DEVELOPMENT AND CHARACTERIZATION OF NICKEL FREE DUPLEX STAINLESS STEEL

THESIS

Submitted in partial fulfillment of the requirement for
The award of the degree of

Master of Technology
In
MATERIALS SCIENCE AND ENGINEERING

Submitted by

ALOK KUMAR

(Roll No: 60602002)

SCHOOL OF PHYSICS AND MATERIAL SCIENCE

THAPAR UNIVERSITY

PATIALA-147004, INDIA

June 2008

Dedicated to

My Loving Parents

CERTIFICATE

This is to certify that the thesis entitled **“Development and Characterization of Nickel free Duplex Stainless Steel”** submitted by **Mr. Alok Kumar**, in the partial fulfillment of the requirement for the award of the degree of M. Tech. in Materials Science and Engineering from the School of Physics and Materials Science, Thapar University, Patiala, is a bonafide record of candidate’s own work carried out by him under our supervision and guidance. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

The thesis work has been carried out from 02.01.2008 to 30.06.2008

LK Singhal
Dr. L. K. Singhal
Director
Jindal Stainless Limited
Hisar

Dr. O. P. Pandey
Prof. & Head
School of Physics and Materials Science
Thapar University, Patiala

Supervisors

Countersigned by:

Dr. O. P. Pandey
Prof. & Head
School of Physics and Materials Science
Thapar University, Patiala

RK Sharma
Dr. R. K. Sharma
Dean, Academic Affairs
Thapar University, Patiala

ACKNOWLEDGEMENT

Words can hardly express my sense of gratitude to my supervisor, Dr. O.P. Pandey, Prof. and Head, School of Physics and Material Science, Thapar University. His wide knowledge and logical way of thinking have been of great value for me. He and the other faculty members, Dr. K. K. Raina, Dr. N. K. Verma, Dr. Kulveer Singh, Dr. Sunil Kumar, Dr. Manoj Kumar, Dr. D. P. Singh, Dr. S. Das and Dr. S. Tiwari, patiently guided me through the study process, never accepting less than my best efforts. Their understanding, encouraging and personal guidance have provided a good basis for the present thesis report. I thank them all.

This thesis could not have been written without the kind help of Dr. L.K. Singhal, Director, Jindal Stainless Limited, Hisar, who guided me during my experimental works. I wish to express thanks to Mrs. Manjusha Jindal, Dr. V. Rao, Mr. C. P. Agarwal, Mr. Rohit Kumar, Mr. Nagrajan P., Mr. K. Ghosh and all members of R&D, Jindal Stainless Limited, who give their support during my experimental work.

I wish to express my warm and sincere thanks to all my friends who devoted their valuable time and helped me in all possible ways towards successful completion of this work. Thanks is very small word for my dearest friends Ms. Deepa Rajwar and Ms. Suksham Charu, whose ideas and concepts have had a remarkable influence on my understanding in the field of Material Science and Engineering. I also want to thanks my dear friend Mr. Vishal Singh; I always find him with me at every difficult moments.

I owe my most sincere gratitude to my parents, sisters, brother and my whole family whose honest support and obstinate love give me energy to complete this work successfully and gave me untiring help during my difficult moments. They have always wanted the best for me and I admire my parent's determination and sacrifice to put me through college. Thanks is a very small word for this.

I thanks to all those who have contributed directly or indirectly to this work.

ALOK KUMAR

ABSTRACT

A new high nitrogen, Ni free duplex stainless steel containing 21wt% Cr, 1.6wt% Cu, 5wt% Mn, 0.2wt% N has been developed. This stainless steel was tested for its mechanical and corrosion behavior in several organic acids, inorganic acids and salts. Result shows that this stainless steel with 58% ferrite has much higher yield strength and corrosion resistance compared to standard austenitic stainless steels: 304, 304L and 316L. This stainless steel also exhibited superior corrosion resistance compared to 304N, 316N and duplex (low Ni) stainless steel containing similar chromium and manganese with 1.5wt% nickel content. The newly developed duplex (Ni free) stainless steel has better corrosion resistance property in sulfuric acid media and in other inorganic media. This duplex stainless steel also behaves better in organic media and craft solutions. This duplex stainless steel can be used in chemical industry, pulp and paper industry, where high strength and good corrosion resistance property are required.

CONTENTS

CHAPTER 1

Introduction

CHAPTER 2

Literature Review

CHAPTER 3

Experimental Procedure & Materials

CHAPTER 4

Results & Discussions

CHAPTER 5

Conclusions and Scope of Future Work

LIST OF TABLES

LIST OF FIGURES

CHAPTER-1

INTRODUCTION

1.1 Stainless steel

Stainless steels are a family of special grade of iron- based alloys that contain at least 11 wt% chromium in their composition necessary to produce passivity. As their name suggest stainless steels can retain the stainless appearance as compared to the rusty look of common carbon or mild steels [1].

Like many scientific discoveries the origins of stainless steel lies in a serendipitous accident. In 1913, Harry Brearley of Sheffield (Britain) found that steel that had been alloyed with a sufficiently high level of chromium was not susceptible to attack from etching acids or moisture. These alloys contained around 13% chromium [2]. The first application of these steels was found in cutlery.

The veracity of stainless steel found in the wide range of its applications from creative expressions in architecture to the hygienic uses in household kitchenware. Stainless steel is more expensive than standard grades of steel but it has greater resistance to corrosion, greater strength to weight ratio, needs low maintenance and has no need for painting or other protective coatings. These factors suggest that the stainless steel can be more economically viable, once service life and life-cycle costs are considered.

1.2 Classifications of stainless steel

Historically stainless steels have been classified by microstructure and are described as austenitic, martensitic, ferritic, and duplex. In addition a fifth family, the precipitation hardenable stainless steels is based on the type of heat treatment [1, 3].

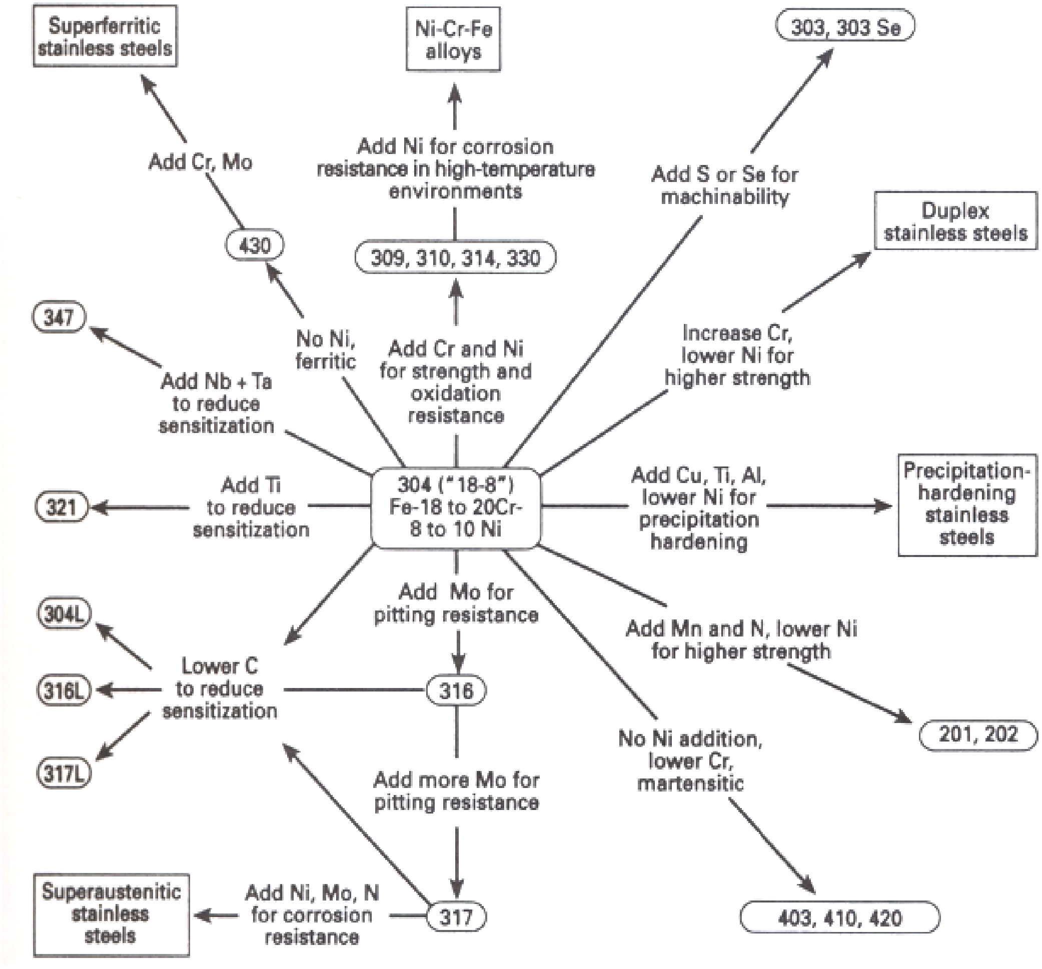


Figure 1.1: Family of stainless steel. [3]

1.2.1 Austenitic stainless steels

As name suggests this stainless steel contains the austenite phase, in which crystals have the FCC (Face Centered Cubic) structure. Austenitic stainless steels constitute the largest stainless family in terms of number of alloys and usage. Generally it contains 16 to 26% Cr, 10 to 22% Ni, and small amounts of other alloying elements such as molybdenum, titanium, niobium, and nitrogen [3]. Austenitic stainless steels cannot be hardened by heat treatment. They are normally used in the quench-annealed state, which means that they are soft and highly formable. Cold working increases their hardness and strength. Austenitic stainless steels found their applications mainly in consumer products, transportation, architecture, food and beverage, chemical and petrochemical, pulp and paper [3].

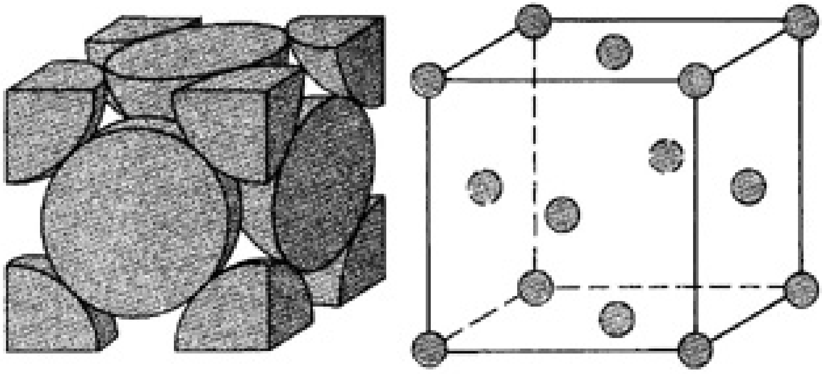


Figure 1.2: Crystal structure (FCC) of austenite.

1.2.2 Ferritic stainless steels

Ferritic stainless steels have the phase with BCC (Body Centered Cubic) crystal structure. These stainless steels are non hardenable iron-chromium alloys, containing 10 to 27% Cr, 0.08 to 0.2% C, and small amounts of ferrite stabilizers, such as aluminum, niobium, and titanium [3]. Ferritic stainless steels successfully used in automotive exhaust system parts, gas turbine silencer housings, annealing boxes, food and beverage industry [4].

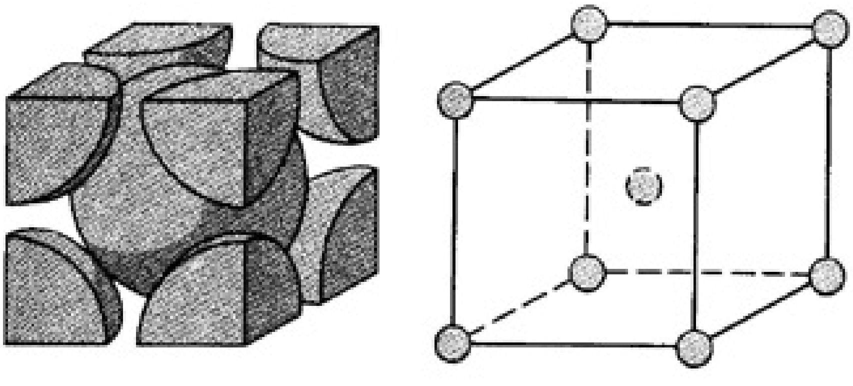


Figure 1.3: Crystal structure (BCC) of ferrite.

1.2.3 Martensitic stainless steels

Martensitic stainless steels are similar in composition to the ferritic group but contain higher carbon and lower chromium to permit hardening by heat treatment. They contain 11 to 18.0% Cr, up to 1.20% C, and small amounts of manganese and nickel [3]. Due to their high strength, martensitic stainless steel used in cutlery, hand tools, dental and surgical industry, mining equipment, rifle barrels [4].

