shown to facilitate cathodic protection of the steel base at pores and cut edges (Townsend et al 1987). This effect probably arises from chloride ion produced by the dissolution of the alumina film (Davies and Hanford 1970).

The corrosion resistance of aluminized coatings stems from the protective oxide on aluminium surface and the relative insolubility of aluminium corrosion products (John D. Sprowl, 1961). Higuchi and Asakawa (1991) have shown that in continuous salt spray testing the relatively higher rate of corrosion is associated with the formation of the bulky and porous corrosion products, while the lower rate of corrosion in alternate salt spray and humidity testing is associated with finer, amorphous corrosion products forming a more protective film. Al coated carbon steel tubes are found to be more corrosion resistant than zinc coated low carbon steel tubes from the result of a neutral salt spray test for 48 h (Guo and Wu 1995).

2.2.9 Interaction of Steel with Molten Aluminium

The aluminium coating on steel consists of an outer most Al layer and an intermediate layer of Fe Al alloy. When steel is dipped in a commercially pure aluminium melt and sufficient time (of the order of 1 min or more) is given, the intermetallic phase formed consists of mostly Fe_2Al_5 phase. The growth of this layer is represented by an expression of the form $\delta^2 = k * t$, where δ is the thickness of the alloy layer, k is a constant known as the growth rate constant and t is the holding time.

The Al layer, which provides corrosion resistance, may be one of several Al alloys. The intermediate alloy layer, which bonds the Al to the steel, consists of intermetallic compounds such as Fe₃Al and FeAl which may be altered in structure and properties by the composition of both the Al layer and the steel base. The steel base may be plain carbon, alloy or stainless steel.

The control of the formation of Fe-Al compound is a major problem in coating the steel with aluminium. For resistance to oxidation and scaling, the compound should not form to such an extent that the surface becomes brittle and spalls. When the aluminium content of the surface zone approaches 50%, a brittle condition exists.

When hot-dipped aluminized steels are heated, a temperature is reached at which a significant rate of coating-substrate interdiffusion is initiated. As a result, the alloy layer increases in thickness and eventually grows through to the surface of the material. When this occurs, the outer aluminium or Al-Si coating will have been consumed in reaction diffusion.

The concentration gradient of aluminium in the material, after diffusion treatment, can be analyzed by using Fick's law of diffusion

$$(\delta C / \delta t) = D * (\delta^2 C / \delta x^2) \quad (2.1)$$

where C is the concentration of the diffusion species, D is the diffusion coefficient of the diffusing species, t is the time and x is the distance.

A simplified approximate solution to the above equation can be obtained if we assume an average of D, i.e. the diffusion coefficient of the diffusing species is independent of its concentration. The solution is of the form

$$(C_x - C_o) / (C_s - C_o) = 1 - \text{erf} (x / (2\sqrt{(D*t)})) \quad (2.2)$$

where C_s is the surface concentration of the diffusing species, C_x is the concentration of the diffusing species at a distance x from the surface, and C_o is the original concentration of the diffusing concentration of the diffusing species in the substrate.

2.3 NITRIDING

Among the processes for the improvement of surface properties of machine components, nitriding holds an important position in industry (Kurney et al 1983). Nitriding is a ferritic thermo chemical method of diffusing nascent nitrogen into the surface of the substrate material. There is no molecular size change and no significant dimensional change, only slight growth due to the volumetric change of the steel surface caused by the nitrogen diffusion. Nitriding of ferrous alloys involves the temperature dependent interaction of substitutional solutes (alloying elements) with interstitial nitrogen. At temperatures as low as 623 K, substitutional atoms are almost immobile. This changes the activity coefficient of nitrogen in iron and so their effects on the amount, size and rate of precipitation of iron nitrides from supersaturated solution are marked (Lightfoot and Jack 1973). Nitrogen has partial solubility in iron. It can form a solid solution with ferrite when nitrogen contents are upto about 6% (Fe_3N).

Nitrided steels are generally medium carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminium, chromium, vanadium and molybdenum which form hard nitrides with surface hardness of 1000-1500 $Hv_{0.1}$ (Goncharenko et al 2003) that are stable up to the nitriding temperatures. Since aluminum is the strongest nitride former, aluminum-containing steels (0.85-1.25% Al) yield the best nitriding results in improving wear and fatigue resistance. This effect is due to the high hardness of aluminum nitride and high internal stress derived from the formation of nitrides, which strain the ferrite lattice and create strengthening

dislocations. Titanium and chromium are also used to enhance the case hardness although case depth decreases as alloy content increases. Molybdenum in addition to its contribution as a nitride former also reduces the risk of embrittlement at nitriding temperatures.

