CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

“Stainless” is a term coined, early in the development of steels, for cutlery products. It was adopted as a generic name and now covers a wide range of steel grades for corrosion or oxidation resistant applications. Stainless steels owe their corrosion resistance to the presence of a “passive”, chromium-rich, oxide film that forms naturally on the surface. Extremely thin, 1-5 nanometers (ie $1.5 \times 10^{-9}$m), and invisible, this protective film adheres firmly and forms an oxide film on the surface (Leif Karlsson et al 2004). Furthermore, the protective oxide film is self-healing. Therefore, even when the steel is scratched, dented, cut, oxygen from the air immediately combines with the chromium to reform the protective layer. However, stainless steels cannot be considered to be “indestructible”.

2.2 HISTORY OF STAINLESS STEEL

In order to obtain a perspective of the development of stainless steel, it is appropriate to look back to the beginning of the century; stainless steel is actually no older than that. The stainless steel was originally discovered and developed in England and Germany during 1910. When steel researchers were experimenting with different types and qualities of alloys, stainless steel was discovered independently, around 1913 by researchers in Britain and Germany. The first true stainless steel was melted on 13th August 1913 in
Sheffield, UK by Harry Brearley. This first stainless steel was martensitic with 0.24%C and 12.8% Cr (Leif Karlsson 2004). Within a year of Brearley's discovery, Strauss & Maurer developed the first austenitic grades while experimenting with Ni additions to find a suitable material for protective tubing for thermocouples and pyrometers in Essen at Germany with 0.25%C, 20%Cr, 7%Ni. During the same period, Dansitzen in US, who studied alloys similar to those that Brearley was investigating, but with lower Carbon (C) and Chromium (Cr) without Nickle (Ni) contents, discovered the ferritic stainless steels. The first duplex stainless steel was produced in Sweden, around 1930, for applications in the paper industry.

The commercial production and use of stainless steels in the United States began in the 1920 by producers like with Allegheny, Armco, Carpenter, Crucible, Firtho Sterling, Jessop, Ludlum, Republic, Rustless in U.S. By the late 1920’s, two types of stainless steel had been found to be most versatile and useful; martensitic stainless steel (chromium content of 13-18 percent) and austenitic stainless steel (18 percent chromium and 8 percent nickel). Today, stainless steel is a generic term given for a group of corrosion resistant steels containing a minimum of 10.5%Cr, which creates a passive, self renewing film of chromium oxide on the steel surface at the atomic level, thereby impeding the iron from rusting.

However, it was not until after the end of World War II that the development in process metallurgy led to the growth and widespread use of the modern stainless steel.

The basic metallurgy of the iron/chromium and iron/chromium/nickel systems was understood by about 1940. By 1950’s stainless steel became standardized in specification that have changed little since that time. As these standard grades became accepted, the emphasis changed to finding cheaper mass- production methods, and popularizing the use of stainless steel.
The next leap in stainless steel development was made possible by the development of Argon-Oxygen-Decarburization (AOD) refining process, in the late 1960’s.

This new refining process was fully adopted in 1970’s and revolutionized the stainless steel melting. The AOD and related process, with different gas injection or gas pressure system, permitted the ready removal of low carbon without substantial loss of chromium to the slag. Further low carbon content was readily achieved in 18 Cr wt% alloys when using high-carbon ferrochromium in furnace charges in place of the much more expensive low carbon ferrochromium. Other elements added to improve particular characteristics include manganese, molybdenum, nickel, copper, titanium, aluminium, silicon, niobium, nitrogen, carbon, sulfur, phosphorus, and selenium. Major alloying elements could be controlled; nitrogen became an easily controlled intentional alloying element and sulphur could be reduced to low levels, which resulted in marked improvement in steel cleanliness.

Over the years, stainless steels have become firmly established as materials for household utilities, fasteners, cutlery, flatware, decorative and architectural hardware. Due to its excellent corrosion resistance dairy, food-processing plants, health, sanitation appliances, chemical plants and petrochemical industries, pharmaceutical and transportation industries started using stainless steel. Some of these applications involved exposure to elevated/cryogenic temperatures as well as highly corrosive atmosphere (Davis 1996).

2.2.1 Classification of Stainless Steel

Over the years since the start of the development of stainless steel the number of grades has increased rapidly. Table 2.1 shows the stainless
steels that are standardized in the US and Europe. The table clearly shows that there are a large number of stainless steels with widely varying compositions.

Stainless steel can be divided into five families. Four are based on the characteristic crystallographic structure/microstructure of the alloys in the family: Ferrite, Martensite, Austenite and Duplex. The fifth family, the precipitation-hardenable alloys is based on the type of heat treatment used than microstructure.

Table 2.1 gives a summary of the compositions within these different categories. The martensitic stainless steels are hardenable, which means that it is possible to modify their properties by heat treatment in the same way as for hardenable carbon steels. The second category, the precipitation hardening steels, can be hardened by heat treatment.

Table 2.1 Types of stainless steel

<table>
<thead>
<tr>
<th>Steel Category</th>
<th>Composition (wt %)</th>
<th>Hardenable</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Cr</td>
<td>Ni</td>
</tr>
<tr>
<td>Martensitic</td>
<td>&gt;0.10</td>
<td>11-14</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td>&gt;0.17</td>
<td>16-18</td>
<td>0-2</td>
</tr>
<tr>
<td></td>
<td>&lt;0.10</td>
<td>12-18</td>
<td>4-6</td>
</tr>
<tr>
<td>Ferritic</td>
<td>&lt;0.08</td>
<td>12-19</td>
<td>0-5</td>
</tr>
<tr>
<td></td>
<td>&lt;0.25</td>
<td>24-28</td>
<td>-</td>
</tr>
<tr>
<td>Austenitic</td>
<td>&lt;0.08</td>
<td>16-30</td>
<td>8-35</td>
</tr>
<tr>
<td>Ferritic-austenitic (duplex)</td>
<td>&lt;0.05</td>
<td>18-27</td>
<td>4-7</td>
</tr>
<tr>
<td>Precipitation hardening</td>
<td>-</td>
<td>15-17</td>
<td>7-8</td>
</tr>
<tr>
<td></td>
<td>12-17</td>
<td>4-8</td>
<td>0-2</td>
</tr>
</tbody>
</table>
The last three categories, ferritic, ferritic-austenitic and austenitic are not hardenable, but are basically used in the as received condition. The ferritic-austenitic stainless steels are often referred to as duplex stainless steels. It may be noted that there is only one category of stainless steels that is non-magnetic: the austenitic steels. All the others are magnetic.

### 2.2.2 Designation of Stainless Steels

Wrought grades of stainless steels are generally designated by the American Iron and Steel Institute (AISI) numbering system, the Unified Numbering System (UNS) or the proprietary name of the alloy. In addition, designation systems have been established by most of the major industrial nations. Of the two institutional numbering systems used in the US, AISI is the older and more widely used. Most of the grades have a three digit designation; the 200 and 300 series are generally austenitic stainless steel, whereas the 400 series are either ferritic or martensitic. Some of the grades have a one or two letter suffix that indicates a particular modification of the composition.

The UNS is broad-based system that comprises a list of all metallic materials, including stainless steel. The system includes a considerably greater number of stainless steels than AISI, because it incorporates all of the more recently developed stainless steel. The UNS designation for a stainless steel consists of the letter S, followed by a five digit number. For those alloys that have an AISI designation, the first three digit of the UNS designation usually corresponds to an AISI number. For stainless steels, that contains high nickel contents (Approx 25, 10, 35% Ni). The UNS designation consist of the letter N followed by a five-digit number.
2.2.2.1 Martensitic stainless steels

Martensitic stainless steels are essentially alloys of chromium and carbon that possesses body centered tetragonal (bct) crystal structure in the hardened condition. They are ferromagnetic, hardenable by heat treatments and generally resistant to corrosion only in relatively mild environments. Elements such as niobium, silicon, tungsten and vanadium may be added to modify the tempering response after hardening. Small amounts of nickel may be added to improve toughness. Sulfur or selenium is added to some grades to improve the machinability.

In the annealed condition, Martensitic stainless steel has tensile yield strength of approximately 275 MPa and can be moderately hardenable. However, martensitic alloys are typically heat treated by both hardening and tempering in order to get yield strength levels up to 1900 MPa depending on carbon level. Primarily these alloys have good ductility and toughness properties, which decrease as strength increases. Martensitic stainless steels are specific when the application requires good tensile strength, creep and fatigue strength properties in combination with moderate corrosion resistance and heat resistance up to approximately 650°C (1200°F). Low-and medium carbon martensitic steels have been used primarily in steam turbines, jet engines and gas turbines.

Martensitic stainless steels are also used in petroleum and petrochemical equipment. Other applications for higher carbon level grades include cutlery, surgical and dental instruments, scissors, springs, valves, gears, shafts, cams and bearings.

Type AISI-420 and similar alloys are used in cutlery, valve parts, gears, shaft, and rollers. One extensive application is a weld overlay on rolls
for steel mill and continuous casters. This type of alloy is quite brittle in the freshly hardened conditions and usually must be tempered to obtain useful toughness properties.

2.2.2.2 Ferritic stainless steels

Ferritic stainless steel is so named because their body center cubic (bcc) crystal structure is the same as that of iron at room temperature. These alloys are magnetic and cannot be hardened by heat treatment. In general, ferritic stainless steels do not have high strength, and have poor toughness, susceptibility due to their yield strength ranges from 275 to 350 MPa at annealed condition.

The ductility and toughness of ferritic stainless steel are affected by many factors. Fundamentally, the strength and ability of the bcc ferrite structure to sustain plastic deformation are temperature dependent, especially below room temperature.

2.2.2.3 Austenitic stainless steels

Austenitic stainless steels have a face centered cubic (fcc) structure. This structure is attained through the liberal use of austenitizing elements like nickel and nitrogen. These steels are essentially non magnetic in the annealed condition and possess good high temperature strength. Molybdenum, Copper, Silicon, Aluminium, Titanium and Niobium may be added to confer certain characteristic such as halide pitting resistance or oxidation resistance.

Austenitic stainless steels compositions are based on a balance between alloying elements that promote ferrite formation. Further manganese promotes the solubility of nitrogen in steel, making possible a low nickel family of austenitic stainless steels that are high in manganese and nitrogen.
Austenitic stainless steels can be best described in terms of the iron - chromium - nickel ternary alloy system. The commercial alloys also contain a certain amount of carbon, silicon, manganese, sulfur and so on. These elements might somewhat alter the phase balance.

In addition to the wrought austenitic stainless steel containing roughly 18-8 Cr-Ni several other groups of austenitic stainless steel are available for specific applications or processing requirements. In particular, the chromium and silicon contents are higher and higher nickel contents are lower in cast alloys compared to wrought alloys.