1.2.4 Duplex stainless steels

Duplex stainless steels have microstructure of approximately equal amounts of austenite and ferrite. These alloys contain roughly 22 to 25% Cr, 5 to 7% Ni, up to 4% Mo, as well as additions of copper and nitrogen [3]. Duplex stainless steels mainly used in petrochemical industries, pulp and paper mill industries, chemical industries, food and beverage equipments, offshore platforms, structural and mechanical components, sulfuric acid plants, multipurpose containers for transportation [3].

1.2.5 Precipitation-hardenable stainless steels

Precipitation - hardenable stainless steels are chromium- nickel alloys containing alloying elements such as aluminum, copper, or titanium, which allow them to be hardened by solution and aging heat treatment [3]. These stainless steels can be used in aircraft and nuclear reactor components, engine parts, valve parts, structural components, bearing plates on bridge [3].

1.3 Nickel price and new development

Austenitic grades have been necessary for the progress of technology during the last 80 years**.** Most of the known austenitic stainless steels such as 304L, 316L; used in the market have nickel contents of about 6 - 22%, which is much higher than the Ni content used in other stainless steel grades (Table 1.1). During the last few years, the worldwide economic situation has resulted in the price of nickel being very - unstable, with a marked tendency to increase [5]. Manufacturers and retailers of stainless steels therefore have difficulty in operating within a fluctuating market, so steel product processing companies, for their part; have difficulty in establishing the prices of the parts produced since they cannot fix the exact price of the raw material until the time of delivery.

Table 1.1: Comparison of Ni wt% used in different common stainless steel grades.

Stainless steel	Austenitic stainless steels	Ferritic stainless steels	Martensitic stainless steels	Duplex stainless steels	Precipitation hardenable stainless steels
Ni wt%	6-22	0.5-1.5	0.5-0.75	3.5-6.5	4

Due to this reason, research on different austenitic stainless steels with low nickel contents is increases. This include 200 series stainless steels (201, 204 Cu) and low Ni duplex stainless steel (2304, LDX 2101), which are more widely used and have been known for some time, are included in various standards and are used because of their specific characteristics. Others have been recently developed with the aim of obtaining some of the basic characteristics of austenitic stainless steel. In fact, by suitably increasing the content of the less costly elements (nitrogen, copper and manganese), it is possible to stabilize the austenitic phase in stainless steel which is equally stable.

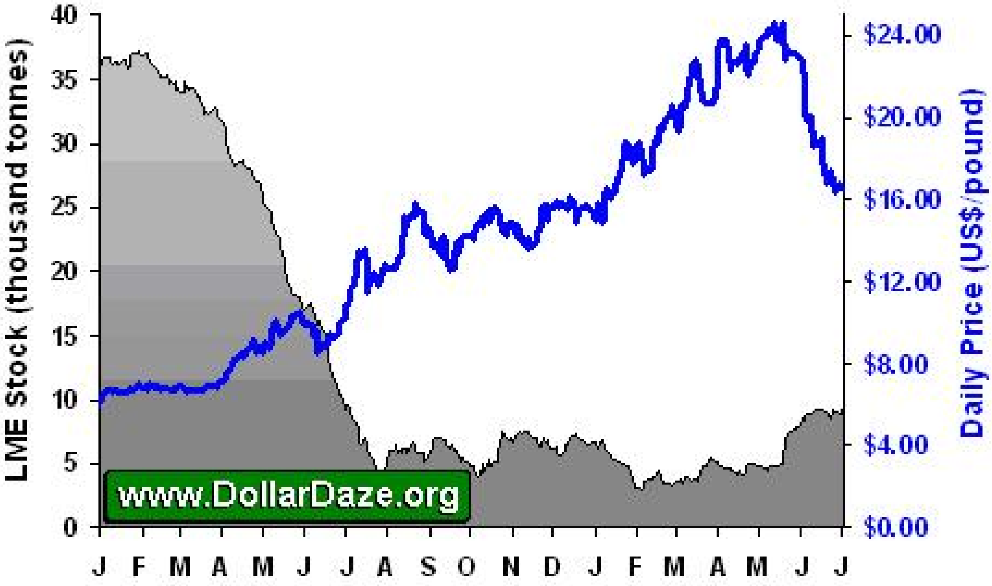


Figure 1.4: 2006-2007 Nickel LME stock and price.

1.4 Comparisons of the properties of stainless steels [6]

If we compare the different physical, mechanical and corrosion resistance properties, we find that the duplex stainless steels are better than other grades, because these group of stainless steels provide similar properties or even better as austenitic stainless steels at low cost.

1.5 Low nickel and/or nickel free duplex stainless steel

From the above discussion about the price of nickel and their content in different stainless steels along with comparison of different properties of stainless steels, it is clear that the duplex family offers a good combination of economy, weldability and toughness and are often selected where both strength and corrosion properties are crucial. Duplex stainless steels are more technically demanding than the standard austenitic stainless steel grades such as type 304 and 316, because they offer high strength and superior corrosion resistance in various aggressive environments.

But currently popular duplex stainless steel also contain some amount of Ni (3.5 to 6.5wt %), which limit their application in general application due to high price. Several laboratories and industries are trying to develop the less Ni content duplex stainless steels. In this order Ni and/ or Mo free duplex stainless steel can be a suitable candidate of low cost stainless steel. In this duplex stainless steel Cr is used to stabilize the ferrite phase and nitrogen is used to stabilize the austenitic phase, in place of costly nickel. Here along with nitrogen, Mn is also used in order to increase solubility of nitrogen in melt and Cu is used to compensate the loss in ductility due the absence of Ni. Addition of nitrogen gives the high corrosion resistance properties to the duplex stainless steel, in different corrosive media and exceptional mechanical properties like high strength [7]. Cr and Cu also improve corrosion resistance.

1.5.1 Phases in duplex stainless steel

The microstructure in duplex stainless steels is usually composed of approximately equal amounts of austenite and ferrite. The austenite looks like island in a ferrite matrix. The austenite ratio can be increased to about 55 - 60 % in order to improve the toughness properties. The desired microstructure is usually obtained by hot working, followed by solution annealing and quenching to ambient temperature.

1.5.2 Mechanical properties of duplex stainless steels

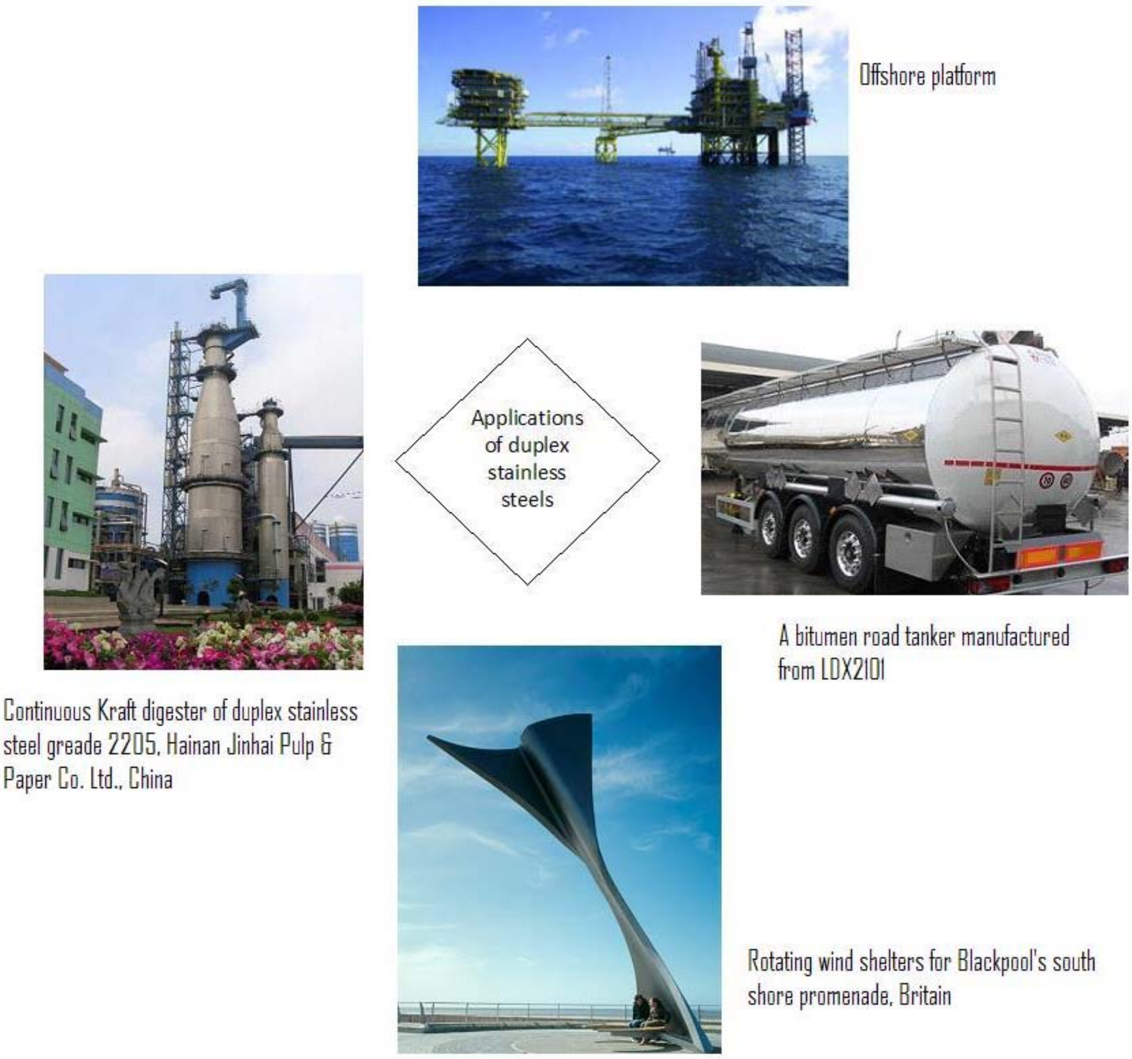
The yield strength of duplex stainless steel (DSS) is 2-3 times higher than that of 18% Cr - 10% Ni austenitic stainless steels. The ferrite usually contributes to the high yield strength, but the strength in duplex stainless steel is also higher than for pure ferritic stainless steels. This can be explained by the small grain size in DSS, caused by mutual hindering of the growth of the ferrite and austenite grains, implying higher strength for the two phase structure than its constituents. It has also been shown that the austenite might be stronger than the ferrite due to interstitial solid solution hardening of nitrogen in the austenite. The high yield strength in duplex stainless steel is the result of [8]:

- Presence of ferrite
- Small grain size
- Formation of hard secondary austenite
- Interstitial and substitutional solid solution hardening

1.5.3 Corrosion resistance properties of duplex stainless steels

Duplex stainless steels are known for their high corrosion resistance properties in different corrosive media like nitric acid, sulfuric acid, sea water etc. They have high resistance to intergranular corrosion even in chloride and sulphide environments, Duplex stainless steel exhibit very high resistance to stress corrosion cracking. Due to these facts duplex stainless steels and/ or low Ni duplex stainless steels found their application in different areas like (Figure 1.5):

- Chemical processing, transport and storage
- Oil and gas exploration and offshore rigs
- Oil and gas refining
- Marine environments
- Pulp & paper manufacturing
- Chemical process plant



Offshore platform

Continuous Kraft digester of duplex stainless steel greade 2205, Hainan Jinhai Pulp & Paper Co. Ltd., China

A bitumen road tanker manufactured from LDX2101

Rotating wind shelters for Blackpool's south shore promenade, Britain

Figure 1.5: Different area of application of duplex stainless steels.

CHAPTER-2

LITERATURE REVIEW

2.1 Duplex stainless steel

Duplex stainless steels, as cast or wrought products, have been used since the middle of 20th century. However, it is only since the late seventies that these alloys became popular by the increased use of "argon oxygen decarburization" (AOD) refining technology combined with continuous casting processes [9]. Duplex stainless steels are a family of grades combining good corrosion resistance with high strength and ease of fabrication. They provide significantly greater strength than the austenite grades while exhibiting good ductility and toughness. The high corrosion resistance and excellent mechanical properties with attractive appearance of duplex stainless steel are the result of chemical composition and balanced microstructure. Due to presence of both austenitic and ferritic phase, the duplex stainless steel shows attractive properties of both austenitic and ferritic stainless steels such as high tensile strength and fatigue strength, good toughness at low temperatures, adequate formability and weldability and excellent resistance to stress corrosion cracking, pitting and general corrosion [10, 11, 12].

Duplex stainless steel find an increasing use as an substitute to austenitic stainless steels, mainly where chloride or sulphide stress corrosion cracking are of concern, e.g., in the oil and gas, paper and pulp, petrochemical industries [13, 14, 15]. In general, the duplex stainless steel with 45% ferrite in matrix exhibits much higher mechanical strength and similar corrosion resistance as compared to standard 304 stainless steels [16].