It is well established that nitriding of plain carbon steels would produce a case of only moderate hardness. This is largely because nitrogen diffuses quickly beneath the surface forming iron nitrides dispersed to greater depths so that surface hardness is comparatively reduced. Since the nitride forming elements have a higher affinity for nitrogen, they prevent the diffusion to a greater depth by forming very hard stable particles near the surface; giving an extremely hard but shallow case (Ashrafizadeh 2003). The depth of nitriding decreases with increasing content of nitride forming elements; the reason for the inhibiting effect of the alloying elements is that they bind the nitrogen as nitrides.

Nitriding is used to confer both wear resistance and fatigue resistance on engineering components. The advantage of nitriding over other surface hardening methods is the reduced risk of distortion through the low treatment temperature, usually 773-813 K, and the elimination of quenching. Among the disadvantages of the nitriding process are long process times, typically 24-72 h, the need to use special steels containing chromium and/or aluminium, and the formation of a brittle white layer which for many applications has to be removed before a nitride component can be put in service (Clayton and Sachs 1976). Due to long process times, increased material and treatment costs of such alloys and a lack of sufficient control over the process, gas nitriding has never been developed to its full potential (Staines 1996). Liquid nitriding has been used particularly in automotive industry, where important combination of increased wear resistance and

fatigue strength results in large scale application such as in crankshafts, cylinder liners, cam shafts and valves (Astley 1973).

2.3.1 Nitrocarburizing

Nitrocarburizing is a thermochemical process, carried out at temperatures in the 833 – 853 K range well within the upper boundaries of the ferritic phase field of iron, and involves the diffusion of carbon and nitrogen into a ferrous matrix (Bell 1976). Once the nitrogen content exceeds the solubility limit in the matrix, a compound (white) layer is formed which is characterized by good tribological features such as high hardness, superior wear and seizure resistance (Wahl 1996 and Pereloma et al 2001). This compound layer consists of ϵ Fe₃N, γ' Fe₄N, Fe₂N, Fe₃C, and Fe₂O₃ and also alloy carbides and nitrides. The best wear resistance properties are achieved when the layer predominantly consists of ϵ Fe₃N. If parts remain within the ferritic phase field during the treatment, quenching stresses and distortion are minimized (Reynoldson 1995). This makes ferritic nitrocarburizing a valuable alternative to carbonitriding when parts must meet tight tolerances (James 1979).

Nitrocarburizing can be applied in the solid, liquid or gaseous states, or using plasma techniques. The treatment media may determine the composition and thickness of the white layer, as well as the depth of the diffusion zone due to the difference in the diffusion rates of carbon and nitrogen. Liquid state techniques use a salt bath and these processes are rapid and generate good quality compound layer. The plasma process offers excellent control of the gas mixture and reduced processing times, energy consumption. Gaseous nitrocarburizing has a good control over the formation of white layer phases. Fluidized bed reactors offer the same advantages as gaseous nitrocarburizing (Reynoldson 1993) with a reduced time process.

Process developments have significantly enhanced the corrosion resistance and aesthetic appearance of treated components to make nitrocarburizing competitive with electroplated finishes (Dawes 1991). Hence, nitrocarburizing is perhaps the most versatile surface treatment for ferritic steel and has a potential for wide application (Somers et al 2000).

2.3.2 Plasma Nitriding

Plasma nitriding of steels developed by Egan (1930) is a well-established commercial surface-hardening process, which provides wear, fatigue and corrosion resistant surfaces (Prabhudev 1988 and Baldwin et al 1998). Depending on the process parameters and the steel composition, a diffusion zone is formed, with N penetrating up to 0.7 mm into the steel. Frequently, a surface compound zone is also formed on top of the diffusion zone, with thickness in the micron range. In the diffusion zone, the microstructure is changed by the introduction of single interstitial N atoms in solid solution and when the solubility limit is reached, very fine coherent nitride precipitates are formed. The hardness is only slightly changed by the nitrogen in solid solution, while the hardness increases substantially when the nitride precipitates form, depending on the nitride-forming alloying elements. In the compound zone, γ (Fe_4N) and ϵ (Fe_{2-3}N) intermetallics as well as nitrides with alloying elements are formed.