Many cast heat - resisting grades of stainless steels also have austenitic structure. The cast heat resisting grades have much higher chromium and nickel contents for scaling resistance and greater high temperature strength compared to the 18 Cr 8Ni types of stainless steel. Thus, alloy carbides which contribute substantially to creep resistance are an important component of the microstructure of the cast austenitic high temperature alloys. The heat resistant austenitic stainless steels are used at temperature as high as 1100°C (2012°F), some times in very aggressive gaseous environments and are expected to provide many years of service. Temperature induced micro structural changes, creep – rupture mechanisms, scaling and oxidation, carburization, decarburization and sulfidation are critical phenomenon that affect the selection and performance of heat resistant austenitic stainless steels.
2.2.2.4  Ferritic-Austenitic (Duplex) steels

The modern duplex steels span the same wide range of corrosion resistance as the austenitic steels. The corrosion resistance of the duplex steels increases in the order “2304” (23Cr-4Ni), “2205” (22Cr-5Ni-3Mo), “2507” (25Cr-7Ni-4Mo). Duplex equivalents can be found to both the ordinary austenitic grades, such as 316L, and to the high alloyed austenitic grades, such as ‘254 SMO’. The corrosion resistance of “2304” type duplex is similar that of 316L while “2205” is similar to “Type” 904L and “2507” is similar to the high alloyed austenitic grades with 6% molybdenum. The ferritic-austenitic (duplex) steels are characterised by high strength, good toughness, very good corrosion resistance in general and excellent resistance to stress corrosion cracking and corrosion fatigue in particular. An increased level of chromium, molybdenum and nitrogen increases corrosion resistance, while the higher nitrogen level also contributes to a further increase in strength above that associated with the duplex structure.

Applications of ferritic-austenitic steels are typically those requiring high strength, good corrosion resistance and low susceptibility to stress corrosion cracking or combinations of these properties. The lower alloyed “2304 type” is used for applications requiring corrosion resistance similar to 316L or lower and where strength is an advantage. Some examples of such applications are hot water tanks in the breweries, pulp storage towers in the pulp and paper industry, tanks for storage of chemical in the chemical process industry and tank farms in tank terminals in the transportation industry.

The higher alloyed “2205 type” is for example used in pulp digesters and storage towers in the pulp and paper industry where it is rapidly becoming a standard grade. It is also used in piping systems, heat exchangers, tanks and vessels for chloride-containing media in the chemical industry, in piping and process equipment for the oil and gas industry, in cargo tanks in
ships for transport of chemicals, and in shafts, fans and other equipment which require resistance to corrosion fatigue. High alloyed grades, e.g. “2507”, are used in piping and process equipment for the offshore industry (oil and gas) and in equipment for environments containing high chloride concentrations, such as seawater.

2.2.2.5 Precipitation – Hardening Stainless Steels

Precipitation Hardening (PH) stainless steel are iron chromium nickel alloys characterized by their high strength obtained by precipitation hardening in a martensitic or austenitic matrix with one or more of the following elements: copper, aluminium, titanium, niobium and molybdenum. Precipitation hardening steels can be grouped into three types Martensite, Semi austenitic and Austenitic – based on their Martensite starts \( (M_S) \) and Martensitic finish \( (M_F) \) temperature resultant behavior upon cooling from a suitable solution – treatment temperature.

The semi austenitic PH steels, such as 17–7 PH, have competitions that are balanced so that their \( M_S \) are well below room temperature. Therefore, they are predominantly austenitic upon cooling from the solution-treatment temperature and are highly ductile and readily formed in that condition. After forming, transformation to martensite is accompanied by a conditioning treatment, which raises their \( M_S \) and \( M_F \) by precipitating carbon alloying elements from solution.

The austenitic PH steel, such as A-286, have \( M_S \) so low that they cannot be transformed to martensite. Strengthening is obtained by the precipitation of intermetallic compounds in an austenitic matrix.
2.3 HIGH NITROGEN STEELS

2.3.1 About Nitrogen

Nitrogen has been described as an essential, important and inexpensive alloying addition to steels, which is fortunate in that all steels contain some nitrogen. The content varies from as little as 0.002% (20 ppm) in Basic Oxygen Furnace (BOF) steels to about 10 times that amount in some Electric Furnace (EF) steels and 150 times that amount in certain stainless grades. Degassed steels can be below 10 ppm. Nitrogen exists in steel as an interstitial quite similar to, but much more soluble than, carbon and as nitrides of iron, aluminum, vanadium, columbium, titanium and a number of other alloying elements. Nitrogen can be either harmful or beneficial to the steel's properties, depending on the form in which it is found. However, enough is now known about nitrogen's behavior that the element's status has progressed from that of an occasional nuisance to a safely controlled, useful alloying addition. During steelmaking, nitrogen can be carried over from raw materials such as coke, it can enter as a constituent, intentional, or otherwise, in alloying additives, and most obviously it can enter by ordinary solution through contact of the liquid steel with air. Nitrogen can also be diffused into the surface of steels to give an extremely hard case.

According to Foct (2003), three class of High Nitrogen Steels (HNS) - austenitic, martensitic and duplex were studied, and three scales of research micro, meso and macro are foreseen to transfer scientific results into application in the past three decades by three universities:

i) The Institute of Kiev, is responsible for the microscopic study on austenitic steel.

ii) The laboratory of Lille, studies the substructure on the mesoscopic scale, and deals mainly with duplex steel.
iii) The University of Bochum, deals with macroscopic properties, mechanical behavior and corrosion resistance and specializes in the field of martensitic nitrogen steel.

2.3.2 History of High Nitrogen Steel

Speidel (1988) reported about HNS, when the nitrogen concentration is higher than 0.4 wt% in austenitic steels, higher than 0.02 wt% in martensitic steel and 0.08 wt% for ferritic steel “High” in this sense intentionally raised N content by appropriate alloying or by pressure or powder metallurgy element.

Corrosion free and high strength high nitrogen steels came up in the recent years. The successful sequence of HNS conference is a proof of that fact. This group of steels has quite a long history.

The scientific studies of nitrogen started before the First World war when Andrew, constructed a small laboratory size arc furnace, which was able to melt iron-carbon alloys under pressure up to 100 bars. This is an important experiment, which gave the first clues as to the strong effect of nitrogen on the mechanical properties and on the direct influence on the austenitic transformation. This new knowledge lead to the first industrial usage of nitrogen steels in the production of stainless steels as a substitute for the available nickel during World War II in Europe. Starting from the fifties, a lot of research was done as to the beneficial effects of nitrogen on the mechanical properties and on a suitable alloy development, as first attempts at a suitable process technology. Besides the strong stabilizing effect on austenitic structure other benefits of nitrogen appeared: interstitially dissolved nitrogen also distinctly improves the strengthening of austenites as well as corrosion resistance (Stein et al 1999)
It is a strange fact, that the beneficial influence of nitrogen on mechanical properties and the favorable behavior as to corrosion fatigue, which had accumulated towards the end of the sixties, did not push forward the usage of high nitrogen steels. May be one of the explanations is based on the fact, that the production of HNS demands very high standards in steel plants and high-pressure melting units looked rather exotic to many people and -by the way - is so even now.

In the meantime, a lot of additional work has been done and today the solubility of nitrogen and nitride as well as the equilibrium stability of certain phases can be fairly well predicted with regard to the most relevant composition and wide temperature range. In addition, it is possible to make some predictions about the physical and mechanical behavior of such steels, which are an important help for future alloy development and application.

2.3.3 Theoretical nitrogen solubility

The equilibrium content of nitrogen in steel depends on three variables: temperature T, nitrogen pressure $p_{N_2}$ and alloy concentration of the steel ‘X’. Due to inter atomic spacing the N-solubility is lowest in ferrite as compared to austenite and the melt. In a nitrogen atmosphere, the dissolution of nitrogen in steel is governed by the reaction.

$$\frac{1}{2}N_2 = [N]_{(\text{Dissolved in liquid Fe})}$$  \hspace{1cm} (2.1)

The value of $K$ equilibrium constant derived from the value of standard Gibbs free energy for this reaction $\log K = -\Delta G^o/RT$ at 1600°C.

$$K = \frac{a_N}{\sqrt{p_{N_2}}} = \frac{f_{N_\text{f}} \cdot %N}{\sqrt{p_{N_2}}} = 0.045$$  \hspace{1cm} (2.2)
K is the ratio of the nitrogen activity in solution $a_N$ and the partial pressure of nitrogen. The Henrian activity coefficient $f_N$ relates the chemical activity of dissolved nitrogen to its concentration $[N]$ in mass%. This implies the validity of Sievert’s law 

$$[N] \sim \sqrt{p_{N_2}} \ .$$

In a dilute solution of nitrogen in pure iron $f_N$ reaches, unity while by adding an alloying element ‘X’ the concentration of dissolved nitrogen is changed and the activity coefficient is adjusted accordingly.

$$f_N^X = \frac{[N]_{Fe}}{[N]_{Fe-X}} \quad (2.3)$$

The influence of dissolved $X$ in mass% on $a_N$ was interpreted by Wagner. A Taylor series expansion leads to first order ($e_N^X$) and second order ($r_N^X$) interaction parameters (Gavriljuk and Berns 1999). The first and second order parameters are reported to have significant influence on the solubility prediction on stainless steels. Based on the experimental chemical composition, the theoretical nitrogen solubility at 1600°C in stainless steel was calculated using equations (2.4) and (2.5).

$$\log f_N^X = e_N^{Cr} \cdot (%Cr) + r_N^{Cr} \cdot (%Cr)^2 + e_N^{Mn} \cdot (%Mn) + r_N^{Mn} \cdot (%Mn)^2 + \quad (2.4)$$

$$%N = \frac{K}{f_N^X} \quad (2.5)$$

### 2.3.4 High Nitrogen Stainless Steel

High nitrogen steels belong to iron-based multicomponent solid solutions which are constructed by substitutional (iron, chromium, nickel, manganese etc.) as well as interstitial (nitrogen, carbon) atoms and, in addition, can be strengthened by the particle of nitrides. The mechanical and
electrochemical properties of nitrogen in solid solutions are mainly
determined by the behaviour of dislocation properties and solutes.

Berns et al (1996) has reported that “high” in High Nitrogen Steel is
not clearly defined; it is 0.1 mass% of nitrogen in creep resistant steels, 0.9
mass% in stainless steel grades or 2 mass% in tool steel refined as HNS.
“High” best refers to “intentionally raised” by appropriate alloying or by
pressure and powder metallurgy. But Speidel (1988) defined HNS as
0.08 wt%N in ferritic and 0.02 wt%N in martensitic and 0.4wt%N is
recommended to become austenitic stainless steel.

Horovitz et al (1996) defined HNS if the nitrogen content is greater
than 0.08% in a ferritic matrix and greater than 0.4% in an austenitic matrix.
Nitrogen and carbon are interstitial elements in relation to the iron crystal
lattice and may be kept in solid solution in the austenite and martensite phases
and precipitates in the matrix as nitrides or carbonitrides.