Generally duplex stainless steels with composition (22-26) % Cr – (5-7) %Ni – (0.15-0.25) % N, have yield strengths two to three times higher than those of austenitic stainless steels and also exhibit greater resistance to stress corrosion cracking in chloride environments than does 316 stainless steel [17]. Nitrogen addition in stainless steel raises the UTS, yield strength and produce a variety of markable properties like high ductility and resistance to stress corrosion cracking [10, 18].

2.2 Classification of duplex stainless steel [9]

In the case of wrought products, three main compositions generally used are:

1) The 23%Cr - 4%Ni - 0.10%N, Mo free grade (SAF2304), can be used to replace the austenitic grades AISI 304 and/or 316.
2) The composition 22%Cr - 5%Ni - 3%Mo - 0.17%N (SAF 2205), which can be considered as the standard duplex stainless steel. The nitrogen content in these standard duplex stainless steels has recently been increased to further improve its corrosion resistance in oxidizing chloride-rich acid media. Its corrosion resistance lies between those of the austenitic grade AISI 316 and the 5 – 6Mo super-austenitic alloys.
3) The composition 25%Cr - 6.8%Ni - 3.7%Mo - 0.27%N, with or without copper and/or tungsten additions (SAF 2507) have been designed to highly corrosive media and named as the super duplex stainless steel, with a pitting index PREN > 40. They are specially designed for marine, chemical and oil engineering applications, requiring both high mechanical strength and resistance to corrosion in extremely aggressive environments.

2.3 Alloying elements and their role in duplex stainless steels [19]

- **Chromium:** Chromium has the BCC crystal structure used in stainless steel to stabilize the ferritic phase. The addition of Cr to steel improves the localized corrosion resistance, by the formation of a passive chromium oxide (Cr_2O_3) film and reduces the rate of general corrosion. In general 22- 24wt% Cr has been used in duplex stainless steels. However, there is a limit to the level of chromium that can be added to such steel, because it enhances the precipitation of intermetallic phases, such a sigma. This phase often lead to reduction in ductility, toughness and corrosion properties.

- **Molybdenum:** Molybdenum is also a ferrite stabilizer and having the beneficial effect on the pitting and crevice corrosion resistance of an alloy in chloride solutions. Cr and Mo extend the passive potential range and reduce the corrosion current density in the active range.
- **Nickel:** Counter to the ferrite stabilizing effect of Cr (Mo and Nb), there is another group of elements which stabilize austenite and having the FCC crystal structure. In order to maintain about 40% to 60% ferrite, balance austenite, the ferrite stabilizing elements need to be balanced with the austenite stabilizers. For this reason, the level of Ni addition to a given duplex alloys will depend primarily on the Cr content. At excessive Ni contents, the austenite level increases to well above 50%, with the consequence that Cr and Mo are enriched in the remaining ferrite. Ni does have some direct effect on corrosion properties, the main role of Ni is to control phase balance.
- **Nitrogen:** Nitrogen has a multiple effect on stainless steels by increasing pitting resistance, austenite content and strength. Nitrogen is a strong austenite stabilizer, so used in low Ni and Ni free duplex stainless steel to stabilize the austenitic phase.
- **Manganese:** Manganese is an austenite stabilizer. Manganese additions to the stainless steel increase abrasion and wear resistance and tensile properties without loss of ductility. Further, Mn increases the solid solubility of nitrogen and thus allows for increased nitrogen contents to eliminate the risk of out-gassing. However, Mn addition in excess of 3% and 6%, for nitrogen level of 0.1% and 0.23% respectively, significantly decrease the critical pitting temperature, probably due to the increased likelihood of MnS inclusions which can act as inclusion sites for pits.
- **Copper:** Copper additions to high alloy austenitic stainless steel are recognized to reduce the corrosion rate in non-oxidizing environments, such as sulfuric acid. In general the addition of Cu to duplex stainless steel is limited to about 2%, since higher levels reduce hot ductility and can lead to precipitation hardening.
- **Silicon:** Silicon is beneficial for concentrated nitric acid service and also enhances the high temperature oxidation resistance. Because Si is generally

considered to enhance the sigma phase formation, it is generally preferred to limit its addition to the 1% level.

- **Carbon:** The carbon content of most wrought duplex stainless steels is limited to 0.02% or 0.03%, primarily to suppress the precipitation of Cr rich carbides which can act as initiation sites for pitting and intergranular corrosion.

2.4 Nickel free duplex stainless steel

In order to find the cost effective alternative of austenitic stainless steels, several work have been done by the many people. Ni free duplex stainless steels have attracted industries and laboratories because of their exceptional properties like high strength, excellent corrosion resistance in many corrosive media, and low cost as compared to conventional austenitic stainless steel. In these stainless steels nitrogen and manganese have been used for the stability of austenite phase in place of Nickel. The high tendency of nitrogen to stabilize the austenitic phase offer to reduce the nickel content in the stainless steel, which solves the purpose of cost reduction. The development of these low Ni or Ni free stainless steels is made possible by the addition of manganese that permits the increase of Nitrogen solubility in the melt and decreases the tendency of Cr_2N formation [16, 20].

Two kinds of nickel-free duplex stainless steels D10 (22.1%Cr - 10%Mn - 0.35%N) and D 10-3(20.1%Cr - 10%Mn - 3%Mo - 0.45%N) have developed by Speidel et al. [18] These alloys can be characterized with high strength and toughness, good corrosion resistance and low alloy element cost. In comparison with the commercial duplex stainless steels with a similar PREN, these duplex stainless steels have yield strength roughly 100 MPa higher and an elongation to fracture of about 40%. Microstructural investigations showed that such alloys have relatively stable austenite content at high temperatures and thus they were also expected to have a good weldability. They found that the experimental molybdenum containing DSS has a similar Tccc (critical crevice corrosion temperature) to the Duplex 2205, while the experimental molybdenum-free DSS was less corrosion resistant and Tccc was below the testing temperature 23 °C in 6%$FeCl_3.H_2O$ solution. Similarly, the presence of a weaker phase in duplex microstructure and a high Mn content in the experimental DSS can result a low Tccc. Due to the absence of nickel, these duplex stainless steels exhibit an excellent resistance to SCC in chloride solutions.

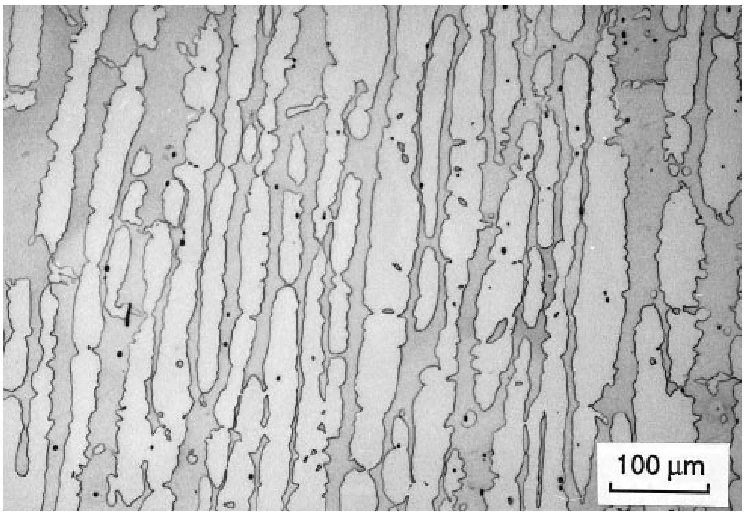


Figure 2.1: Typical duplex microstructure of the experimental steels D10.
(The light colored austenite is evenly distributed as islands in the ferritic matrix)

Finally, these alloys can be cost - efficient because of the total absence of the expensive element nickel and therefore can find applications where high strength and moderate corrosive resistance are required, for example, as reinforcing bars in the building industry.

Hyuk Sang Kwon et al. [16] have developed a new high Mn–Ni free duplex stainless steel containing 18%Cr - 6%Mn - 1%Mo - 0.2%N by examining the effects of manganese on the corrosion and mechanical properties of high Mn stainless steels containing 18%Cr - (4-11)%Mn - (0-2)%Ni - (0-1)%Mo - 0.2%N. According to them the alloy with 45% ferrite is an optimum alloy with much higher mechanical strength and similar corrosion resistance compared with those of standard SS304. In addition, the alloy was free of precipitation of sigma phase and Cr-nitride when exposed to high temperatures due primarily to relatively low contents of Cr, N and Mo. They noticed that with an increase in Mn content, the resistance to pitting and metastable pitting corrosion of high Mn DSS decreased since the number of (Mn, Cr) oxides, acting as preferential sites of pitting, increased with the Mn content.

S.S. Kim at el. [21] have investigated the effect of different Mn contents on tensile and corrosion behavior of CD4MCU cast duplex stainless steels. They found that with increasing Mn contents from 0 to 2%, the improvement in YS and the UTS values was not significant. The tensile elongation was on the other hand, greatly impaired with the addition of 0.8%Mn. They also found that the addition of 0.8% Mn to CD4MCU alloys greatly degraded the resistance to both pitting corrosion and stress corrosion cracking in 3.5% NaCl + 5% H_2SO_4 solution.

C. D. Van Lelyveld et al. [22] have examined the two duplex stainless steels, alloyed with Mn and N, for the purpose of improving their strength while maintaining reasonably high ductility and toughness. They found that the warm working is an effective thermo - mechanical treatment for improving the mechanical properties of the experimental duplex stainless steels. It results that great increase in strengths, with only a slight lowering of the ductility. Corrosion behavior was adversely affected by warm working although to a far lesser extent than for cold working. The Mo containing alloys responded particularly well to warm working.

2.5 Detrimental phases in duplex stainless steels

Hyuk Sang Kwon et al. [10] have investigated the precipitation behavior of secondary phases (nitrides, sigma phase etc) in newly developed Ni free duplex stainless steel. This may deteriorate mechanical and corrosion properties in the duplex stainless steels. To analyze the precipitation behaviour, experimental duplex stainless steel was aged for 3 h at 800 ^oC, 700 ^oC & 600 ^oC, respectively. XRD analysis (Figure 2.2) showed that sigma phase was not precipitated at these temperatures.

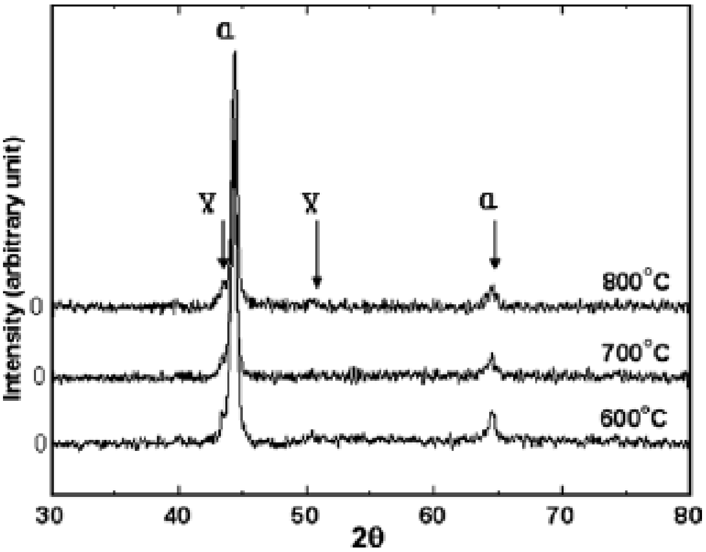


Figure 2.2: XRD of Ni free duplex stainless steel.

I Calliari et al. [12] have investigated the kinetics of precipitation of secondary phases in a duplex stainless steel (SAF 2205) after isothermal and continuous cooling treatment. They found that the precipitation sequence is different in these two situations. During isothermal aging the χ-phase always precipitates before the σ-phase, but during continuous cooling, the χ-phase appears only at low cooling rates. The chemical composition of both secondary phases varies with the cooling rate. They Mo and Cr content in the precipitating phase decreases with increasing cooling rate.

Henrik Sieurin et al. [23] have also investigated the sigma phase precipitation in duplex stainless steel 2205. They suggested that in order to avoid more than 1% sigma phase in duplex stainless steel, the cooling rate from the solution treatment temperature should exceed 0.23K/s. The aging time at the most critical temperature 865 °C must not exceed 134 second.

Chi-Shang Huang et al. [24] have investigated the effects of nitrogen and high temperature aging on σ phase precipitation of 2205 duplex stainless steel. They concluded that σ phase is a phase rich in chromium and molybdenum.