The advent of plasma nitriding (Edenhofer 1974) has led to an increased interest in the application of the process to plain carbon (non-alloyed) steels for obvious advantages offered by these materials. Such treatment would affect the surface related properties such as resistance to applied loads; to adhesive and abrasive wear, to rolling contact fatigue and to corrosion.

2.3.3 Gas Nitriding

Gas nitriding is a casehardening process whereby nitrogen is introduced at surface of a solid ferrous alloy by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia. The nitriding temperature for all steels is between 763 K and 863 K. Because of the absence of a quenching requirement with attendant volume changes, and the comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than either carburizing or conventional hardening. Some growth occurs as a result of nitriding but volumetric changes are relatively small.

2.3.3.1 Single and Double Stage Nitriding

Either a single or a double stage processes may be employed when nitriding anhydrous ammonia. In the single stage process, a temperature in the range of about 768 K to 798 K is used and the dissociation rate ranges from 15 to 30%. This process produces a nitrogen rich layer known as the white nitride layer which is extremely hard but very brittle. The double stage process has the advantage of reducing the thickness of the white nitrided layer. The first stage of the double stage process is a duplication of the single stage process except for time. The second stage may proceed at the nitriding temperature employed for the first stage or the temperature may be increased from 823 K to 838 K. However, at either temperature, the rate of dissociation in the second stage is increased to 65 to 80% (preferably 75 to 80%). Generally an external ammonia dissociator is necessary for obtaining the required high second stage dissociation.

The principal purpose of double stage nitriding is to reduce the depth of the white layer produced on the surface of the case. Except for a reduction in the amount of ammonia consumed per hour, there is no

advantage in using the double-stage process unless the amount of white layer produced in single stage nitriding cannot be tolerated on the finished part or unless the amount of the finishing required after nitriding is substantially reduced.

2.4 DUPLEX TREATMENT

The coatings field is developing rapidly which has led to the development of duplex treatment. It is a combination of two surface engineering processes involving coating by deposition of a material followed by a thermochemical process such as nitriding or carburizing. The new challenges or the complex loading situations can be met only through realizing the potential of duplex treatment. Indeed, there are great technical and economic benefits available through the application of duplex surface engineering technologies in many new market sectors (Bell 1998). Limitations to the further advancement of manufacturing industry in the 21st century are most likely to be surface-related.

2.4.1 Aluminizing and Nitriding

Chudina (1994) studied the surface treatment of low carbon steel by laser alloying and subsequent nitriding. The microhardness and wear resistance were increased to a greater extent. The steel surface was alloyed with vanadium or chromium without laser beam path overlapping and subjected to nitriding at 783-813 K for 25-30 h to increase the crack resistance.

Tsuji et al (1995) studied the surface hardening of 5Cr-1.25Mo-1V-die steel by aluminum vapor deposition, diffusion annealing and ion nitriding. The diffusion was carried out at temperatures from 1123-1323K for 1 h. The

Al rich layers of the steel were nitrided at 923K for 2 h. The hardness of the coated layer was found to be 1300-1400 HV_{0.1}.

Lee et al (1996) have carried out duplex plasma surface treatment by calorizing and plasma nitriding on mild steel and high-alloyed tool steel to improve their elevated temperature wear properties. Calorizing was done at 1323 K for 5 h, which created a FeAl compound layer of 120 µm thickness. On subsequent plasma nitriding of the calorized layer, the surface hardness was increased to above 1200HV_{0.1} with the nitriding depth of 80 µm.

Tsuji et al (1999) have conducted the duplex treatment studies on the SKD61 die steel. The nitriding zone consists of the Al-diffused nitriding layer and the nitriding layer of the matrix. The Al-diffused layer showed the hardness of about 270 Hv_{0.1} and the matrix showed the hardness of about 610 Hv_{0.1} corresponding to the die steel quenched.

Bindumadhavan et al (2000) reported that aluminizing followed by diffusion treatment and nitriding of plain carbon steel could provide an alternative to the use of expensive nitridable steels for piston ring application. The specimens were dipped in molten Al-Si bath at 988 K for 3 min, diffused at 1173 K for 8 h and gas nitrided. Surface hardness was increased by this process from 580 to 1208 Hv_{0.1} for EN32B steel and from 650 to 1454 Hv_{0.1} for 15CR3 steel. It has also been found that the nitrided case depth obtained (0.11-0.13 mm for EN32B steel and 0.10-0.14 mm for 15CR3 steel) matches well with the general requirements of the piston ring industry.