Kamatchimudali and Baldevraj (2004.) reported that the beneficial
effect on nitrogen alloying in stainless steel is manifold. The combination of
properties such as improved strength, fracture toughness, wear resistance,
magnetic properties and corrosion resistance of HNS has given unique
advantages and offers a number of prospective applications to day in many
industries and engineering applications. The attainment of very high yield
strength levels by judicious combinations of the basic hardening mechanism
by solid solution hardening, grain boundary hardening, work hardening, and
precipitation hardening is one of the major remarkable developments of HNS
alloys.

Bahrami and Hendry (1995) have reported that nitrogen, as an
interstitial alloying element is well known for its beneficial effects in stainless
steel. Phase stability, high strengthening effect, and corrosion resistance have
made nitrogen an attractive candidate for high temperature and corrosion resistance applications. Carbon gives better phase stability than nitrogen in austenite, but carbon forms many precipitates such as carbide and carbonitrides. The addition of nitrogen is reported to delay carbide precipitation, and in high nitrogen steels results in the disappearance of carbide phases.

In austenitic stainless steels, very high strength can be achieved by additional cold work. When nitrogen is in solid solution, however, such an enhancement in martensitic steels is restricted by low ductility, which is due to self trapping of dislocations. This behaviour is the result of tetragonality in nitrogen alloyed martensitic stainless steel and must be overcome before engineering application. Carbon in creating similar structure has additional disadvantages, being very unstable on tempering and forming large particles. However, in martensitic stainless steels nitrogen addition results in a finer and uniform structure causing retention of properties on tempering, and maintaining the advantages discussed above.

2.3.5 Martensite transformation in HNSS

Martensite transformation in stainless steel is similar to iron carbon alloys (Davis 1996). When the temperature of metal capable of undergoing a martensite reaction is lowered, it eventually passes through an equilibrium temperature separating the stability ranges of two phases. Below this temperature, the free energy of the metal is lowered if the metal changes its phase from stable at high temperatures to stable at low temperature. The free energy difference is the primary driving force for a martensitic reaction. The phase change that occurs in a martensite transformation is brought about by the movement of the interface separating parent phase austenite from the
product phase martensite. As the interface moves, atoms in the lattice structure of austenite fcc phase are distorted and realigned into the lattice of the martensite (bcc) phase as shown in Figure 2.1.

The nature of the individual atomic movements in the region constituting the interface is not known, like in deformation twinning. Nevertheless, it is undoubtedly true that the displacement of atoms, relative to their neighbors, is small in magnitude and probably more complicated than those in deformation twinning. Because of the manner in which martensite forms, no composition change occurs as the parent lattice (fcc) is converted into the product phase and diffusion in either the parent phase or product phase is not required for the reaction to continue. Martensite reactions are, accordingly commonly referred to as diffusionless phase transformation because the interstitial holes which house dissolved carbon and nitrogen are much smaller in the bcc structure than in the ‘fcc’ structure. More C or N can dissolve in ‘fcc’ than ‘bcc’.

Figure 2.1  Supersaturated C or N distorts the martensite unit cells along three possible directions.

The strength obtained by heat treatment depends on the interstitial (carbon, nitrogen) content of the alloy. Increasing interstitial content increases the strength but decreases ductility and toughness.
2.3.6 **Martensite transformations in nitrogen alloyed stainless steel**

As the martensitic transformation is a diffusionless transformation, i.e. it is accompanied by atomic displacements less than the inter atomic distance, the atomic distribution in ferrous martensite is inherited from the parent austenite phase. However, the quenching of steels to room temperature does not retain the initial atomic configurations of nitrogen and carbon atoms, as they existed in the austenite. This occurs in such a way that the fcc austenite experiences a polymorphic transformation to a body centered tetragonal (bct) martensite as ‘c’ shown in Figure 2.2. A unit cell of this crystal structure is simply ‘a’ body centered cube (bcc) that has elongated along one of its dimensions ‘c’. The fact is in accordance with enthalpy of migration of nitrogen and carbon atoms in α-iron they are mobile at room temperature. That is why the crystal structure of nitrogen martensite as well as of carbon martensite at room temperature is far from the freshly formed one and has to be characterized as an aged structure.

![Figure 2.2](image)

**Figure 2.2** The three possible directions of unit cell ‘a’ and ‘c. The large locked-in stresses result ‘c’ >’a’. 
A rarely virgin iron based martensite can be observed if the start temperature of martensitic transformation is below -50°C. In martensitic steels, the micro structural refinement and homogeneity obtained by N alloying, results in better high temperature mechanical and corrosion/oxidation properties.

2.4 EFFECT OF ALLOYING ELEMENTS IN NITROGEN ALLOYED MARTENSITIC STAINLESS STEEL

Each alloying element in steel has a specific effect on the properties of the steel. It is the combined effect of all the alloying elements and, to some extent, the impurities that determine the property profile of a certain steel grade. In order to understand why different grades have different compositions a brief overview of the alloying elements and their effects on the structure and properties will be given. The effects of the alloying elements on some of the important materials properties will be discussed in more detail in the subsequent sections. It should also be noted that the effect of the alloying elements differs in some aspects between the hardenable and the non-hardenable stainless steels.

General purpose of alloying additions is to fulfill one of more of the following functions:

i) Increase the hardenability
ii) Reduce distortion due to heat treatment
iii) Provide improved toughness at a particular hardness level
iv) Increase the dry wear/abrasion resistance at a given hardness level
v) Increase the elevated temperature, strength and hardness
vi) Increase the corrosion, erosion resistance.
In this aspect, as reported by Anil Kumar Sinha (2003) some of the alloying elements that influence the property of steel are shown in Table 2.2.

**Table 2.2 Effect of alloying elements on specific parameters.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Elements (in order of decreasing effectiveness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardenability</td>
<td>Mn, Mo, Cr, Si, Ni, V</td>
</tr>
<tr>
<td>Minimum distortion</td>
<td>Mo (with Cr), Cr, Mn</td>
</tr>
<tr>
<td>Toughness</td>
<td>Ni (produces general toughness), V, W, Mo, Mn, Cr</td>
</tr>
<tr>
<td>Wear resistance</td>
<td>V, W, Mo, Cr, Mn</td>
</tr>
<tr>
<td>Hot hardness</td>
<td>W, Mo, Co, V, Cr, Mn</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>Cr, Mo, N,</td>
</tr>
</tbody>
</table>

Solubility of N is increased by the addition of alloying elements such as Cr, Mn, Mo, since these elements decrease the chemical potential of N. The larger the stability of nitrides of the transition metals, the smaller is the ‘d’ electron density: example Ti, V, Cr, Zr, Nb, Mo nitrides are much more stable than Mn, Fe nitrides Ni and Cu nitrides are unstable. In contrast, with carbides there is often a structural compatibility between the crystallographic lattices of solid solutions and nitrides which often are Hagg’s compounds. One may therefore expect that nitrides should be more coherent with the matrix than carbides and that the interfacial energies \( \Gamma \) should therefore obey this inequality, \( \{ \Gamma_{\text{carbide/matrix}} > \Gamma_{\text{nitride/matrix}} \} \). Hence, the driving force for growth of nitrides is comparatively less than that of carbides (Foct 2003).

As reported by Horovitz et al (1996) alloying is the easiest way of enhancing the nitrogen solubility. Apart from elevated pressure, the solubility of nitrogen in the steel may be raised by introducing alloying elements into the melt. Alloying elements like Ti, Zr, V, Nb, Cr, Mn and Mo are added to
enhance nitrogen solubility, while in the order of W, Mo, Mn, Cr, Nb, V, Zr and Ti nitrogen is increasingly attracted to the melt as shown in Figure 2.3 (Gavriljuk and Berns 1999).

![Figure 2.3 Effects of various alloying elements on nitrogen solubility](image)

**Figure 2.3 Effects of various alloying elements on nitrogen solubility**  
*Simmons (1996)*

### 2.4.1 Chromium

Chromium (Cr) is one of the most versatile and widely used alloying element in producing Nitrogen Alloyed Martensitic Stainless Steel (NAMSS). Its contents are generally in the range of 10.5% to 18 wt% leading to the formation of passive chromium rich oxide film on the surface of the alloy. Minimum 10.5 wt%Cr is required to obtain passivity and Cr of 12wt% produces semi ferritic microstructure. Martensitic stainless steels have their chromium content in the range of 10.5–18 wt%. When the chromium content is below 12 wt% it is possible to obtain a martensitic microstructure since the steel can be made fully austenitic at elevated temperatures. Such steels solidify as δ-ferrite and are completely transformed to austenite as shown in Figure 2.4 (γ-gamma loop) at high temperature,
followed by relatively rapid cooling for transformation into non-equilibrium martensite.

However, this is the limit to the level of chromium that can be added to martensitic stainless steel, as the beneficial effect of even higher levels is negated by the enhanced precipitation of intermetallic phases such as sigma, secondary (retained) austenite etc. These phases often lead to reduction in ductility, toughness and corrosion properties.

At this concentration, Cr increases hardenability, corrosion, wear and oxidation resistance, improves high temperature strength with Mo, and enhances the abrasion resistance. It is a strong carbide/nitride former and chromium carbides/nitride are hard and wear resistant. Cr is susceptible to temper embrittlement while heat treating. Electrochemically Cr extends the passive range and reduces the rate of general corrosion.

Figure 2.4 shows part of the Fe-Cr constitution diagram according to Bungardt et al (1993). Chromium is a ferrite former by analogy with iron and ordinary steels; the bcc ferrite precipitated from the melt is known as \( \delta \)-ferrite, while ferrite resulting from transformation of austenite during cooling is called \( \alpha \)-ferrite. The two types of ferrite show differing grain structure \( \delta \)-ferrite is often coarse when compared with \( \alpha \)-ferrite and its morphology retains features of the solidification microstructure. Low carbon Fe-Cr stainless steels have either a ferrite or martensitic, possibly semi-ferritic, microstructure depending on composition.

Between the austenite phase field and the fully ferritic domain, there is a narrow range of compositions which defines the semi-ferritic alloys. As reported by Berns and Kraff (1988) a microstructure consisting partly of \( \delta \)-ferrite remains unchanged following solidification, the remainder being
martensite. 12%Cr martensitic stainless steel makes use of the strengthening effect of fine carbide precipitated upon tempering.

![Fe-Cr constituent diagram with <0.01 wt%](image)

**Figure 2.4** Fe-Cr constituent diagram with <0.01 wt%.

Chromium content greater than approximately 14 wt% gives a completely ferritic stainless steel over the whole temperature range corresponding to the solid state and hence cannot be hardened on quenching.

Cardoso et al (2003) has reported that C, Cr strongly influence the microstructure transformations that can occur during hot forming process. These transformations may lead to duplex microstructure formation of δ-ferrite + martensite.

### 2.4.2 Manganese

Generally manganese is added to stainless steels to assist in deoxidation, during melting and to prevent the formation of iron sulfide inclusions which can cause hot cracking problem. It is also a “austenite”
stabilizer and when added in higher levels replaces some of the nickel in the AISI-200 series grade stainless steels.