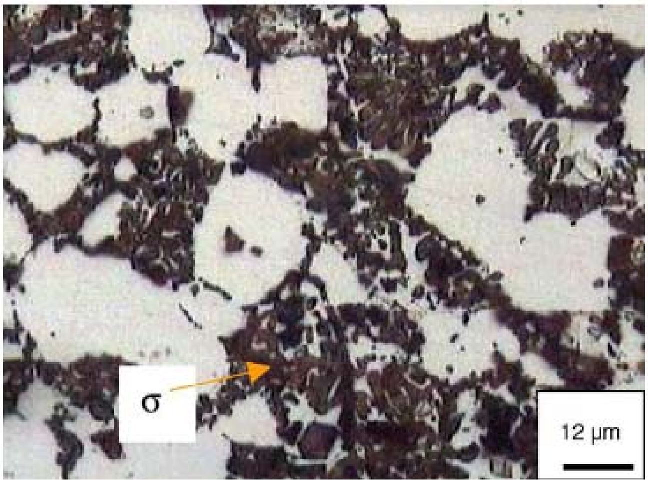


Figure 2.3: Optical microscopic observation of sigma phase.
(By Groesbeck etchant: 4 g NaOH+4g $KMnO_4$ + 100 ml, H_2O)

Its quantity will increase with aging time. When they aged samples under 800 and 900 °C, they found that after 10 h, saturation is reached, and less than 700 °C aging, no saturation state was found within the period of time when this experiment was conducted. They noticed that the σ phase precipitates more rapidly under 900 °C aging, and more slowly under 700 °C aging, which needs to take as much as 10 h. The higher the aging temperature, the bigger the σ phase grains precipitating. Under the same aging conditions, the higher the nitrogen content, the lower the σ phase content in DSS, which is most obvious under 700 °C aging, followed by 800 °C, and under 900 and 950 °C aging, this phenomenon is least obvious (Figure 2.4). Therefore, slowing down of σ phase precipitation by adding nitrogen was most effective under 700 °C, whereas this effect was not obvious under 900 and 950 °C (Figure 2.5).

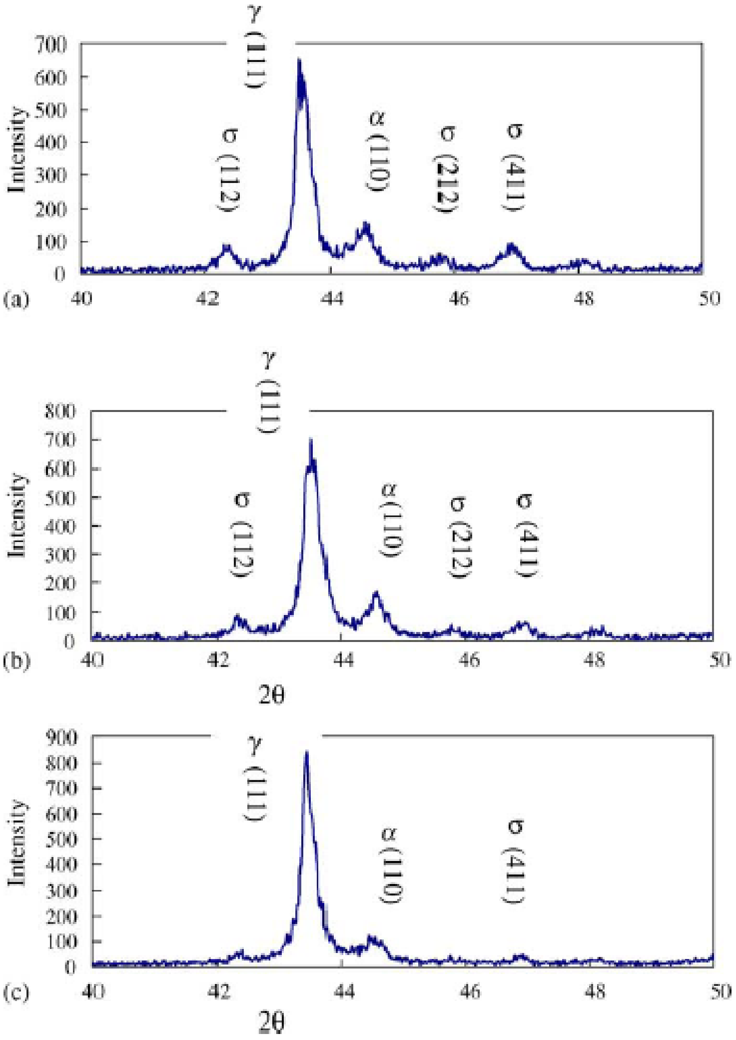


Figure 2.4: X-ray diffraction pattern of duplex stainless steel after 800 ◦C×24 h aging: (a) 0.14%N, (b) 0.18% N and (c) 0.22%.N

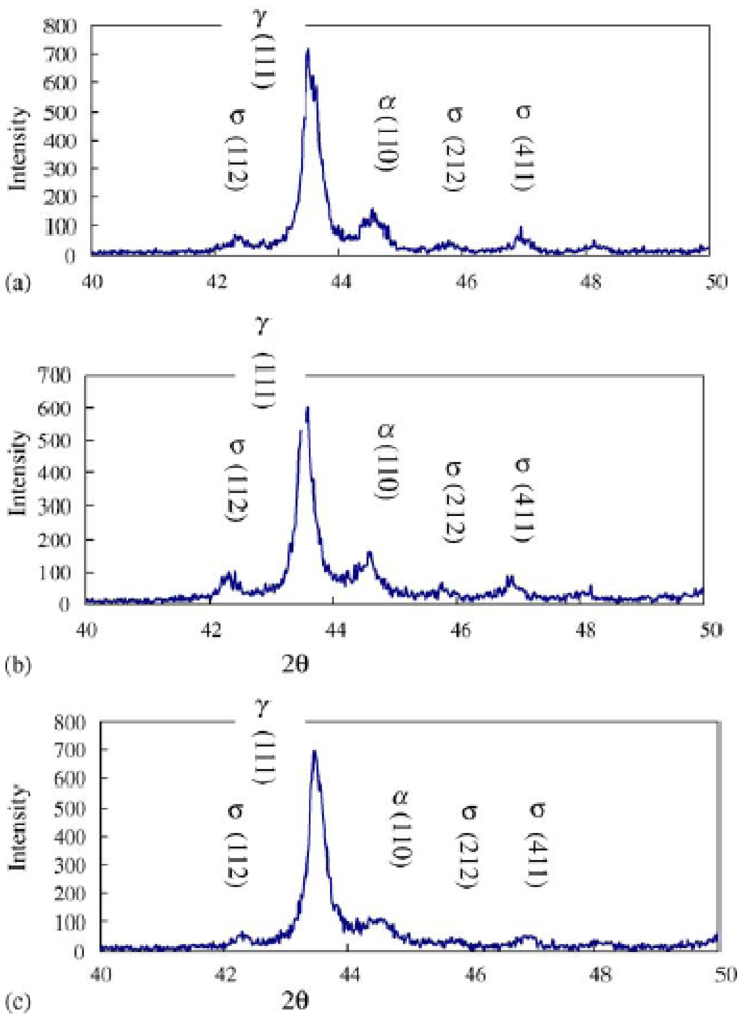


Figure 2.5: X-ray diffraction pattern of duplex stainless steel after 900 ◦C×24 h aging: (a) 0.14%N, (b) 0.18% N and (c) 0.22%.N

M. Pohl et al. [25] investigated the effect of sigma phase precipitation on the properties of duplex stainless steels. They found that the high amount of alloying elements causes a complex precipitation and transformation behavior, which requires necessary heat treatment. The precipitation of σ-phase induces most extensive change in properties. This hard and brittle phase causes a reduction in toughness in duplex stainless steel.

2.6 Corrosion in duplex stainless steels

Hosni M. Ezuber et al. [26] have investigated the effects of sigma phase precipitation on seawater pitting of duplex stainless steels SAF 2205 and 3RE60. They found that the seawater pitting corrosion of 3RE60 and SAF 2205 DSS depends largely on the inappropriate heat treatment duration (volume fraction of sigma phase precipitation) and test temperature. The intensity of the pitting attack is markedly increased with increasing seawater temperature and/or inappropriate heat treatment duration. Microscopic examinations revealed that pits on HT SAF 2205 are taking place at the austenite ferrite boundaries, with the result that their propagation occurs more obviously into the ferrite phase, indicating the beneficial presence of 0.22% of nitrogen.

Z. Cvijovic et al. [27] have compared the pitting corrosion behavior of two cast duplex stainless steels of types 22.5%Cr - 7.8%Ni - 2.3%Mo - 3.5%Cu - 0.1%N and 26.6%Cr - 7.6%Ni - 2.5%Mo - 2.9%Cu - 0.12%N, in 0.5 M NaCl water solution under different microstructural conditions achieved by annealing in the range from 900 ^{o}C to 1200^{o}C. They concluded that σ phase has the most deleterious effect. Annealing at higher temperatures improves the pitting resistance. A maximum improvement of corrosion stability can be achieved by annealing at 1200^{o}C.

F. J. Botana et al. [28] have investigated the effect of chemical composition on the pitting corrosion resistance of non-standard low-Ni, high-Mn-N duplex stainless steels having composition: 0.5%Si – 8%Mn - (0.5-2.7)%Ni - %Cu - (18-24)%Cr - (0.3-4)%Mo - (0.09-0.34)%N. The result obtained shows that these alloys have higher pitting corrosion resistance in chloride environments than equivalent standard duplex or austenitic stainless steels. These materials have also a strong dependence between E_p and Mo content. In order to achieve improved pitting corrosion resistance, Mo content should be higher than 1%. The best result they obtained for alloys with Mo content between 3% and 4%.

J. M. Sykes et al. [29] have investigated the effect of phase compositions on the pitting corrosion of 25 Cr duplex stainless steel in chloride solutions. They found that the pitting and critical pitting temperature of UNS S32550 duplex stainless steel was strongly influenced by the solution treatment temperature. Raising the annealing temperature lowers both parameters. They obtained maximum CPT was 62^{o}C by annealing for 2 hour at 1020^{o}C followed by water quenching. Pitting corrosion of

UNS S32550 in chloride solution takes place preferentially in the ferrite phase rather that in the austenite phase. High annealing temperatures (above 1060^{o}C) increase the ferrite content and dilute the key alloying elements in the ferrite lowering the corrosion resistance of ferrite.

CHAPTER-3

EXPERIMENTAL PROCEDURE AND MATERIALS

This chapter describes the materials of present investigation and experimental details of melting, casting, chemical analysis, phase analysis, heat-treatment, microstructural analysis, corrosion testing, tensile and V-notch Charpy testing at room temperature.

Thermocalc software have been used to know the phase diagram and hence the heat treatment temperature. Optical microscopic observation has carried out to characterize the microstructure and phases of duplex (Ni free) stainless steel. Fracture surface of tensile tested samples have been analyzed by SEM to know the mode of fracture.

For comparative study, along with duplex (Ni free) stainless steel five other alloys named as duplex (low Ni), 316N and 304N has also designed. Duplex (Ni free) and duplex (low Ni) are the dual phase stainless steel: they have both austenite and ferrite phase at room temperature, while other two alloys: 316N and 304N have only austenite phase.

3.1 Instrument used in experiments

The instruments used in entire process of development and characterizations are:

3.1.1 Instruments for chemical analysis

- Optical Emission Spectroscopy, model: ARL 4460, for the detection of C, Cr, Mn, Mo, Ni, Cu, Si, P
- Spectro Lab, model: M7, for the detection of C, Cr, Mn, Mo, Ni, Cu, Si, P
- XRF, Sequential 9800, for detection of Ni
- LECO, Model: CS 44 L, for detection of C and S

- LECO, model: TC 436 AR, for detection of N and O

3.1.2 Melting unit

- Power – Trak induction furnace, model: 125-30R

3.1.3 Forging

- General forging unit

3.1.4 Cutting machine

- Metkon servocut - A250, with coolant

3.1.5 Heat treatment unit

- Okey electric furnace, model: 7009

3.1.6 Grinding, mounting and polishing unit

- Metkon Finopres hot mounting machine
- Metkon Gripo 2V wet grinding and polishing machine

3.1.7 Ferritoscope

- Fischer feritoscope, model: MP 30, Version 2.0

3.1.8 Tensile testing machine

- FIE, Universal testing machine, 100KN, model: UTN. 100T

3.1.9 Impact testing machine

- FIE, Impact testing machine, model: IT-30

3.1.10 Hardness tester

- Wilson M.I.C.I. Rockwell hardness tester, reference standard: IS 1586 (2000)

3.1.11 Microscopes

- Zeiss optical microscope, model: Axiovert 2000; MAT, magnification 50X - 1000X
- LEO scanning electron microscope, model: EV 040-7636 with OXFORD NICAx-sight EDS

3.1.12 XRD

- Rigaku model Geiger diffractogram, with Cu Kα radiation (λ= 1.54 Å), Cu target with inbuilt Ni filter

3.1.13 Weighing machine

- Mettler Toledo balance, model:AB265-S

3.2 Materials

The raw material for present work was obtained from Jindal Stainless Limited, Hisar, Haryana. Major part of material was taken from stainless steels scarps, because it reduces the amount of pure metal for alloying. We have mainly used the 304L, 316L, 430 and maruti scrap (mild steel). The other benefit of taking scarp is the low cost as compared to pure metal used for alloying. The scraps used for making alloy, were first subjected to chemical analysis, in order to confirm the composition (Table 3.1). After the confirmation melting was carried out in 100 Kg induction furnace in open atmosphere. The amount of material used for making the alloys in 100 kg induction furnace, are shown in table 3.2

Table 3.1: Approximate chemical composition of scraps used.