Liu et al (2004) carried out pack aluminizing on low carbon steel (0.2% C) and pure iron at 1223 K for 6 h followed by plasma nitriding at 833 K for 8 h. On aluminizing, a layer of 100 µm thick with a hardness of 300±10 Hv_{0.1} was obtained. After plasma nitriding, a dark hard surface region 20 µm to 40 µm thick was formed with hardness as high as 1300±50 Hv_{0.1}

Koji Murakami et al (2004) have combined aluminizing with ion nitriding to achieve high hardness of about 1500 Hv_{0.1}. An excessive Al concentration will hinder nitriding, causing the modified layer to become fragile and delaminate easily from the substrate.

2.4.2 Aluminizing and Chromizing

Kim et al (2000) developed a new pack process for simultaneous deposition of Cr and Al on low alloy steel. This process is characterized by the pack composition using elemental Al and Cr₂O₃ powder as the Al and Cr sources. Cr₂O₃ is converted by aluminum halide (or Al) to Cr halide (or Cr), which is deposited along with aluminum onto the metal surface. At a higher weight ratio of Cr₂O₃ to Al, the aluminum content in the coating layer decreased with increasing temperature, while the Cr content increased. The decrease in aluminum content is mainly related to the activated conversion of Cr₂O₃ to chromium halide by aluminum in the diffusion layer.

Heo et al (2000) investigated the codeposition of Cr and Al on austenitic stainless steel by using the conversion reaction of Cr₂O₃ to halide. A codeposited coating layer had a high oxidation resistance. Zheng and Rapp (1998) developed a two-step pack-cementation process (Al-Cr coating) on carbon steels involving the first treatment at 1198 K and the second at 1423 K. A dense and uniform coating with surface compositions of approximately Fe₃Al plus several wt. % Cr with high hardness was obtained.

2.4.3 Chromizing and Nitriding

Do Yon Chang et al (1999) conducted duplex plasma surface treatments of chromizing and plasma nitriding on various alloys such as mild steel (AISI 1020), AISI H13 and 1Cr-0.5Mo steel (ASTM A213). Chromizing by pack cementation process at 1473-1573 K for 5 h created a Cr diffusion

layer of approximately 150-300 μm thickness. Subsequent plasma nitriding at 803 K for 1 h on the Cr-diffused layer induced formation of a duplex-treated surface layer with a high hardness of 1500 $\text{Hv}_{0.1}$ due to the formation of CrN and Fe_xN phases. The wear volume of the duplex-treated AISI 1020 and H13 steels after a wear test at 873 K were reduced by a factor of 8 and 3 respectively when compared to the chromized specimens.

Baggio-Scheid (2003) developed new duplex surface treatments consisting of chromium pack diffusion and plasma nitriding of mild steel. Chromizing was carried out at 1173 K-1573 K for 5h and plasma nitrided for 1 h at 723 K. Chromium-diffused layers of upto 150 μm was obtained. The subsequent plasma nitriding increased the surface hardness to 1400 $\text{Hv}_{0.1}$ due to the formation of CrN and Cr_2N . The increase in hardness and corrosion resistance has led the possibility to use this material as substitute for tool steel applications.

2.4.4 Chromizing and Boriding

Sang Yul Lee et al (2004) conducted studies on pack cementation of chromizing and boronizing on AISI 403 stainless steel. Chromizing at 1373 K for 2 h created a Cr diffusion layer of 130 μm thickness. Subsequent boronizing at 1223 K for 9 h on the Cr diffused layer induced formation of duplex layer of approximately 50 μm thickness with high surface hardness of 2300 $\text{Hv}_{0.1}$. The duplex treated specimen showed a much-improved high temperature oxidation resistance, which could be attributed to the high Cr content (20 at. %). The wear volume of duplex treated specimen after a wear test at 773 K, when compared with boronized specimen, was reduced by a factor of 1.5.

2.4.5 Aluminizing and Boriding

Maragoudakis (2002) developed a simultaneous one-step boroaluminizing process for 2.25Cr-Mo steel at 1223 K for 6 h. Three distinct regions were found in the coating consisting of an outer Al-rich layer, a transition region containing Al and Fe and an inner layer containing mostly B and Fe.

Xinmin Luo et al (2005) conducted studies on duplex treatment of aluminizing and boronizing. Plain carbon steels and alloyed steel were dipped in molten aluminium bath at 993 K, diffusion-treated at 1203 K for 5 h and boronized at 1223 K for 6 h. Good anti corrosion ability, higher wear-resistance and excellent anti-oxidization at elevated temperatures were achieved with brittleness (Ji et al 2002).