Manganese (Mn) is the most prevalent alloying element in steel, after carbon and it is generally used in stainless steels to improve hot ductility and surface quality in all ranges of carbon. Its effect on the ferrite/austenite balance varies with temperature: at low temperature, manganese is an austenite stabiliser but at high temperatures, it stabilizes ferrite. It is the most cost effective hardenability intensifier and promotes finer grain sizes and deep hardening effect in steels. As grain size reduces yield strength increases with improvement in impact properties. Very high manganese contents suppress the gamma phase (γ) and alpha transformation entirely, and such steels will be fully austenitic at room temperature. In all cases, manganese lowers the Ms temperature, and high manganese steels will tend to contain residual austenite. Although it is carbide former, it produces no secondary hardening during tempering. Mn is a solid solution strengthener in steel and is very effective in increasing the hardenability, but >2% results in increased tendency towards cracking and distortion during quenching. Enhances susceptibility to temper embrittlement when presents in excess of 0.30%. In addition, Mn increases the solubility of nitrogen and is used to obtain high nitrogen contents in austenitic steels.

2.4.3 Molybdenum

Molybdenum (Mo) being a strong ferrite stabilizing element, it slows ferrite separation from austenite to greatly enhance the martensitic phase. It produces fine grained steel, increases the martensitic hardenability (0.5wt% or less), and improves the fatigue strength. In combination with Cr, Mo eliminates the tendency of embrittlement and it must be balanced by the addition of austenite stabilizing elements (Figure.2.5) such as manganese, nitrogen or nickel. Depending on the corrosive environment, the amount of
molybdenum used ranges between 0-3 wt%. Molybdenum also promotes the formation secondary phases while tempering of quenched steels in ferritic, ferritic-austenitic and austenitic steels. In martensitic steels, it will increase the hardness at higher tempering temperatures due to its effect on the carbide precipitation.

Mo increases the hardness as a function of cold work and after solution treatment, no delta ferrite is found in 0.01 and 2.0 wt%Mo in Cr-Mn-Ni steel. The hardness is drastically decreased in 40% cold worked 0.01%Mo contained stainless steels after aging at 550°C but Mo containing steel remains strong after aging at higher temperature. The additions of Mo retard recrystallisation of the work-hardened steel so that high dislocation density remains in the steel after prolonged aging at 660°C.

![Figure 2.5 Effect of molybdenum on the austenitic phase stability field in the Fe-Cr phase diagram](image-url)
Mo increases the corrosion resistance for transportation of oil and gas. Alloying with molybdenum reduces the general corrosion rate at elevated temperatures and reduces the sulfide stress corrosion cracking susceptibility. Coefficient of Mo is 3.3 times that of chromium, while it has a similar effect on ferrite stability as chromium, in corrosion. The mechanism by which molybdenum increases the pitting resistance of an alloy has been examined by a number of workers and has been found to suppress active sites by formation of an oxy hydroxide or molybdate ion.

Shigeru Hirata et al (2002) reported about Mo and N, which form an interstitial-substitutional pair, which changes the dislocation structures. Yield and tensile strength increases with increasing Mo up to 1.0%, and this strengthening effect of Mo saturates at more than 1.0%Mo content.

2.4.4 Carbon

Carbon (C) is an interstitial element and strong austenite former, promotes an austenitic structure. Carbon dissolves in iron, but the solubility limit depends on crystal structure. Carbon contents lower than 0.1 wt% has the effect to shift the austenite stability region in the phase diagram of the alloy toward higher temperatures and higher nitrogen contents. Carbon content higher than 0.1 wt% from the other side causes a shift of the solubility curve for $M_{23}C_6$ precipitation towards higher temperature as shown in Figure 2.6. Both cases promote precipitation of undesired phases such as $M_{23}C_6$ and/or $Cr_2N$ at temperatures lower than 950°C and thus decrease the toughness and corrosion resistance of the alloy. The reduction in carbon content from 0.2 to 0.1 wt% has a negative influence on the mechanical strength (less solid solution hardening). A carbon content nearly 0.1% is required in order to have good stable austenite; the reduction on tensile
strength can be compensated by adding more nitrogen in solid solution. Impact energy varies with varying nitrogen in increasing order (Paolo Cobelli et al 2002).

**Figure 2.6 Phase fields in the ternary iron-chromium-carbon at 13wt%Cr**

Prabhudev (1998) stated that when carbon content is increased austenite also stimulates to start martensite $M_s$ (Martensite start) early and finishes $M_f$ early by 550° to 650°C for 0.5% C and that is why more residual or retained austenite forms. Such a steel should be subjected to subzero treatment to convert retained austenite to martensite.

Apart from carbon, elements like manganese, silicon, nickel, chromium, molybdenum, and tungsten tend to lower the $M_s$ proportional to the alloying elements dissolved in austenite. Of all the alloying elements carbon has by far the best in decreases the $M_s$ and other alloying elements are in the order of Mn, Cr, Ni, Si, Mo, W. In hot working with 0.15% C in plain carbon steel increases the power by 20% more at 850°C and for cold working process, energy strongly depends on the carbon content.
Carbon atoms are soft in the first coordination sphere and hard in the second one, so that C-C pairs in adjacent sites exist and the Fe₄C structure is hardly possible (Gavriljuk 2007). As for as martensitic stainless steel is concerned carbon can vary from 0.07 to 0.15wt% as interstitial but other interstitials like N, and substitutional solid solutions like W, Ti, Nb, V it can vary proportionate to alloying elements.

2.4.5 Nitrogen

According to various researchers, including Speidel (1988) High Nitrogen Steel must have 0.08 wt%N in ferritic and 0.02 wt%N in martensitic phases and 0.4wt%N is recommended to become austenitic stainless steel. Nitrogen (N) exists in steel as an interstitial quite similar to carbon, but much more soluble than carbon. Since atomic size of the nitrogen (0.071 nm) is less than carbon (0.077 nm) and as nitrogen forms nitrides of iron, aluminium, vanadium, columbium, during heating before quenching, a certain part of nitride particles dissolve in austenite and it is preserved in a solid solution after rapid cooling.

Bahrami et al (1995) reported about nitrogen saying that it delays the carbide precipitation, and in high nitrogen steel results in the disappearance of carbide phases. When nitrogen is in solid solution, such an enhancement in martensitic steel is restricted by low ductility, due to self trapping dislocations. Nitrogen addition in martensitic stainless steel results in a finer and more uniform structure, retaining the properties on tempering.

Apart from these benefits Gavrirljuk et al (2007) explains about nitrogen and its three main features that differ from carbon are:
- It is a higher stability of nitrogen austenitic and martensitic steels in relation to phase transformation and precipitation reaction.

- The alloying of austenitic steels with nitrogen maintains the high fracture toughness in spite of the increase in the yield and ultimate strength, as it was obtained by Frehser and Kubish (1988) is the first time, and also provides a better combination of strength and plasticity of tempered martensitic steels.

- Nitrogen improves corrosive properties of steels, mainly the resistance to pitting and crevice corrosion, whereas carbon accelerates the degradation of steel in aggressive environments.

It has been known that adding nitrogen to austenitic steel bears considerable advantages. Simultaneously the positive effects of nitrogen can also be used in martensitic steel as reported by Paolo Cobelli et al (2002) and is shown in Figure 2.7.

![Effects of nitrogen in martensitic steel](image)

**Figure 2.7** Effect of Nitrogen on Martensitic Steel
Kamatchimudali and Baldevraj (2004) reported that nitrogen has a tendency to enhance metallic bond rather than covalent bond like carbon. More ‘s’ electrons are concerned around N atoms in hybridation than in carbon atoms. This increase of free electron in outer most orbital compared to that in carbon is due to the lattice dilation in N which results in enhancing the strength of austenite. Enrichment of free electron by N in the hybridized orbit gives a short range atomic order, which promotes a more homogeneous substitutional atomic distribution.

Nitrogen in solid solution is the most beneficial alloying element in promoting high strength in austenitic stainless steels without affecting their good ductility and toughness properties as long as the solubility limit of N in austenitic does not exceed (<0.9wt.%N). As the solubility limit is exceeded, Cr\(_2\)N precipitates or gas porosity formation takes place (Hanninen 2001). Additions of nitrogen in NAMSS improve the retention of hardness upon tempering and the strength at higher temperature.

As reported by Berns and Lueg (1988) nitrogen is a very potent solid solution hardener which delivers high strength without significant reduction in fracture toughness but also enhances the corrosion resistance of steel (Speidel 1988). However, nitrogen increases the activity of carbon and decreases the activity of Cr (Leda 1988). Whereas nitrogen atoms avoid to occupy neighboring sites in the austenitic lattice and prefer the atomic distribution like that in the ordered ‘\(\gamma\)’ phase Fe\(_4\)N (Gavriljuk 2007).

Hanninen et al (2001) reported that, replacement of Ni and improvement of mechanical and corrosion properties have been the targets in austenitic stainless steel. In martensitic steels, the micro structural refinement and homogeneity obtained by N alloying result in better high temperature mechanical and corrosion/oxidation properties.
Nitrogen content in the martensite is lesser than in austenite because the martensite forms from the fractions of austenite of having less nitrogen content for which the $M_S$ temperature is high (Prokoshkina et al 2002).

Girodin et al (2002) reported that XD15NW nitrogen martensitic stainless steel replaces the X105CrMo17 steel (AISI 440C) for cryogenic bearing applications with improved corrosion resistance, better metallurgical and mechanical properties, improved tribological behavior and fatigue life, but corrosion resistance is weakened due to large $M_7C_3$ carbide precipitates.

As far as N equivalent for Ni is concerned, it is stated that 0.05%N is found to be equivalent to 1% Ni in its austenite stabilizing effect. It is reported that nitrogen addition is carried out using high pressure nitrogen gas upto 10 atm. Maximum nitrogen solubility achieved is 0.53% in Vacuum Induction Melting (VIM) at 10 bar pressure and 4% in Hot Isostatic Pressing (HIP) at 200 atmosphere pressure.

Alberto Akikazu et al (1996) reported that as far as N solubility is concerned under 0.9MPa pressurized induction furnace obtained, nitrogen solubility of 0.5 mass% with low carbon of 0.004% for 18Cr1Mo stainless steel.

Prokoshkina (2002) reported about micro hardness, it increases proportionately with to nitrogen and the nitrogen solubility depends on pressure and temperature, so that it obeys the Sieverts law while dissolving nitrogen in a melt of Fe, Fe-O, and Fe-Cr in argon and nitrogen atmosphere with different pressures from 0.1–3.2 MPa at 1630°C. In this respect, carbon and nitrogen are strong austenite stabilizers in Fe-Cr alloys (Figure 2.6 and Figure 2.8), However, in martensitic stainless steels, both the carbon and nitrogen contents have to be kept as 0.1 wt%. This is because hardness of martensite increases sharply with carbon concentration and therefore raises
the probability of sulfide stress corrosion cracking. On the other hand, carbon and nitrogen in the presence of 11-13 wt% Cr and 0-3 wt% Mo, can lead to the formation of a range of precipitates such as $M_23C_6$ and $M_2X$, which diminish the effective chromium and molybdenum concentrations in solid solution and therefore decreases the corrosion resistance.