Alloys	**Alloying elements (wt %)**									
	C	**Mn**	**S**	**P**	**Si**	**Ni**	**Cr**	**Cu**	**Mo**	**N**
430	0.05	0.6	0.005	0.03	0.4	0.15	16.2	-----	-----	------
316L	0.020	0.82	0.003	0.032	0.53	10.09	16.22	0.34	2.02	0.0432
304L	0.022	1.35	0.006	0.037	0.33	8.39	18.23	0.41	0.09	0.0838

Table 3.2 Materials and their quantity used for making the experimental alloys.

Materials	**Amount used in alloy making**			
	Duplex (Ni free)	**Duplex(low Ni)**	**304N**	**316N**
430 scrap	79 kg	79 kg	------	17.7 kg
316L scrap	------	------	------	80 kg
304L scrap	-------	------	75 kg	-------
Maruti scrap (Mild steel)	-------	-------	15.7 kg	-------
Mn metal	3 kg	3.7 kg	------	------
Nitrated Fe-Mn	3 kg	2 kg	1.8 kg	1.4 kg
Low C Fe-Cr	13 kg	13 kg	7 kg	-------
Low C Fe-Si	0.5 kg	0.5 kg	0.4 kg	0.3 kg
Molybdenum oxide	0.1 kg	0.1 kg	------	0.9 kg
Ni	-------	1.6 kg	------	------
Cu	1.6 kg	0.3 kg	-------	------

Where,

Each 100 kg of Low C Fe-Si contains: 0.02wt% C, 77wt% Si

Each 100 kg of Low C Fe-Cr contains: 0.1wt% C, 70wt% Cr

Each 100 kg of Molybdenum oxide contains: 0.018 wt% C, 59.60 wt% Mo

Each 100 kg of Nitrated Fe-Mn contains: 0.058 wt% C, 87.30 wt% Mn and 8 wt% N

3.3 Alloy designing

The experimental alloys: duplex (Ni free) , duplex (low Ni), 304N and 316N stainless steel, were designed with the help of Schaeffler diagram having compositions as shown in table 3.4 and two other standard grades 304L, 316L have also been taken for comparison. The values of Ni and Cr equivalents for Schaeffler diagram are shown below [30, 31]:

$$\%\,\text{Ni equivalent} = \%\text{Ni} + \%\text{Co} + 30\,(\%\text{C}) + 25\,(\%\text{N}) + 0.5\,(\%\text{Mn}) + 0.3\,(\%\text{Cu})$$

$$\%\,\text{Cr equivalent} = \%\text{Cr} + 2\,(\%\text{Si}) + 1.5\,(\%\text{Mo}) + 5\,(\%\text{V}) + 5.5\,(\%\text{Al}) + 1.75\,(\%\,\text{Nb}) + 1.5\,(\%\,\text{Ti}) + 0.75\,(\%\text{W})$$

Table 3.3: $Ni_{equivalent}$ and $Cr_{equivalent}$ for Schaeffler diagram.

Alloys	Duplex (Ni free)	Duplex (low Ni)	304N	316N	304L	316L
$Ni_{equivalent}$	9.6625	9.397	12.943	12.732	11.943	12.282
$Cr_{equivalent}$	21.94	22.48	19.535	19.71	19.025	20.31

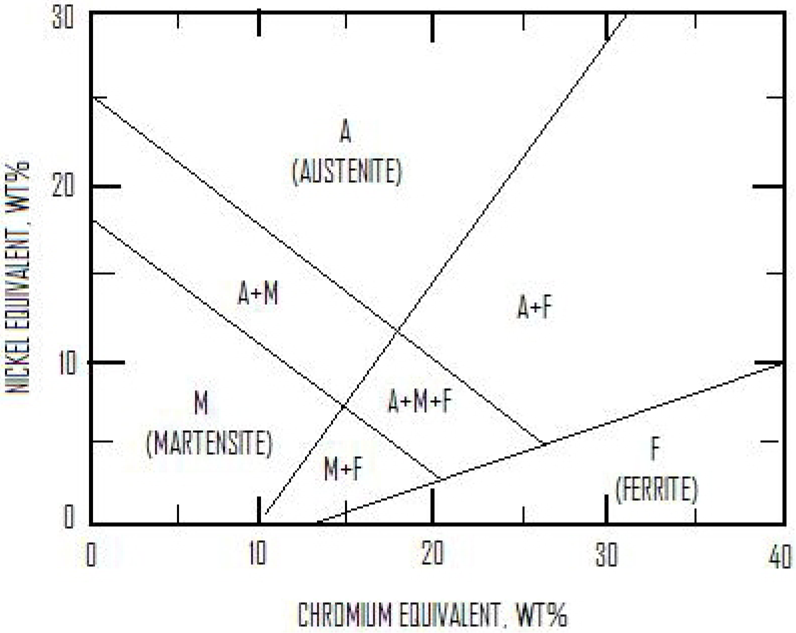


Figure 3.1: Schaeffler diagram.

Table 3.4: composition of alloys produced and used in the study.

Alloys	**Alloying elements (wt %)**									
	C	**Mn**	**S**	**P**	**Si**	**Ni**	**Cr**	**Cu**	**Mo**	**N**
Duplex (Ni free)	0.030	4.97	0.002	0.032	0.27	0.17	21.40	1.65	0.021	0.2313
Duplex (low Ni)	0.035	4.34	0.002	0.035	0.24	1.84	22.00	0.34	0.051	0.1694
304N	0.027	2.35	0.003	0.031	0.45	6.44	18.50	0.31	0.09	0.1770
316N	0.020	1.72	0.004	0.030	0.55	8.29	15.88	0.29	1.82	0.1158
304L	0.022	1.35	0.006	0.037	0.33	8.39	18.23	0.41	0.09	0.0838
316L	0.020	0.82	0.003	0.032	0.53	10.09	16.22	0.34	2.02	0.0432

3.4 Melting and casting

The melting of the alloys was carried out in a 100 kg induction furnace in open atmospheric and casting was carried out in the form of small ingots of 40 mm diameter and 66 mm length. The ingots obtained were hot forged in the 300 mm × 35 mm × 7 mm dimension plates.

Figure 3.2: Melting of alloy in 100 kg Induction Furnace.

Figure 3.3: Cast samples of duplex (Ni free).

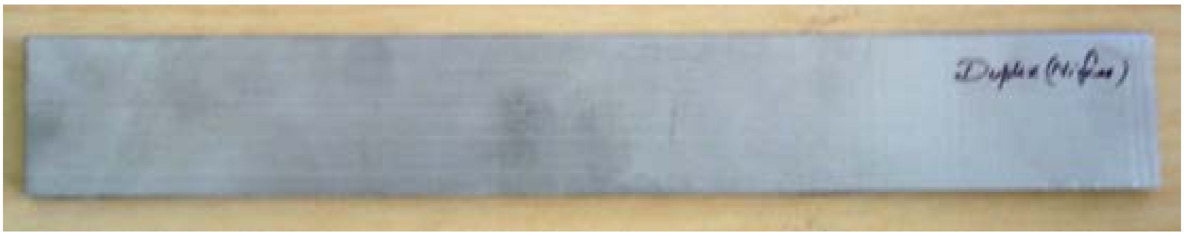


Figure 3.4: Forged samples of duplex (Ni free).

3.5 Heat treatment

For getting the desire phases in stainless steels, the forged samples were solution annealed and then water quenched. Thermocalc software was used to draw the phase diagram (Figure 3.5a - 3.5d) and to calculate the annealing temperature (Table 3.5). The annealing temperatures were selected according to thickness of samples. In general soaking time selected is:

Time (min) = 1.5 × thickness of sample with bright surface
Time (min) = 1× thickness of sample with black surface

Table 3.5: Heat-treatment temperature for alloys.

Alloys	Duplex (Ni free)	Duplex (low Ni)	304N	316N	304L	316L
Heat-treatment temperature (^oC)	1030	1080	1050	1050	1050	1050

After heat treatment the ferrite percentage was calculated with the help of Ferritoscope (Table 3.6) in order confirm the percentage of ferrite and austenite in alloys.

Table 3.6: % ferrite measured in experimental alloy.

Alloys	Duplex (Ni free)	Duplex (low Ni)	304N	316N	304L	316L
% ferrite	58	60	7.9	5.9	5.8	3.0

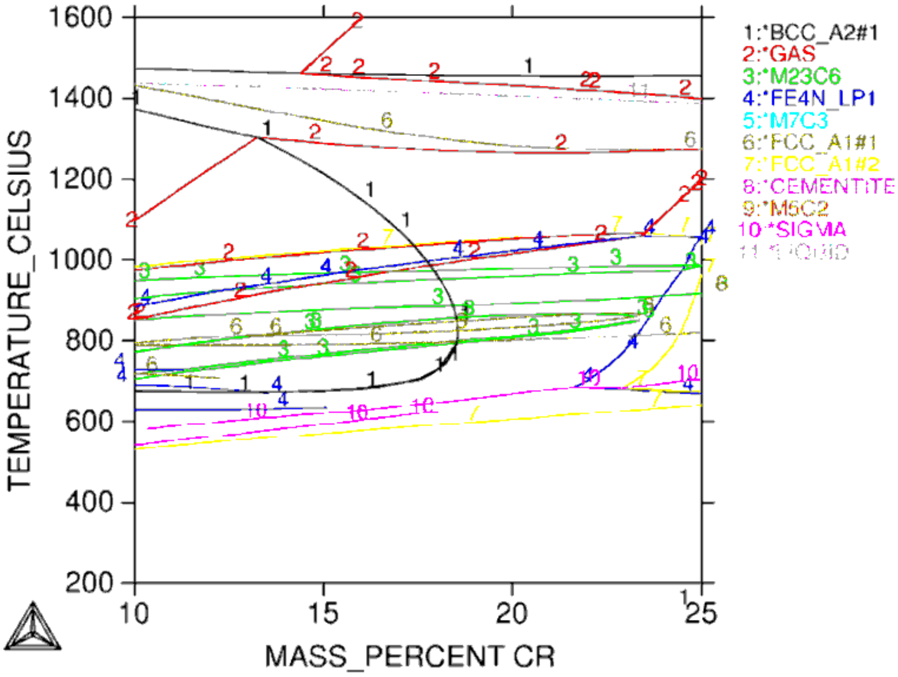


Figure 3.5a: Phase diagram of duplex (Ni free).

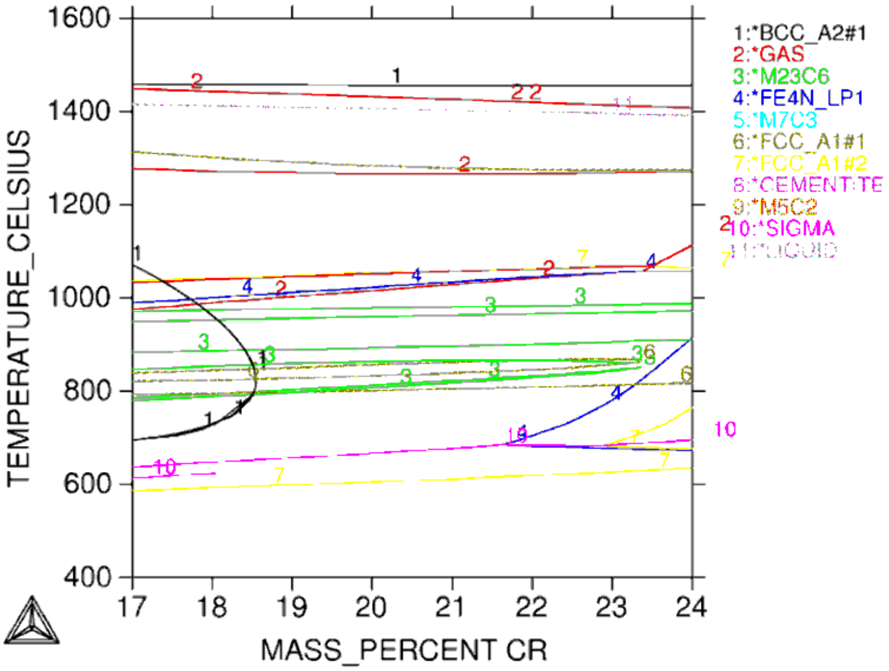


Figure 3.5b: Phase diagram of duplex (Ni free).