![Figure 2.8 Fe-Cr-N phase diagrams at 1100°C derived by thermo calculation](image)

Nitrogen increases the resistance to localized corrosion, especially in combination with molybdenum. In ferritic stainless steels, nitrogen will strongly reduce toughness and corrosion resistance. In the martensitic and martensitic-austenitic steels, nitrogen increases both hardness and strength but reduces the toughness. Nitrogen alloying leads to indirect or direct saving of traditional and high cost alloying elements such as Ni, Co, Mo, Nb etc., Nitrogen has lower relative energy consumption and it promotes the sustainable energy development.
One kg of nitrogen replaces about 6-20 kg of costly nickel (Foct et al 1989) and one wt%N replaces about 2/3 of Carbon and 30 wt% of Cr in preventing pitting corrosion (Speidel et al 1988)

Tsolo Rashev (2002) reported that nitrogen steel produced under pressure are eco-friendly and “care for the materials from birth to birth”. Nitrogen is the only alloying element that is in complete conformity to the ecological principle. There are no data about any harm caused by the nitrogen gas to human health of to the flora and fauna.

2.4.6 Nickel

Nickel (Ni) has the strongest effect in this respect and also has a tendency to improve toughness. Nickel is an essential alloying element in 300 series stainless steel grades to promote an austenitic structure. In Figure 2.9 it can be observed that the increase in wt% of Ni increase the (γ) austenite loop size and it is also a ferritic strengthener. Its good ductility, toughness even at cryogenic temperature and flexible heat treatment of low carbon nickel steels make them good case hardening materials. In combination with Cr, Ni produces alloy steels with increased hardenability, impact strength and fatigue resistance than are possible with carbon steels. If carbon and nitrogen is, kept low austenite can be stabilized using substitutional solutes. Without nickel, austenite forms in areas with a high density of nitride particle residuals from the initial microstructure, which leads to large, wide spaced bands of martensite in the nickel free alloy (Berns et al 1996). Ni concentration increases gradually with increasing reversion austenite treatment temperature, indicating that the stability of reversed austenite becomes lower with increasing the reversion treatment temperature owing to the rise in Ms temperature due to decrease in the Ni concentration (Dong-Seok Leem et al 2001).
Figure 2.9  Influence of nickel on the range of the austenite phase filed in the iron-chromium system

Ni reduces the corrosion rate and is thus advantageous in acid environments. In precipitation hardening steels, it is also used to form the intermetallic compounds that increase the strength. Apart from these advantages, nickel is having some detrimental effect also. Speidel (1988) and others reported that nickel is more often classified as cancer and allergy provoking element, so that Cr-Ni stainless steels are preferably avoided for medical application. Nickel is costly metal, thus it is replaceable by other alloying elements like Co, Mo and Nb.

2.4.7  Cobalt

The metallurgical behavior of cobalt is similar to that of its sister element Ni. Cobalt (Co) is unique among alloying constituents in steel in that it is the only element that decreases the hardenability of steel by accelerating the decomposition of austenite. Cobalt is only used as an alloying element in martensitic steels where it increases the hardness and tempering resistance,
especially at higher temperatures. It forms a complete series of solid solution with iron at elevated temperature and is extremely soluble. Co does not form carbide (Anil Kumar Sinha 2003).

2.4.8 Vanadium

Vanadium (V) is a deoxidizer; it dissolves to some extent in ferrite, imparting strength and toughness. Vanadium has ability to retard grain growth at elevated temperature, has beneficial affinity for C and N, and promotes fine grain size, which increases the hardenability and improves wear resistance through the precipitation of its carbide and nitride. It is also a micro alloying element and forms carbide/nitrides. Vanadium increases the abrasion wear resistance, edge holding quality and high temperature strength (Anil Kumar Sinha 2003).

Paolo Cobelli et al (2002) reported that Vanadium increases the hardness of martensitic steels due to its effect on the type of carbide present. It also increases tempering resistance. Vanadium stabilises ferrite and will, promote ferrite in the structure. It is only used in hardenable stainless steels. The effect of vanadium as grain refining and precipitation hardening element was investigated. Vanadium higher than 0.5wt% and carbon contents higher than 0.12wt% must be avoided, due to unfavorable dispersions of precipitates that cause deterioration in toughness and corrosion resistance. A positive grain refining effect coupled with a relatively good toughness has been observed by alloying with low vanadium (0.3wt%) and low niobium (0.02wt%), but a comparison between the grain size and mechanical properties achievable, show niobium to be the most promising grain refining element in high nitrogen, nickel free austenitic stainless steel when a good toughness is also required.
2.4.9 Niobium

Niobium (Nb) is both a strong ferrite and carbide former. As titanium, it promotes a ferritic structure. In austenitic steels, it is added to improve the resistance to intergranular corrosion but it also enhances mechanical properties at high temperatures. In martensitic steels, niobium lowers the hardness and increases the tempering resistance. In U.S., it is also referred to as Columbium (Cb).

Nb has the drawback of decreasing the toughness at all the annealing temperatures. Among all alloys, the one with lowest carbon and lowest niobium content shows the highest toughness, Nb content higher than 0.02wt% increases the ductile to brittle transition temperature. Nb content higher than 0.05 wt% has no significant effect in reducing the austenite grain size below ~3µm after recrystallisation at low temperature. Indeed, a negative effect on toughness and ductile to brittle transition temperature was seen. Nb lower than 0.05wt% seem to be not enough to prevent excessive grain growth up to 6-7 µm in size. Nb gets refine the grains in austenite. (Paolo Cobelli et al 2002)

2.4.10 Copper

Copper (Cu) enhances the corrosion resistance in certain acids and promotes austenitic structure. In precipitation hardening steels, copper is used to form the intermetallic compounds that are used to increase the strength.

2.4.11 Titanium

Titanium (Ti) is a strong ferrite former and a strong nitride/carbide former, thus lowering the effective carbon content and promoting a ferritic structure in two ways. In austenitic steels, it is added to increase the resistance
to intergranular corrosion but it also increases the mechanical properties at high temperatures. In ferritic stainless steels, titanium is added to improve toughness and corrosion resistance by lowering the amount of interstitials in solid solution. In martensitic steel, titanium lowers the martensite hardness and increases the tempering resistance. In precipitation hardening steel, titanium is used to form the intermetallic compounds that are used to increase the strength.

2.4.12 Silicon

Siwka (2002) has reported that silicon (Si) increases the resistance to oxidation, both at high temperatures and in strongly oxidizing solutions at lower temperatures. It promotes a ferritic structure. Increase in the silicon concentration in Fe-N-Si alloy reduces the solubility of nitrogen

2.4.13 Aluminium

Aluminium (Al) improves oxidation resistance, if added in substantial amounts. It is used in certain heat resistant alloys for this purpose. In precipitation hardening steels aluminium is used to form the intermetallic compounds that increase the strength in the aged condition.

2.4.14 Sulphur

Sulphur (S) is generally kept low levels as it can form sulfide inclusions. It is added to certain stainless steels, the free-machining grades, in order to increase the machinability. At the levels present in these grades sulphur will substantially reduce corrosion resistance, ductility, and fabrication properties, such as weldability and formability.
2.5 EFFECT OF MICROSTRUCTURE ON PROPERTIES OF NAMSS

Kaluba et al (1999) reported that NAMSS of 0.31C0.39N15.9Cr0.95Mo steel with nitrogen and 0.39C15.89Cr0.84Mo steel without nitrogen steels where heat treated in furnace at 1050°C, the nitrogen steel shows higher hardness which can be related to the presence of residual austenite in the microstructure. Austenitization begins at 856°C for nitrogen steel and 816°C for nitrogen free steel. After solution treatment and quenching the steels were partially or entirely transformed into martensite, although the typical lath-shaped morphology was easily revealed only at relatively high austenitizing temperature. Very often, a special kind of interaction between the particles and a moving α/γ interface is observed. The final structure at room temperature consisted of lath martensite and no retained austenite was observed, even at early stages of the transformation.

Gocmen et al (1999) has reported that microstructure development and strength of new 12%Cr is characterized by increased weight fraction of nitrogen (0.15%) and vanadium, which is essentially based on the influence of solubility products of the fcc-MN phase and can be realized to provide a superior combination of grain coarsening resistance and high temperature strength over conventional 12%Cr steel. Nitride precipitation by ausageing enables to make full use of martensite hardening. Ausageing can be useful to optimize the properties and to control microstructure stability.

Gavriljuk and Berns (1999a) reported on 9-12%Cr martensitic steel, it was precipitated by tempering and found hexagonal M₂X precipitates were found after 400°C along with fine cubic (NbV)X particles precipitated beyond 700°C. Cubic (FeCr) (CN) and (NbV) (CN) precipitates were identified after ageing at temperatures up to 500°C, while beyond 600°C, M₂₃C₆ precipitates in the structure of tempered martensite were replaced by Cr₂ (CN) particle.
The sequence of precipitation during the tempering of three steels 15Cr1Mo0.6C (C), 15Cr1Mo0.6N (N), 15Cr1Mo0.6C0.6N (C+N) studied are as follows:

**C Martensite**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>ε-carbide (FeCr)(_3)C</td>
</tr>
<tr>
<td>300°C</td>
<td>θ-(FeCr)(_3)C</td>
</tr>
<tr>
<td>600°C</td>
<td>θ-(FeCr)(_3)C+ε-(CrFe)(_7)C(_3)</td>
</tr>
</tbody>
</table>

**N Martensite**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>ε-carbide (FeCr)(_2)N</td>
</tr>
<tr>
<td>300-600°C</td>
<td>ζ-(FeCr)(_2)N</td>
</tr>
<tr>
<td>650°C</td>
<td>ζ-(FeCr)(_2)N+ε-(CrFe)(_2)N</td>
</tr>
</tbody>
</table>

(orthorhombic nitride)

**C+N Martensite**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>200-400°C</td>
<td>ε-carbide/nitride (FeCr)(_3)C+fcc-(CrFe)N→ θ-(FeCr)(_3)C+ε-(CrFe)(_2)N</td>
</tr>
<tr>
<td>500-600°C</td>
<td></td>
</tr>
<tr>
<td>650°C</td>
<td></td>
</tr>
</tbody>
</table>

Prokoshkina et al (2002) has reported that in the as cast condition, all Fe alloys had ferrite structure, nitrogen free Fe-13%Cr steel was ferrite-martensitic, the same steel with 0.16%N was martensitic, and with 0.7%N was austenitic-martensitic structures.

Horovitz et al (1996) reported that microstructures of the samples 16Cr0.11Ni0.13C0.19N, 15Cr0.11Ni0.16C0.16N and 13Cr0.17N0.11C (Fe-Cr-N added) steels and AISI 420 showed ferrite with high density of precipitates for austenitizing temperatures lower than 900°C. As the austenitizing temperature is increased, formation of martensite and increasing dissolution of precipitates were observed. AISI 420 steel quenched from 1000°C contains martensite and primary carbides M\(_{23}\)C\(_6\) type. In the microstructure of 16Cr0.11Ni0.13C0.19N steel containing nitrogen, primary
precipitates are, probably, nitrides or carbonitrides (MX, MX type). Higher austenitizing temperatures favored the formation of increasing quantities of retained austenite, which decreased the hardness. The steels containing nitrogen showed lath martensite, with a dislocated substructure, typically for low carbon martensite. After tempering microstructure of the AISI 420 steel at 500°C showed that tempered martensite with undissolved primary and secondary carbides resulting from martensite decomposition. NAMSS 13Cr0.17N0.11C shows no visible secondary precipitation.

Bahrami et al (1994) reported that in 9Cr1Mo1Ni0.016C0.3N NAMSS produced by nitrogenizing at 1000°C and solution treated at 1200°C exhibited lath martensite. 0.3N, 0.1N steel when nitrogenized resulted in an inhomogeneous distribution of nitrogen and precipitates formation near the surface. Solution treated at 1200°C revealed a uniform microstructure and nitrogen distributed uniformly through the bulk material. This was confirmed by micro hardness measurements. The same steel was tempered from 400 to 750°C in various levels. At 400°C tempering, there was no significantly change in the microstructure, however there was some rearrangement of dissolution. At 500°C, did not alter the microstructure of nitrogen sample with some recovery and dissolution rearrangement on mechanical properties. Lath morphology and the high dissolution density network remains unchanged are able see from the microstructure. At 550-750°C tempering range the lattice parameter decreases significantly indicating an increase in thickness of the precipitates and compared with nitrogen free materials the hardness remains high.

Beneteau et al (2005) discussed in particular about, the high temperature treatment involving the austenitic transformation and the partial dissolution of the primary carbides and nitrides on Fe Cr15 - 16.5, Mo1.5 -
1.9\%, \ V0.2- 0.4\%, \ C0.37 - 0.45\%, \ N0.16 - 0.25\%. \ Which \ leads \ to \ the 
following \ consequences \ in \ the \ final \ properties:

i) \ the \ high \ solutionizing \ of \ the \ precipitates \ stabilizes \ the 
austenite \ and \ increases \ the \ fraction \ of \ retained \ austenite \ after 
quenching.

ii) \ the \ high \ solutionizing \ of \ the \ precipitates \ is \ beneficial \ for \ the 
corrosion \ resistance \ because \ the \ chromium \ content \ in \ the 
matrix \ increases \ and \ the \ size \ of \ the \ precipitates, \ preferential 
sites \ for \ pitting \ corrosion, \ decreases.

As \ could \ be \ expected, \ the \ final \ fraction \ of \ carbides \ M_{23}C_6 \ is \ lower 
for \ the \ higher \ temperature \ (1075^\circ C). \ It \ must \ be \ pointed \ out \ that \ during \ slow 
cooling \ from \ 1050^\circ C \ the \ phase \ fraction \ of \ carbides \ M_{23}C_6 \ rises \ again, \ due \ to 
growth \ of \ existing \ precipitates \ and \ nucleating/growth \ of \ new \ ones. \ The 
dissolution \ of \ the \ nitrides \ begins \ between \ 850^\circ C \ and \ 900^\circ C, \ at \ the \ beginning 
of \ the \ austenitic \ transformation.

The \ M_S \ temperature \ decreases \ as \ solution \ time \ increases. \ Indeed, 
due \ to \ the \ precipitates \ dissolution, \ the \ increase \ of \ substitutional \ and \ overall 
interstitial \ C \ and \ N \ atoms \ in \ solid \ solution \ leads \ to \ a \ decrease \ of \ the \ M_S 
temperature. \ Moreover, \ the \ lower \ M_S \ for \ a \ solutionizing \ at \ 1075^\circ C \ can \ be 
linked \ with \ the \ higher \ carbides \ dissolution \ at \ the \ beginning \ of \ the \ isothermal 
stage.

Dissolution \ of \ M_{23}C_6 \ starts \ in \ the \ ferrite, \ and \ continues 
simultaneously \ to \ the \ transformation \ from \ ferrite \ to \ austenite. \ The \ dissolution 
of \ Cr_2N \ starts \ when \ austenite \ forms \ and \ continues \ in \ the \ austenite \ matrix. 
Dissolution \ of \ M_{23}C_6 \ precipitates \ prior \ to \ the \ Cr_2N \ because \ of \ the \ higher 
diffusivity \ of \ carbon \ compared \ to \ nitrogen. \ These \ different \ dissolution \ rates
led to the observation of two stages in the ferrite to austenite transformation. The austenitic transformation begins in carbon rich areas around the $M_{23}C_6$.

Speidel (1988) discussed that low tempering temperature (upto 400°C) do not significantly change the microstructure, however there is some rearrangement dislocation. High nitrogen 9-12% chromium steels very nearly meet the strength and toughness at 400°C. From 400 to 600°C the nitrogen must be primarily located in finely precipitated carbonitrides. The results so far indicate that nitrogen is not helpful when precipitated out in carbonitride particles and thus, microstructures with nitrogen in solid solution are being developed.

Toro et al (2001) discussed that, second phase particles (Chromium nitrides and carbonitrides) are expected to be more abundant in samples tempered at 600°C.

The corrosion - erosion resistance of nitrided AISI 410S stainless steel containing 0.42wt% N at the surface decreased with tempering temperature in the range 200 - 600°C, (Tora et al 2003) mainly as a consequence of precipitation of cubic $CrN$ nitrides between 400 and 600°C and hexagonal $Cr_2N$ nitrides at 550 and 600°C. Precipitation of hexagonal $\varepsilon$ nitrides at 200°C did not affect the surface properties significantly. Finely dispersed cubic $CrN$ nitrides were observed in nitrided specimens tempered between 500 and 600°C, with a mean size between 5 and 20 nm. These precipitates were located both inside the grains and at the interfaces between martensite laths. Coarse, hexagonal $Cr_2N$ nitride was observed in specimens tempered at 550° and 600°C preferentially at the lath boundaries. The substitution of chromium by iron in these precipitates was not significant. The corrosion erosion resistance of the nitrided steel was superior to that of conventional AISI 420 for tempering temperatures of 200 and 400°C. The main reason for this difference was attributed to the occurrence of large Cr
depleted areas around $M_{23}C_6$ type precipitates in the conventional steel. After tempering at 600 °C, both steels showed similar surface properties.

Wu et al (2000) reported that with different quantities of Ni% 1.44 to 3.04, Cr% 8.52 to 14.74, Mo% 0.83 to 2.54, has influence of $M_S$ temperature and retained austenite. Retained austenite levels are relatively low for materials with a high $M_S$ temperature when materials are all cooled to room temperature. This is because more time available for the phase transition of martensite. The presence of molybdenum, retained austenite levels increase with the amount of nickel; also, austenite levels are somewhat higher when molybdenum is present.

Leda (1988) has reported that the influence of austenitization temperature on austenite grain growth in several Fe-Cr-C-N alloys. Alloys with high nitrogen content have smaller austenite grains. Also Fe-Cr-N alloys show smaller grains as the nitrogen content increases. From the SEM observations, it may be deduced that in high nitrogen alloys and steels a thin layer of austenite covers the grains boundary surface. Carbides in nitrogen alloys and steels are smaller and more uniformly distributed. As the austenitization temperature increases, the Cr content in carbide decreases.

In lattice, smaller lattice parameters of carbides are an indication of lower Cr content in them. Thus, it may be stated that in N alloys and steels the carbides contain less Cr. Nitrogen dissolved in austenite decreases the Chromium activity causing an additional flow of Cr from carbides into nitrogen saturated austenite.

The $M_S$ temperatures in N steels and alloys are shifted towards lower temperatures and no increase of $M_S$ is found after high austenitization temperature. After austenitization at 1030°C nitrogen stimulates plate martensite formation, but after quenching from 1200°C this tendency
vanished in austenite with very low SFE caused by N and Cr, and undergoing transformation at very low temperatures rather lath martensite formation are preferred.

While tempering, the carbides in N samples are finer and more uniformly distributed. Nitrogen increases the activity of carbon, which is the reason of easy nucleation. About the precipitates, when the activity of the main element in the precipitation reaction increases, smaller precipitates are formed and if the activity of the main element decreases larger carbides and nitrides precipitate.

2.6 EFFECT OF HEAT TREATMENT ON THE PROPERTIES OF NAMSS

Henninan et al (1999) has reported that 9-12 wt% Cr (Cr12Mo1V) stainless steel replaces the 2/3 of carbon content or carbon totally replaced by N have excellent mechanical and creep property based on their fine and homogeneous distribution of Cr$_2$N and (Nb,V) (C, N) carbonitrides precipitates in tempered lathe and /or plate martensite microstructure.

Gocmen et al (1999) reported about heat treatment, tempering, and yield strength on 1.5Mo (12%Cr 1.5%Mo 0.7%V 0.15%N 0.03%C and 11-12%Cr 1.5%Mo 0.01%C 0.15%N) and an alloy with 4.5 Mo (8-12%Cr 4.5%Mo 0.7V 0.01%C 0.16%N) respectively.

While normalizing treatment, dissolutions of carbide, nitride occurs in austenitization process. The interstitial gap is depends on the normalizing time. Characteristics of normalizing treatment in HNS is strong dependence of the martensitic hardness upon normalizing temperature for the investigated high nitrogen – high vanadium containing variants. Above 1175°C has to be applied in order to achieve martensite, which is close to conventional
12Cr steel containing carbon 0.12wt%, and about nitrogen 0.05 wt% steels. Low soluble nitrides in N-V containing 12Cr steels can be very effectively precipitated in the austenite before the martensitic transformation by means of an isothermal ageing treatment.

The tempering characteristics of HNS 9-12%Cr steels can be influenced by alloying, but also through an ausageing treatment before martensitic transformation. Alloying with nitrogen and vanadium can expand secondary hardening up to 650°C, the tempering behavior appears less affected by the elements Ni, Mn, and Co. However an increase of Mo up to 4.5wt% results in an intensified secondary hardening reaction at 600°C. This type of secondary hardening is also observed in analogous high carbon steels and is known to be due to the precipitation of Mo.

Secondary hardening in the temperature range between 450 and 539°C appears to be significantly intensified by C in high N steels. Low carbon variants (12%Cr 1%Mn 0.8%V 0.15%N 0.01%C) do not exhibit a well “peaked” maximum of secondary hardening. The secondary hardening is most effectively expanded towards 650°C by precipitation of very small sized nitride <5nm. Effect of the heat treatment on the yield strength of an alloy at low and high temperature generally decreases with increasing tempering temperature.

Bottger et al (1999) has reported that increasing the Mo fraction of the alloy enables to attain high strength values with higher tempering temperature (710 – 740°C).