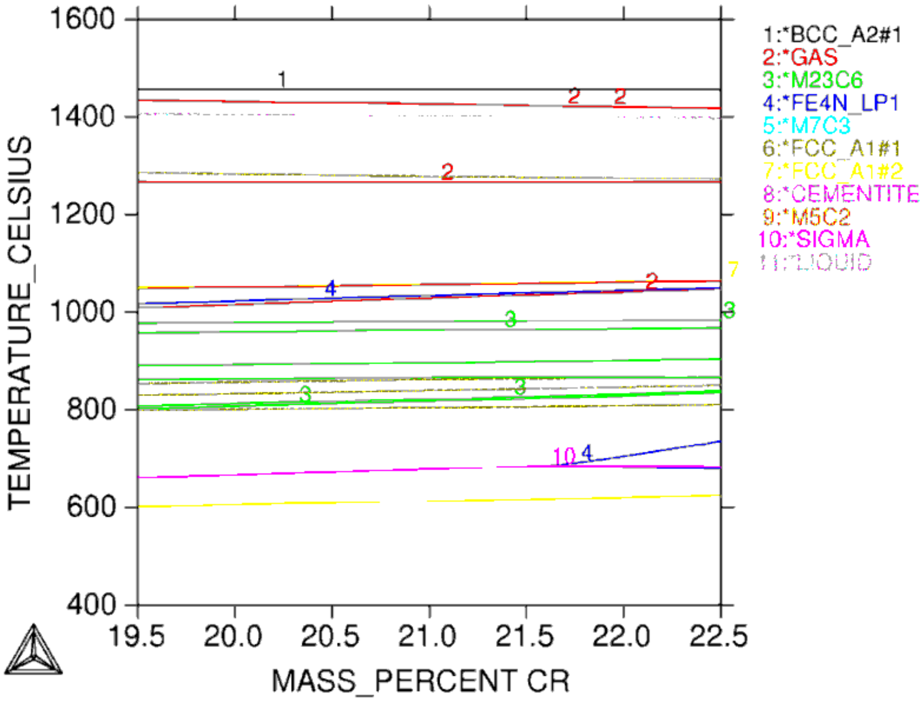


Figure 3.5c: Phase diagram of duplex (Ni free).

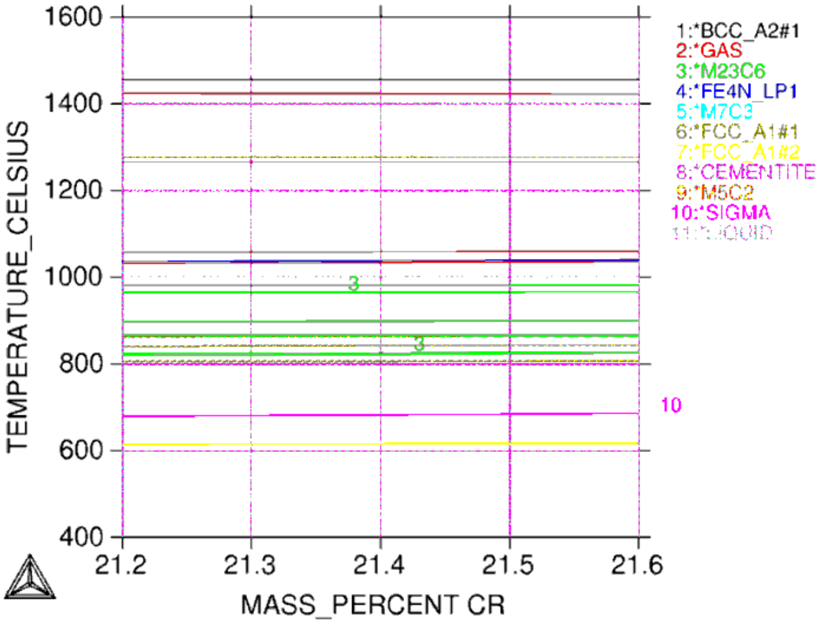


Figure 3.5d: Phase diagram of duplex (Ni free).

3.6 Optical metallography

Heat-treated samples were prepared for microstructural analysis. Specimens were hot mounted in epoxy and then wet-grinded on 120, 240, 400, 800 and 2400 grit silicon - carbide papers. After this diamond polishing of samples was carried out. After polishing the samples were washed thoroughly in running water and then cleaned with methanol. For microstructure hot modified Murakami (30 gram KOH +150 ml distilled water + gram K_4 Fe $(CN)_6$) etchant, for duplex stainless steels and an electrolytic etchant (10% oxalic acid) for austenitic stainless steel were used. Microstructure was examined under the magnification 100 X, 200X and 500X.

3.7 XRD analysis

XRD of Duplex Ni free sample has been carried out to confirm the intermetallic phases like σ phase in annealed condition. For this purpose the annealed (at 1030^{o}C) sample of dimension 1cm X 1cm, has been prepared.

3.8 Impact testing

V-notched Charpy testing of duplex Ni free alloy has been carried out at room temperature. The samples for this have been prepared as ASTM standard (Figure 3.6). The details of sample prepare are given in following figure:

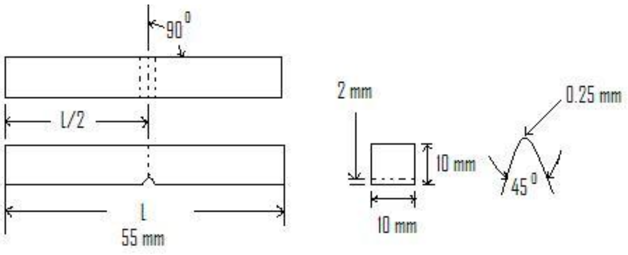


Figure 3.6: Schematic diagram of impact sample.

3.9 Mechanical testing

The tensile testing was carried out, using 100,000 N hydraulic-driven Universal testing Machine, for the examination of mechanical properties of experimental alloys.

Flat tensile specimens were prepared as per ASTM standard A 370. The details of specimen are shown below:

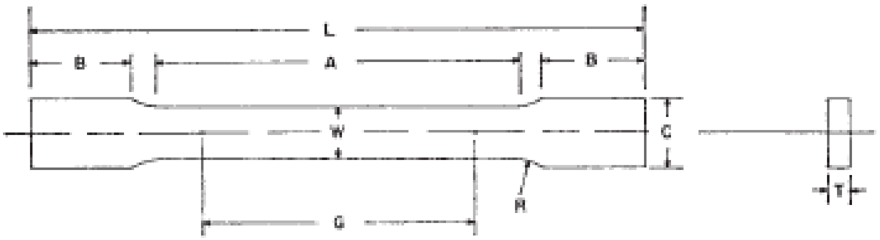


Figure 3.7: dimensional details of tensile specimen.

Where,

G = gauge length = 50 mm
W = width = 12.5 mm
T = thickness = thickness of material
R = radius of fillet = 13 mm
L = overall length = 200 mm
A = length of reduced section = 60 mm
B = length of grip section = 50 mm
C = width of grip section

3.10 SEM analysis

To know the mode of fracture, the SEM (Scanning Electron Microscope) analysis of the fracture surfaces of tensile tested specimens were carried out. For this the samples of length 1.50 cm that include the fracture surface were taken. These samples were then ultrasonically cleaned in acetone and then dried. The fracture surfaces of samples were analyzed in at 1000 magnification.

3.11 Hardness testing

Rockwell hardness of experimental alloys has been measured in annealed condition.

3.12 Corrosion testing

Stainless steels are mainly used in, chemical industry, construction and house hold application. Where they face different types of corrosive environment and there for suffers from the different types of corrosion. So it is must to check corrosion behavior of duplex stainless steel in these corrosive media and compare with other grades. In this order corrosion tests of duplex (Ni free), duplex (low Ni), 304N, 316N, 304L and 316L were carried out in different boiling corrosive media (Table 3.7 - 3.9). The corrosion rate was calculated in "millimeter per year" (mmpy) by using following formula (from ASTM A262):

$$\text{mmpy} = \frac{7290 \times w \times 12}{t \times d \times A}$$

Where,

w = weight loss in gram
t = time of exposer in hour
d = 7.8 g/cm^3 for duplex stainless steels
= 7.9 g/cm^3 for molybdenum free austenitic stainless steels
= 8.0 g/cm^3 for molybdenum containing austenitic stainless steels
A = Area of specimen in cm^2

Table 3.7: Inorganic media used for corrosion testing.

S.No.	Medium for corrosion test	Test condition	Duration
1.	50% Nitric acid	Boiling point	48 hour
2.	50% Orthophosphoric acid	Boiling point	48 hour
3.	3% H_2SO_4	Boiling point	48 hour
4.	5% H_2SO_4	Boiling point	48 hour

Table 3.8: Organic media used for corrosion testing.

S.No.	Medium for corrosion test	Test condition	Duration
1.	20% Acetic acid	Boiling point	48 hour
2.	5% Acetic acid + 5% Formic acid	Boiling point	48 hour
3.	2% Formic acid	Boiling point	48 hour
4	5% Formic acid	Boiling point	48 hour
5.	25% Lactic acid	Boiling point	48 hour
6.	1% Oxalic acid	Boiling point	48 hour
7.	25% Citric acid	Boiling point	48 hour

Table 3.9: Other media used for corrosion testing.

S.No.	Medium for corrosion test	Test condition	Duration
1.	1% Acetic acid + 1% NaCl	Boiling point	48 hour
2.	10% Acetic acid + 5% NaCl	Boiling point	48 hour
3.	3.5% NaCl	Boiling point	48 hour
4.	5% H_2SO_4 + 20% $(NH_4)_2SO_4$	Boiling point	48 hour
5.	White liquor	Boiling point	48 hour
6.	Black liquor	Boiling point	48 hour

For corrosion testing in boiling media, samples were prepared by following steps:

1. Samples were cut in dimension 1 inch × 1 inch, with servo-cut
2. Heat treatment: Heat treatment of samples have been carried out according to following details:
    - For duplex (Ni free) at 1030^0C for 6 minutes
    - For Duplex (low Ni) at 1080^0C for 6 minutes
    - For 304N, 316N, 304, 304L, 316L at 1050 for 1.30 minutes
3. Quenching: water was used for quenching
4. Pickling: For removing the scales annealing has been carried out.

    Pickling chemical: 10% HNO_3+ 2 to 3 drops of HF

5. Grinding and polishing: Samples were grinded at Silicon carbide paper from 120 to 2400 grit. After grinding, samples was polished at cotton with diamond paste (Solar diamond, grade: 1-0S) of particle size.
6. Cleaning: After polishing samples were thoroughly cleaned in running water and then cleaned in ultrasonic bath with methanol, to remove the organic impurities and trace of Cl. Now samples were dried with cold dryer.
7. Weighing: Samples were then weighed at up to five decimal.

The apparatus (Figure 3.8) used for corrosion test has details as: An Allihn condenser with four bulbs with overall length was about 260 mm and length of condensing section was 155 mm.

- A 1000 ml Erlenmeyer flask with opening of 50 mm wide.
- The cradle was used having 38 mm and 38 mm diameter with 31 holes to increase the circulation of testing solution around the specimen.
- Boiling chips was used to prevent bumping.
- An analytical balance was used, capable of weighing to the nearest 0.00001 g.

Figure 3.8: Setup corrosion testing in boiling media.

CHAPTER-4

RESULT AND DISSCUSSION

4.1 Microstructural characterizations

A typical microstructure of the experimental duplex (Ni free) stainless steels is shown below (Figure 4.1). In this figure the austenite (light portion) is evenly distributed as island in the matrix of ferrite. After solution annealing at 1030°C the volume fraction of ferrite was measured about 58%, with the help of Ferritoscope. The microstructure reveals that the individual phases are free from the precipitation of intermetallics.

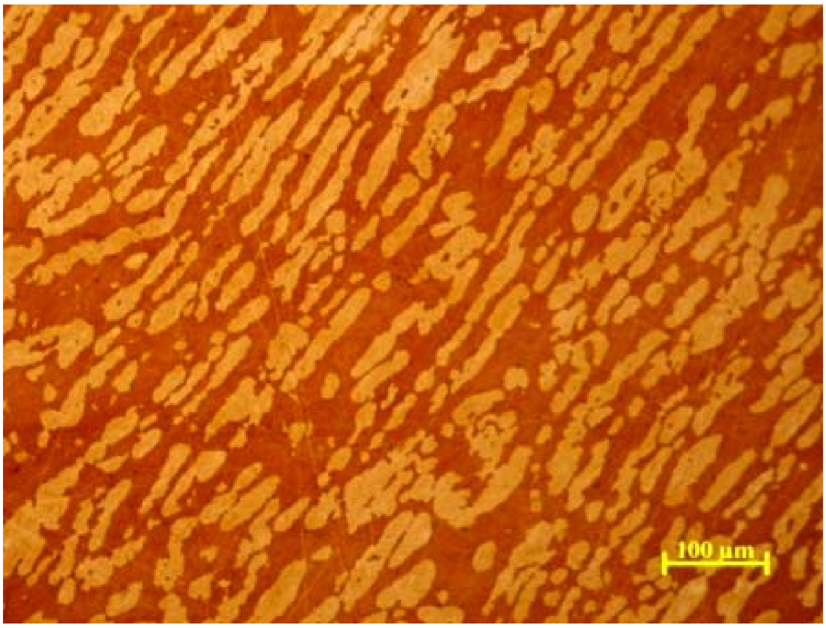


Figure 4.1: Microstructure of Ni free duplex stainless steel heat treated at 1030°C.