Gavriljuk and Berns (1999) have reported between carbon and nitrogen martensite that the values of their hardness are changed in opposite directions during tempering. 15Cr1Mo0.6C (Carbon) steel in as quenched state and after low temperature ageing, the C martensite has a highest
hardness (685 HV) which decreases after tempering above 200°C. The secondary hardening caused by the precipitation of stable chromium carbides is not significant in the carbon steel. In 15Cr1Mo0.6N (nitrogen) steel comparatively low hardness (550 HV) of nitrogen martensite in the as quenched state increases permanently up to 500°C (650 HV) and after this exceeds the hardness of carbon martensite by about 100HV. The low hardness of the water quenched 15Cr1Mo0.6C0.6N (carbon + nitrogen) martensite is approximately 545HV obviously due to the high fractions of retained austenite.

Horowitz et al (1996) has reported that the production of NAMSS in a 15kW induction furnace, under nitrogen atmosphere, using magnesia crucible whose capacity is 16kg. The injection of nitrogen was done by an alumina lance for 16Cr0.11Ni0.13C0.19N steel, by a porous plug for 15Cr0.11Ni0.16C0.16N steel, by an Fe-Cr-N master alloy of steel 13Cr0.17N0.11C steel (almost equal to AISI 420 but reduced carbon and nitrogen (0.11 C% and 0.17N%) Ni free and AISI 420 for comparison. It is noticeable that the AISI 420 steel is harder than the NAMSS at higher austenizing temperature. After tempering, the high nitrogen steels showed higher hardness (545 HV) than the AISI 420 and for tempering temperatures between 300 and 550°C the hardness is 515 HV. Moreover, secondary hardening at temperatures around 500°C, can also be seen, its hardness being 580 HV but there is no change in AISI 420. This should be probably due to coherent precipitation inside martensite during tempering.

Prokoshkina et al (2002) studied with micro ingot of pure Fe, Fe-O, Fr-Cr steel produced under nitrogen atmosphere. In the as-cast condition, all Fe alloys had ferrite structure, Nitrogen free Fe-13%Cr steel was ferrite-martensitic, the same steel with 0.16%N was martensitic, and with 0.7%N was austenitic. The distribution of hardness along the length of the initial cast
ingot was non-uniform due to dendritic liquidation of alloying elements. After hardening and quenching, the hardness of all materials increased, phase content changes, lattice parameter increases. The nitrogen content in solid solution increased because part of the nitride particles dissolved in the austenite on heating and remaining in a solid solution after rapid cooling.

Bernauer et al (1999) reported on martensitic stainless steel with nitrogen of Cr13, Cr15, Cr17. N is added to Cr13 steel in order to raise the hardenability in relation to the annealing temperature and demonstrates a significant increase in the hardness (60HRc) due to alloying with nitrogen, while nitrogen free steel shows 57HRc.

Bahrami et al (1994) reported on 9Cr0.016C0.3N martensitic stainless steel nitrogenized at 1000°C and solution treated 1200°C sample showing a uniform nitrogen distribution. The nitrogen solubility is higher at 1200°C than 1050°C solutionizing temperature, so that the hardness also increased. Additions of nitrogen prevented grain growth and originated a finer structure. Some dependence of strength on grain size is expected.

However, the hardness (at 500°C) for nitrogen alloys is always higher. Material containing 0.27%N shows tensile and yield strength of 1429 and 1224MNm⁻² respectively. If tempered at 500°C, values of 1596 and 1348 MNm⁻² at 550°C as martensite decomposes very small precipitates nitrides or carbonitrides (type M₂X) are formed. At 600°C tempering temperature can be explained by finer precipitation, in combination with high dislocation density and the small martensite lath size, and at 720-750°C the dislocation density is considerably reduced (and also precipitates have grown); in this condition, nitrogen in the lattice is a minor factor and the main controlling parameter is the interaction of dislocation with finely dispersed particle. Increasing the nitrogen content results in a reduction in the inter particles distance, which increases the strength of the material.
2.7 EFFECT OF THERMO MECHANICAL WORKING PROPERTIES ON NAMSS

Balachandran et al (2000) has reported that tensile and yield strength increase with nitrogen content at almost similar rate in steels with about 0.1%C. Carbon has little effect on yield strength of the as forged steels. However, carbon decreases strength due to lamellar nitride precipitate formation. The fractography of low carbon steels showed completely dimple rupture, and some of the steels show elongated dimple, slip step within the dimple and serpentine glide, characteristics of highly ductile steel. At higher carbon content, the fracture was quasi cleavage type with shallow dimple, indicative of poor plasticity.

Prokoshkina et al (2002) reported that High Temperature Thermo mechanical Treatment (HTMT) cycle leads to an increase in the steel hardness on 13Cr0.12C0.16%N, and significantly changes the grain structure and phase content in comparison to quenching. The average grain size in the initially cast and then hot deformed steels corresponds to the grain size in the quenched steels that testifies to an absence of recrystallization. Partially recrystallized (~15%) structure was observed only in initially forged very fine-grained (3-5µm) steel. After hot deformation, lattice parameters and X-ray line width increase significantly in comparison to the as-cast condition. The tempering treatments lead to internal stress relaxation, lowering of lattice parameters and X-ray line width. In vanadium-free steels, the martensite decomposed at temperature as low as 100°C but in vanadium-containing steels, the martensite decomposition began at 200°C.

Cardoso et al (2003) discussed that AISI416 stainless steel alloying elements (specially carbon and chromium) strongly influence the microstructure transformations that can occur during hot forming process. These transformations may lead to duplex microstructure formation
(δ-ferrite+martensite), which can affect adversely the forming characteristics, with a possibility of inducing cracks and rejection of material. Additionally, after heat treatments hot workability in the temperature range of 1000-1250°C evaluated by hot torsion tests with emphasis in maximum strength and ductility.

Kabutkina et al (2002) reported that Cr11N1, Cr11Mo1N1 martensitic stainless steels in the course of the strengthening process removal of cold work effects, is observed and possible phase transformation (such as precipitation and dissolution of nitrides and carbide-nitrides, or the γ→α transformation) has also occurred. Quenching of these steels after hot deformation results in martensitic transformation based on the chemical composition.

Alloying of Cr11N1 steel with molybdenum (1.4%Mo) increases the true strain of hot deformation, inhibits the process of nitrides and carbide-nitrides precipitation and growth, and widens the permissible range of hot deformation temperatures in the cycle of thermo mechanical treatment assuring the high strength state of material after quench hardening to be obtained. The course of phase transformation (i.e. ageing processes and the γ→α austenitic-ferritic transformation) during hot deformation of nitrogen steel with 11%Cr leads to decrease in strain stress diagram and a decrease in the strength level. Deformation at high temperatures (>1000°C) is undesirable because of the formation of large sized precipitated particles and the growth of grains.

Thermo Mechanical Treatment (TMT) process in the austenitic condition, by the gradual reduction of size, inhomogeneities of composition caused by segregation during casting. Heat treatment process after hot forging leads to the breaking down of the original coarse cast structure by repeated recrystallization of the steel. In addition, the inevitable non-metallic
inclusions, i.e. oxides, silicates, sulphides, are broken up, some deformed, and distributed throughout the steel in a more uniform manner.

### 2.8 WEAR RESISTANT PROPERTIES OF NAMSS

Brandes and Brook (1992) reported that adhesive wear or sliding wear is, by transference of material from one surface to another due to the process of solid-phase welding. Adhesive wear is often used, loosely, to describe other metal-to-metal wear mechanisms, including the removal of particles detached by fatigue arising from cyclic contact stresses and in which no adhesion occurs.

Berns (1996) has reported that martensitic stainless steels have been used in components operating under wear, corrosion and erosion + corrosion conditions found in distillation towers, slurry pumps and mixers of chemical products.

Guenbour (1988) has reported that HNS materials show high mechanical properties and moderate corrosion resistance, but when under erosion action by the presence of hard particles in aqueous solutions their performance is reduced due to a synergistic effect between wear and corrosion mechanisms.

Kim et al (2003) nitrided AISI 420 (12-14Cr, 0.15%C, 1%Si, 1%Mn) with hot wall nitriding reactor in different treatment time (1-16h, 4h) and temperature (400°C, 350-500°C). A low-pressure RF (Radio Frequency) discharge using pure nitrogen is an effective medium for nitriding martensitic stainless steel. With a treatment time of 4 hours at 400°C, the nitrogen-rich layer was 20µm thick and had a hardness of approximately 4.3 times higher than that of the untreated material. The alloy AISI 420 was more susceptible to the formation of CrN and ferrite than AISI 304. The transformation was
evident after 9 h treatment at 400°C and completed after only 4 h at 450°C. This has a deleterious effect on the hardness again, so that 4 h, 400°C is close to the optimum treatment conditions. Under these conditions, the treated layer retains its martensitic structure, but with a larger lattice parameter than the bulk. The situation was very similar to that obtained with austenitic stainless steel, and the analogy prompted the use of term the newly identified phase ‘expanded martensite’. The fact that treated layer retains a bcc structure is interesting in view of previous evidence that nitrogen changes structure to fcc. The activation energy obtained for AISI 420 is much lower than that of austenitic stainless steels which indicates easy formation of a thicker diffusion layer.

Toro et al (2001) reported on AISI 410S with 0.035%N gas nitrided at 1200°C under 0.25MPa high purity nitrogen atmosphere and oil quenched martensitic stainless steel performed with erosion tests for 96 hours. Nitrided, direct quenched and 200°C tempered AISI 410S steel was more resistant to corrosion+erosion than AISI 410 and 420 quenched and tempered at the same temperature.

Stein et al (1999) reported 15Cr1Mo and nitrogen 0.2 to 0.5% influences more corrosion resistant cold work tool steels and its hardness value above 58HRc and excellent resistance against wear as well as pitting corrosion. Nitrogen bearing precipitations in hot work tool steels are responsible for an improvement of hot strength compared to similar carbon steel. The life time of tool like forging dies made out of conventional X17CrMoVN5-1 with 0.22%N therefore clearly is improved compared to those made out of AISI H 13 materials.

Bernauer et al (1999) reported on martensitic stainless steel Cr15 steel, with nitrogen are super imposed for wear resistance, hardness and corrosion resistance.
2.9 EFFECT OF CORROSION RESISTANCE PROPERTIES ON NAMSS

Alberto Akikazu Ono et al (1996) reported about polarization result on 13-16%Cr, 0.11-0.13%C, 0.16-0.19%N, nitrogen martensitic stainless steels and AISI 410 and 420, analyzed with 0.5M H$_2$SO$_4$. The results suggest that nitrogen and carbon have different influences on the passive current density; AISI 410 and 420 steels shows highest passive current density. Nitrogen present in the C alloy seems not to have great effect on the passive current density of the alloy, which have less than 0.2%N and no molybdenum addition. Nitrogen when present in solid solution, increases the critical current density while, it decreases after tempering. This can be explained due to the decrease of the nitrogen content in the matrix promoted by the precipitations of nitrides or carbonitrides. Nitrogen increases the pitting potential of the martensitic stainless steels, even without molybdenum addition. The tempering treatment of 500°C has an important influence on the corrosion behavior of the high nitrogen martensitic stainless steels.

The mass loss of the alloy in heat treated and quenched condition, after 120 min immersion tests in 0.5M H$_2$SO$_4$ solution, increases with the Cr content of the steels, like other Fe-Cr alloys. The Nitrogen bearing alloys at tempered condition show higher mass loss while AISI 410 and 420 alloys in the hardened and tempered condition the mass loss is similar. Nitrogen affects the corrosion behavior of these steels, decreasing the mass loss of the steels when it is present in solid solution. It increases the mass after tempering and is due to decrease in nitrogen content in the matrix promoted by the precipitation of nitrides or carbonitrides.

Horovitz et al (1996) reported on anodic polarization curves for AISI 420 and 13%Cr 0.17%Mn 0.11%C steels. The passive current value for the nitrogen steel is lower, in hardened and hardened and tempered
conditions, than those for the AISI 420 steel, indicating that the nitrogen steel possesses higher corrosion resistance. Precipitation of incoherent M$_{23}$C$_6$ type carbide in the quenched and tempered AISI 420 steel is responsible for the substantial decrease in the corrosion resistance, as it leaves the matrix depleted from chromium, while small coherent and well distributed precipitates with lower Cr content, present in the nitrogen steel, contributes to a better corrosion resistance. TEM structure shows that samples quenched from 1000ºC and tempered at 500ºC has lath martensite with dislocated substructure.

Bernauer et al (1999) reported that martensitic 15 wt%Cr steels with nitrogen have better wear resistance, hardness and corrosion resistance. These properties are achieved by a high corrosion resistant hard matrix and an optimized distribution of hard particles. This is particularly used for bearing and surgical instruments. Martensitic 17 wt%Cr steels are characterized with an outstanding corrosion resistance and highest homogeneity and purity.

Li and Bell (2006) studied about corrosion properties of plasma nitrided at 420, 460, 500ºC AISI 410 martensitic stainless steel with chemical composition of 0.15%C, 0.33%Si, 0.43%Mn. 12.20%Cr and 0.27%Ni. Corrosion test performed electrochemically at room temperature with 3.5% NaCl solution by polarization technique. Immersion technique (mass loss) was performed with 1%HCl in an acidic water for up to 100 hrs. Plasma nitriding improves the corrosion resistance of the 410 stainless steel in 1% HCl and in 3.5% NaCl aqueous solution. In immersion tests in 1% HCl, the nitrided samples showed reduced corrosion weight loss and corrosion rate. In polarisation corrosion test in 3.5% NaCl solution, the nitrided samples had higher corrosion potentials, higher pitting potentials and lower current densities. The improvement in corrosion resistance was attributed to the formation of a compound layer containing iron nitride of C-Fe4N and
\(\varepsilon\)-Fe\(2\)–3N in the surface of the 410 martensitic stainless steel. The formation of chromium nitride was of less importance in affecting the corrosion resistance of the 410 steel when a compound layer containing \(\gamma\) and/or \(\varepsilon\) iron nitride was formed on the plasma nitrided surface.

Makoto Ogawa et al (2002) have reported that HNS, which contains 1% nitrogen and less than 0.1% Mn, can manufacture. These HNS show good localized corrosion relative low Cr and Mo content. Supersaturated nitrogen causes gasification or nitride precipitation by melting or heating up to just below the above mentioned temperature. HNS containing above 1% in nitrogen content suppress the blow hole generation at weld metal and Cr nitride precipitation at HAZ. The pitting corrosion resistance equivalent of the weld metal is also predicted by Cr, Mo and nitrogen content, segregation followed by depletion of these elements in the weld metal should be taken into account.

Yoshikuni Nakao et al (2002) have reported Nitrogen has the effect of not only to delay the progress of corrosion by dissolving as ammonium ion (\(\text{NH}_4^+\)) when the pit generates, but also to suppress the precipitation of the intermetallic compound in the materials. The same way Cu, Mn had susceptibility to crevice corrosion even if PRE 52 or more. Si and Mn that promote precipitation of sigma phase must be reduced to promote crevice corrosion resistance. The reason for this was that the precipitation of sigma phases was observed in the microstructure of this material and the corrosion attack was observed in the matrix immediately surrounding the sigma phase where Cr and Mo depletion took place. Therefore, it is necessary to add more Mo and nitrogen instead of Cr to improve the crevice corrosion resistance. The effect of nitrogen was examined for the range of 0.1–0.3 mass%.

Hanninen et al (1999) reported that high nitrogen stainless steel, nitrogen alloying increases especially, the resistance to localized corrosion
such as pitting corrosion and crevice corrosion together with Cr and Mo. Other benefits of nitrogen alloying are sensitization resistant to stress corrosion cracking and resistance to wear. Nitrogen alloying can exert a possible positive role:

i) nitrogen enrichment through anodic segregation

ii) formation of a protective surface layer consisting of Cr rich oxide

iii) dissolution of nitrogen during active corrosion forming ammonia ions, which passivate the pits, crevice and cracks

iv) dissolution of nitrogen forming nitrates or nitrites, which act as local inhibitors. Additionally nitrogen expands the passive region by reducing passivation potential and increases the transpassive potential (pitting corrosion). For pitting and crevice corrosion PRE index for nitrogen proposed by Truman and Tsug (1988) is 13 to 16. Mn which is most probably related to MnS inclusions acting as pitting corrosion initiation sites and can be balanced by the beneficial effect on N. Pitting corrosion strongly affects the microstructural inhomogeneity.

Toro et al (2001) discussed about spalling of chromium carbides precipitated at prior austenite grain boundaries that could be a consequence of the exposure of these carbides due to localized corrosion of chromium-depleted matrix. Precipitation of carbide and nitride in martensitic stainless steels could also contribute to the increase in the pitting susceptibility.

Stein et al (1999) reported that for martensitic stainless steel 12Cr High Nitrogen Martensitic Steel (HNMS) the benefits from nitrogen in solid
state are not to attain strength or hardness but a distinct improvement of corrosion resistance in martensitic stainless steel. This steel with 15Cr1Mo and nitrogen 0.2% to 0.5% influences more corrosion resistant on cold work tool steel and is well known under brand name of CRONIDUR, its hardness value is above 58HRc and has excellent resistance against wear as well as pitting corrosion.

Berns et al (1998) reported on HNS tool steel whose the corrosion resistance is significantly high. The improved wear properties of HNS are presumably attributed to the much finer and much more homogeneously distributed precipitates of nitrides and carbides. The reason for the improved corrosion resistance is brought about by sufficient contents of Cr, Mo and N, as far as these elements are dissolved within the solid solution.

2.10 WELDING OF NAMSS

Makoto Ogawa et al (2002) have reported that, High Nitrogen Steel (HNS), which contains nitrogen about 0.5 to 0.7mass% in nitrogen content along with high Mn content, were developed. 0.8% nitrogen content, which was beyond the solubility at the molten state, could be welded with no pores by choosing appropriate welding methods and conditions so as to form a small and shallow molten pool. 1% nitrogen content are to suppress the blow hole generation at weld metal and Cr nitride precipitation at HAZ.

Bonnefois et al (1988) has reported that nitrogen influences strongly both the solidification mode and the ferrite content of the weld metal, and studied the effect of higher nitrogen and manganese (often used to increase the solubility of nitrogen) in stainless steels and found a negligible effect of manganese, a lower effect than previously observed for nitrogen. Increased ferrite content is the result of welding thermal cycles. Cooling rates
are too high to allow complete $\alpha \rightarrow \gamma$ retransformation of high temperature ferrite.

As reported by Gavriljuk and Berns (1999) which implies that a take-up of nitrogen in the hot spot is opposed by losses outside of it. Since the weld pool is covered by the arc, the loss of nitrogen may be contained. It is recommended to keep the weld pool small. Nitrogen contained in the penetration zone and may be in some of the Heat Affected Zone (HAZ) will be flushed in to the weld pool, the composition of which is adjusted by the alloy content of the filler metal. Higher Cr, Mn, Mo content will reduce the effusion of nitrogen. In TIG weld nitrogen fluxes to be expected (between heat source, shielding gas, hot spot, weld pool and penetration zone) in the direction of lower nitrogen activity.

According to Kikuchi et al (1996) nitrogen content of the weld pool at full penetration may be influenced by the partial pressure $p_{N2}$ and the additions of Ar will give a sufficient $p_a$ to suppress bubbles pressure and pores during solidification. In MIG welding of a CrNiMo austenitic stainless steel in a pressure chamber filled with nitrogen of up to 6 bar increased the nitrogen content of the weld metal to 0.6 mass%. Nitrogen promotes austenite strength and corrosion resistance. It is therefore important to at least maintain the nitrogen content of the base metal in the HAZ and the weld metal. In some cases, an increase may be beneficial for suppressing ferrite. This initial nitrogen content is accumulated in the weld pool at full penetration.
Meyer et al (2001) has reported that 3Cr12 (12Cr 1.5Mn 1.5Ni 0.03C 0.03N) chromium steel weld, the phase composition of the heat affected zone at high temperature depends on the relative amount of austenite and ferrite stabilizers in the steel. Grain growth occurs during the heating cycle and close to the peak temperature when the phase composition is fully ferritic. The influence of martensite grain growth may only account for part of the observed loss of toughness in the HAZ of weld.

Gooch and Ginn (1988.) studied the influence of carbon and nitrogen carbon and nitrogen affect the impact properties of the heat-affected zone in 11-12% chromium steels in two different ways. First, the hardness of the intergranular martensite that forms in the high temperature heat affected zone increases with increasing carbon and nitrogen contents, which is harmful to the impact properties. Second, both carbon and nitrogen are strong austenite stabilizers and can restrict δ-ferrite grain growth by producing a dual phase at the high peak temperatures reached during welding. An optimum amount of carbon and nitrogen exists where the detrimental effect of a harder HAZ exceeds the beneficial effect of a finer structure.

Zaayman (1992) has reported that the ideal amount of carbon and nitrogen is strongly dependent on the content of other alloying elements in weld.

2.11 ETCHANTS FOR PHASE IDENTIFICATION

Horovitz et al (1996) selected the Vilella reagent solution for 30 seconds as etchants for 13-16Cr, 0.6-0.19N, and 0.11-0.16C HNMSS to study the surfaces by SEM.
Yuji Ikegami (1996) selected aqueous solution of 10% oxalic acid as etchant to observe microstructure on thermo mechanical treated samples of 16 – 21Cr 0.33 – 0.655N containing Cr-Mn-Ni austenitic stainless steel.

Alejandro Toro et al (2003) opted for the chemical etching with Kalling’s 1 reagent for 3-5 min to find the different intermetallic phases of nitrides in AISI 410S stainless steel.