The absence of precipitation of intermetallic phases has also been confirmed by XRD analysis of this sample (Figure 4.2). The absence of σ phase may be due to the high nitrogen content [24]. Ihsan- ul- Haq et al have reported that the low Cr and Mo content (18.08wt% Cr – 1.01wt% Mo), decrease the chance of formation of σ phase [16]. The absence of σ phases in newly developed duplex (Ni free) stainless steel may be due to low content of Cr and Mo and high percentage of nitrogen.

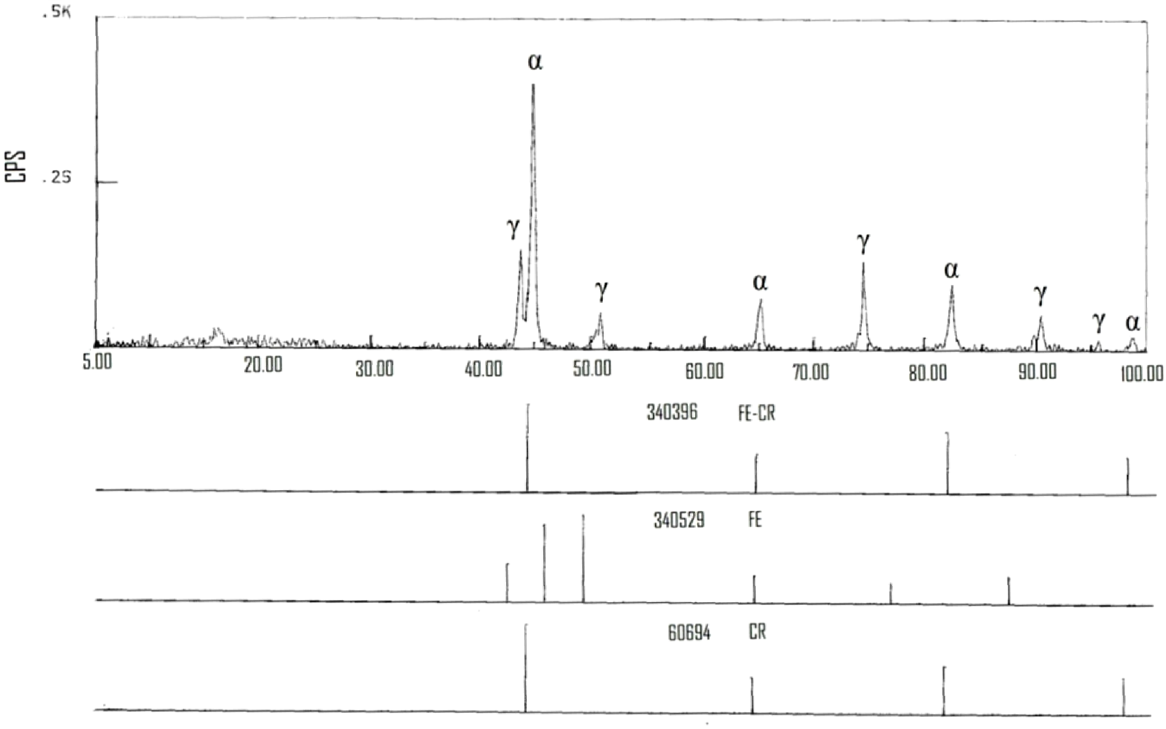


Figure 4.2: XRD of annealed sample of duplex (Ni free).

4.2 Comparison of hardness of experimental alloys

The high hardness (Table 4.1) of duplex (Ni free) stainless steel as compared to duplex (low Ni) stainless steel, of 304N, 316N, 304L and 316L, may also be due to the nitrogen which promotes the hardening by interstitial solid solution strengthening and grain refining [32]

Table 4.1: Comparison among the hardness of experimental alloys.

Grades	Duplex (Ni free)	Duplex (low Ni)	304N	316N	304L	316L
Rockwell Hardness	98	97	93	83	85	81
Brinell Hardness	228	222	200	159	165	153

4.3 Mechanical properties

Mechanical properties (Table 4.2) of duplex (Ni free) stainless steel were investigated in solution annealed condition at room temperature and compared with duplex (low Ni) stainless steel, 304N, 316N, 304L and 316L. The duplex (Ni free) stainless steel has comparatively high yield strength and UTS as compared to the duplex (low Ni) stainless steel, 2304, 2205, 304N, 316N, 304L and 316L.The cause of this high yield strength and UTS of duplex (Ni free) stainless steel may the high Nitrogen content as compared to other alloys used in comparison [10, 18]. The ductility of duplex (Ni free) stainless steel is found comparable to other standard duplex stainless steels.

Table 4.2: Comparison of mechanical properties of experimental alloys with 2304 and 2205. [18]

Grade	**0.2%YS (MPa)**	**UTS (MPa)**	**% Elongation**
Duplex Ni Free	562	686	42
Duplex low Ni	501	644	38
2304	480	663	40
2205	540	758	41
304N	351	667	64
316N	316	582	60
304L	304	565	63
316L	221	685	63

In order to know the mode of fracture in (duplex Ni free) stainless steel, the SEM analysis of fracture surface has been carried out at 1000X and compared with fracture surface of other experimental alloys.

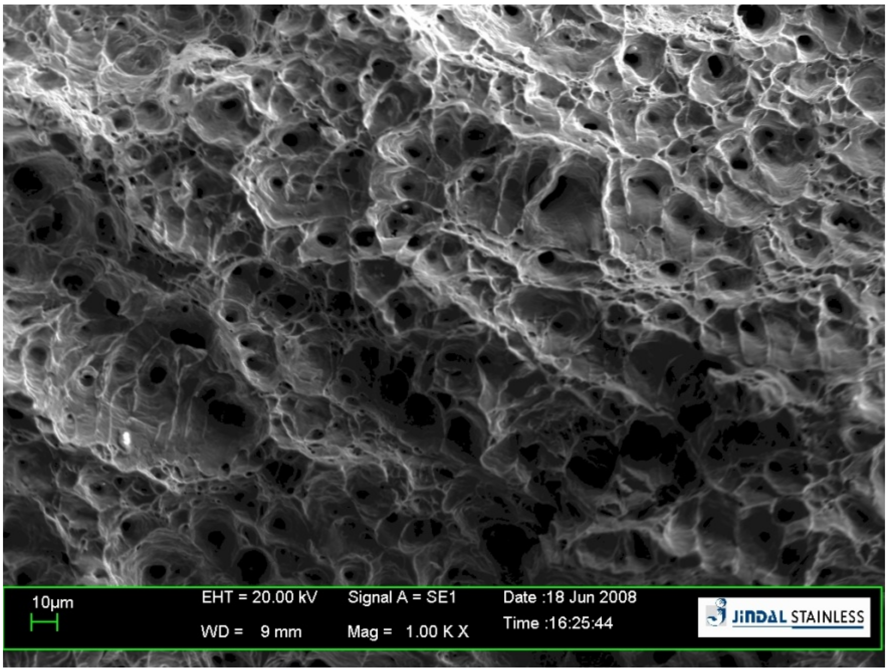


Figure 4.3: SEM picture of fracture surface of duplex (Ni free).

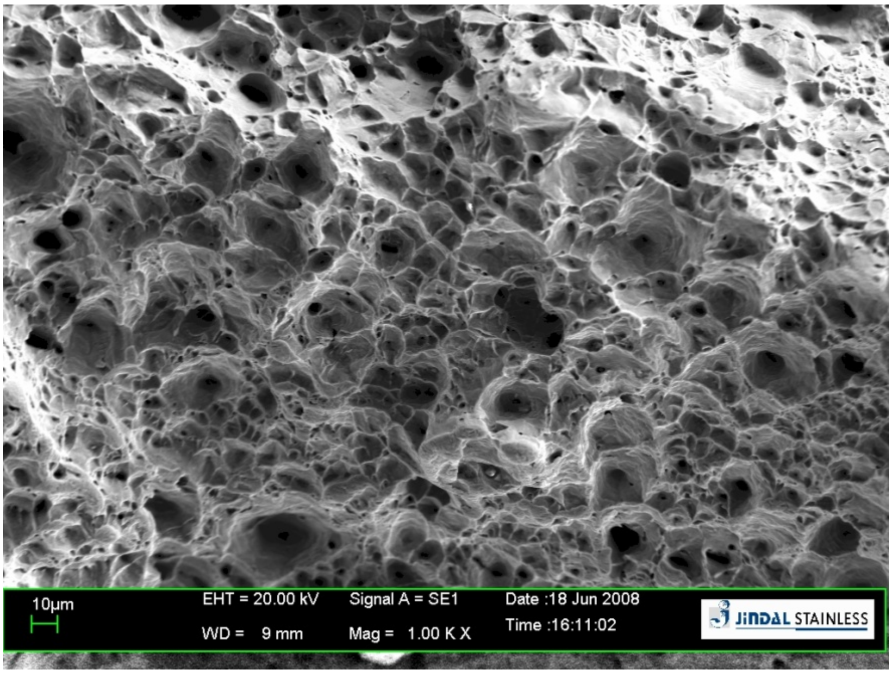


Figure 4.4: SEM picture of fracture surface of duplex (low Ni).

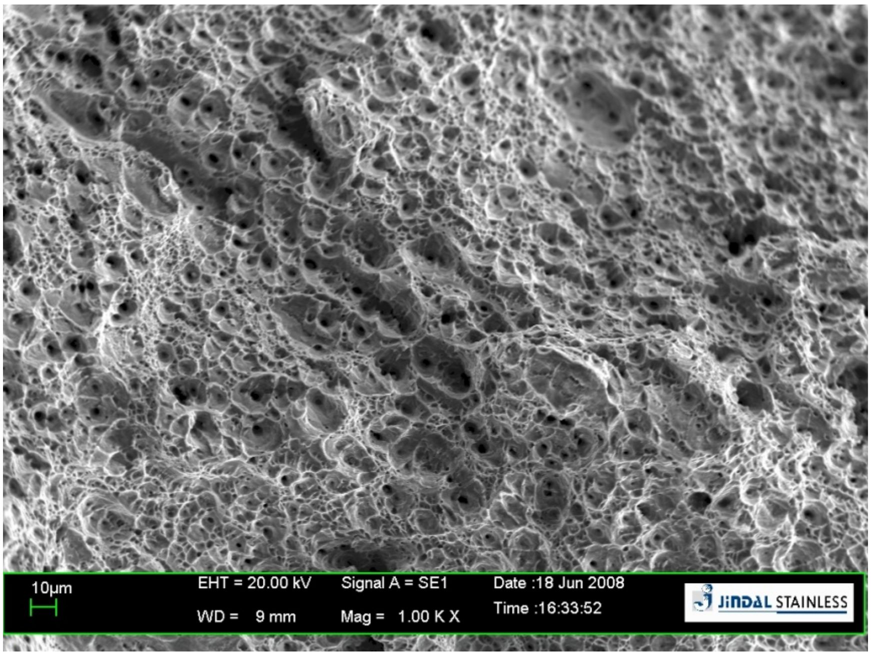


Figure 4.5: SEM picture of fracture surface of 304N.

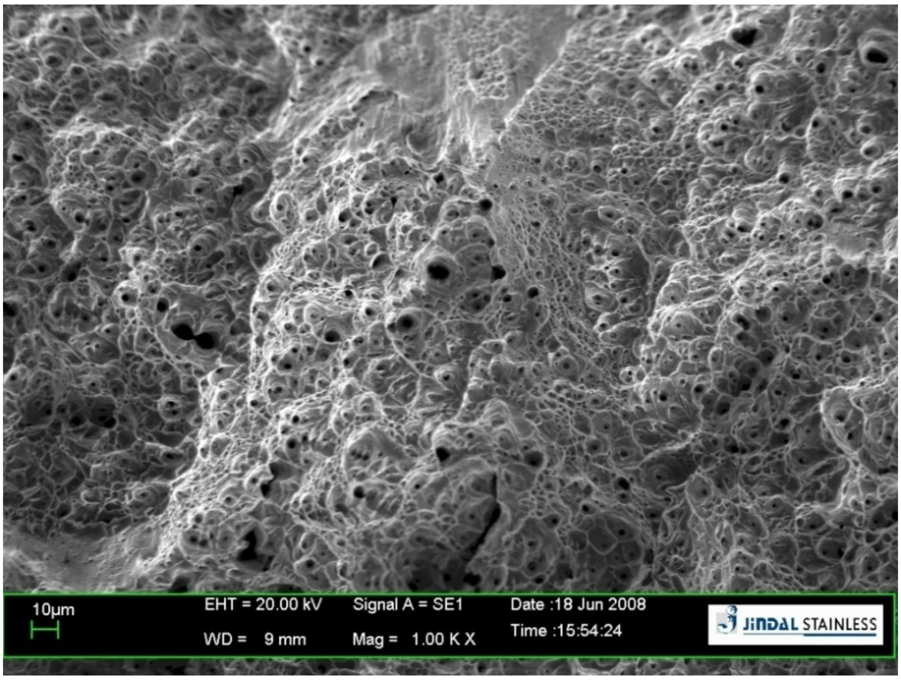


Figure 4.6: SEM picture of fracture surface of 316N.

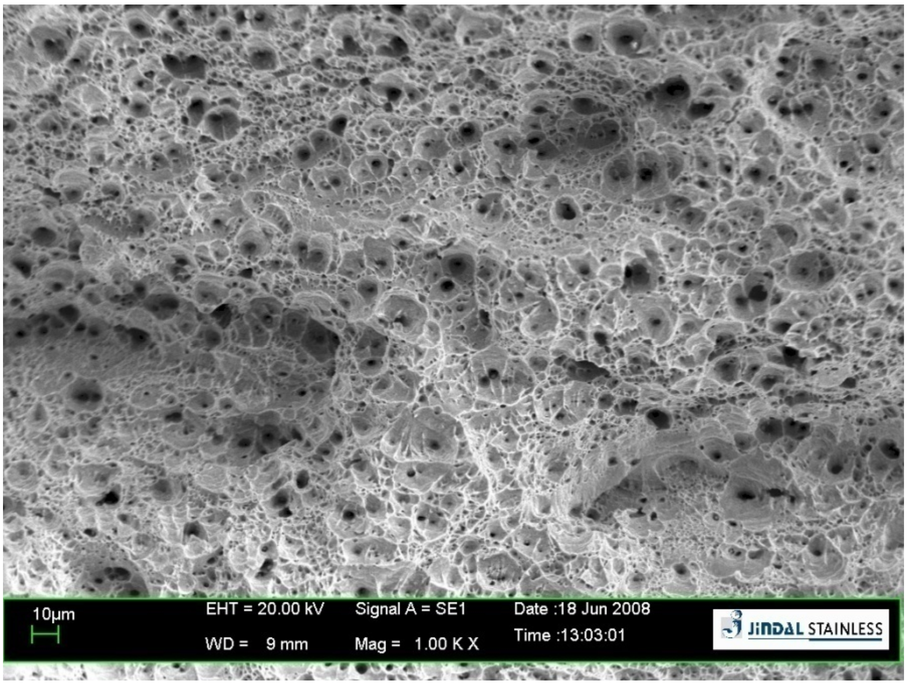


Figure 4.7: SEM picture of fracture surface of 304L.

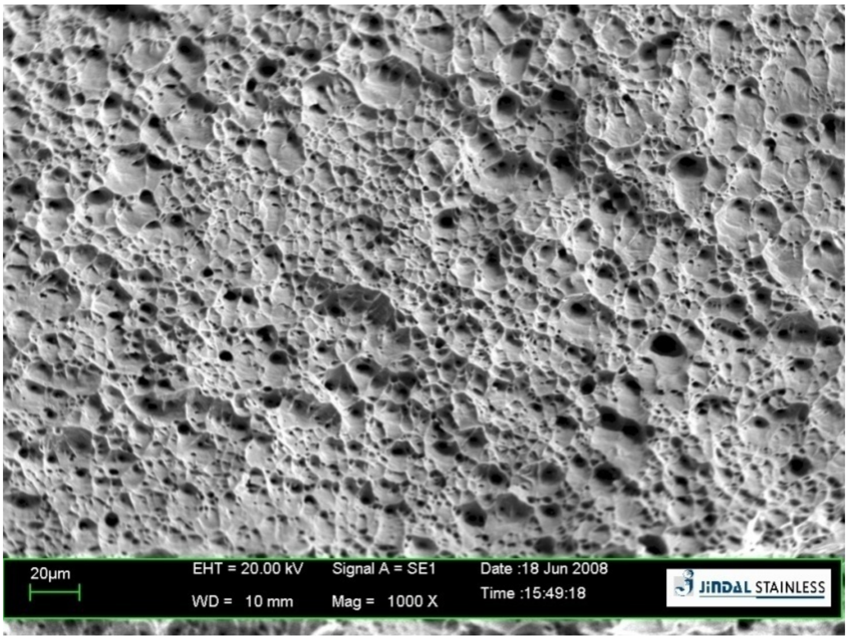


Figure 4.8: SEM picture of fracture surface of 316L.

Figure 4.9: Tensile tested samples.

4.3.1 Analysis of fracture surface

1) Duplex (Ni free) stainless steel

This stainless steel exhibits a very good property in terms of yield strength and ultimate tensile strength. Moreover, percentage elongation is also very good. The SEM micrograph (Figure 4.3) of this steel exhibit the dimple structure (which is typical characteristic of ductile material). The micro-voids observed uniformly exist and each micro-void more or less contains precipitate. The SEM fractograph indicates that these dimples are of uniform size and are aligned in a preferred direction. Because of uniform dimple size, the strength of the material observed is very good.

2) Duplex (low Ni) stainless steel

This stainless steel is very good in nature as far as strength is concerned and exhibits good mechanical property. However, when compared with the duplex nickel free alloy, the SEM fractograph (Figure 4.4) exhibits different morphological features. The dimples observed are non-uniform in size which varies from few microns to hundreds of microns. The SEM fractograph indicates that there are some trapped gases inside the material which tries to bubble out from the matrix (right hand side top corner). Moreover, fractured surface appears to be of heterogeneous in nature.

3) 304 N stainless steel

This stainless steel exhibit very good elongation apart from yield strength and ultimate tensile strength. Such type of steels can be very much useful where flow ability in the material is required. The SEM microstructure (Figure 4.5) is very much different as compared to above two stainless steels. The sizes of the dimples are very small and the strength is also very small as compared to the other two materials described above. The existence of pores at some places leads to lower strength. The flow pattern indicates that the material can be very much suitable for utensils and other pattern making devices.

4) 316 N stainless steel

This SEM microstructure (Figure 4.6) is also similar to the 304N stainless steel but the dimple size observed is smaller. Because of this variation in structure, the strength of the material should exhibit better mechanical strength as compared to 304N. Since the amount of porosity observed in this material is on higher side as compared to 304 N steel, it may start yielding much earlier. Moreover, the dimples are also of smaller size.

5) 304 L stainless steel

This stainless steel exhibits uniform dimple structure (Figure 4.7) with micro-voids of different sizes. Since the structure is homogeneous with uniformly distributed pores which are because of the micro-voids. The material can be used for several structural devices. The shapes of the dimples observed are heterogeneous in nature and each micro-void provides good ductility. The material exhibits better elongation.

6) 316 L stainless steel

This stainless steel has quite different microstructures (Figure 4.8) as compared to the other steels in a way that the fractured surface is different. It appears that huge amount of gaseous substances have been pored inside the melt. The poor yield strength is because of these trapped gases. However, the ultimate strength is very good. This indicates that substance can be rolled very easily as compared to the other steels. The dimples observed are uniformly distributed throughout the segment.

4.3.2 Impact testing

The average energy absorbed in V-notch Charpy test at room temperature (Table 4.3) is higher than energy absorbed in standard 2304 and 2205 duplex stainless steel. The high yield strength, high tensile strength coupled with high ductility account for this high value of absorbed energy in Charpy test.

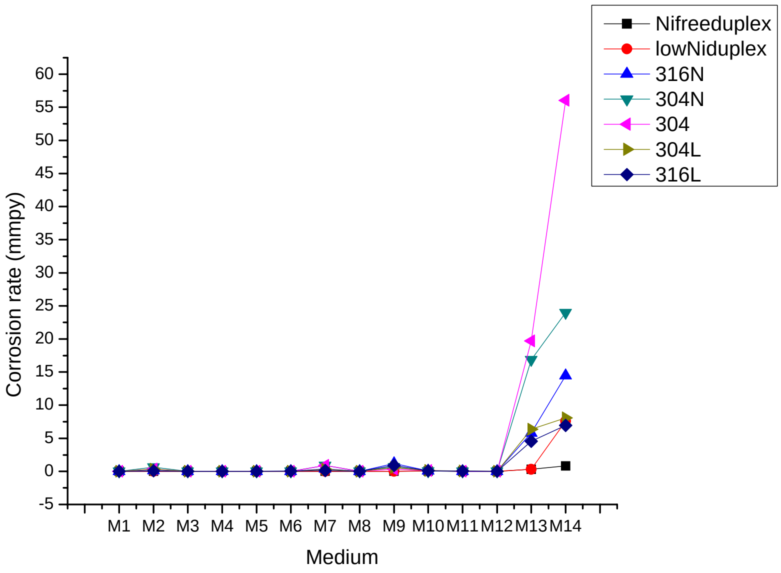
Table 4.3: Comparison of energy absorbed in Charpy test among experimental duplex (Ni free) and standard [18] duplex stainless steels.

Grades	Energy (Joule) absorbed in Charpy test
Duplex (Ni free)	274, 296, 298
2304	280
2205	280

Figure 4.10: Impact tested samples.

4.4 Corrosion in different boiling media

The corrosion test has been carried out in different media (Table 4.4a – 4.4c) at boiling temperature. The tests results (Figure 4.11) shows that the duplex (Ni free) stainless steel has better corrosion resistance property as compared to duplex (low Ni), 304N, 316N, 304, 304L and 316L, in organic, inorganic and other corrosive media.



M1	20% Acetic acid
M2	5% Acetic acid + 5% Formic acid
M3	1% Acetic acid + 1% NaCl
M4	10% Acetic acid + 5% NaCl
M5	3.5% NaCl
M6	2% Formic acid
M7	5% Formic acid
M8	25% Lactic acid
M9	1% Oxalic acid
M10	50% Nitric acid
M11	50% Orthophosphoric acid
M12	25% Citric acid
M13	5% H_2SO_4 + 20% $(NH_4)_2SO_4$
M14	3% H_2SO_4

Figure 4.11: Comparison of corrosion rate of experimental alloys, in different media

Table 4.4a: Comparison among rate of corrosion duplex (Ni free) with duplex (low Ni), 316N, 304N, 304, 304L and 316L in different medium.

S. No	**Medium**	**Temp.**	**Time**	**Duplex (Ni free)**	**Duplex (Low Ni)**	**316N**	**304N**	**304**	**304L**	**316L**
1.	20% Acetic acid	B.P.	48 h	0.0024088 **(A^+)**	0.004482 **(A^+)**	0.001374 (A^+)	0.003816 **(A^+)**	0.006921 **(A^+)**	0.006643 **(A^+)**	0.004877 **(A^+)**
2.	5% Acetic acid + 5% Formic acid	B.P.	48 h	0.0040263 **(A^+)**	0.004652 **(A^+)**	0.131702 **(A)**	0.633612 **(C)**	0.358459 **(B)**	0.290855 **(B)**	0.104844 **(A)**
3.	1% Acetic acid + 1% NaCl	B.P.	48 h	0.002592 **(A^+)**	0.005417 **(A^+)**	0.006676 **(A^+)**	0.004122 **(A^+)**	0.008663 **(A^+)**	0.007899 **(A^+)**	0.005475 **(A^+)**
4.	10% Acetic acid + 5% NaCl	B.P.	48 h	0.0101314 **(A^+)**	0.008149 **(A^+)**	0.018174 **(A)**	0.014236 **(A^+)**	0.025254 **(A)**	0.025787 **(A)**	0.019486 **(A)**
5.	3.5% NaCl	B.P.	48 h	0.0033428 **(A^+)**	0.008027 **(A^+)**	0.003336 **(A^+)**	0.003226 **(A^+)**	0.0022 **(A^+)**	0.004514 **(A^+)**	0.003423 **(A^+)**
6.	2% Formic acid	B.P.	48 h	0.00003 **(A^+)**	0.007677 **(A^+)**	0.031871 **(A^+)**	0.001402 **(A^+)**	0.007573 **(A^+)**	0.006088 **(A^+)**	0.002029 **(A^+)**

Table 4.4b: Comparison among rate of corrosion duplex (Ni free) with duplex (low Ni), 316N, 304N, 304, 304L and 316L in different mediums

S. No	**Medium**	**Temp.**	**Time**	**Duplex (Ni free)**	**Duplex (Low Ni)**	**316N**	**304N**	**304**	**304L**	**316L**
7.	5% Formic acid	B.P.	48 h	0.0014882 **(A^{+})**	0.01529 **(B)**	0.385705 **(B)**	0.894964 **(B)**	0.89914 **(C)**	0.295371 **(C)**	0.12457 **(B)**
8.	25% Lactic acid	B.P.	48 h	0.0021785 **(A^{+})**	0.005449 **(A^{+})**	0.015031 **(A)**	0.003424 **(A^{+})**	0.005171 **(A^{+})**	0.004453 **(A^{+})**	0.016376 **(A)**
9.	1% Oxalic acid	B.P.	48 h	0.0105166 **(A^{+})**	0.016124 **(A)**	1.209288 **(D)**	0.663307 **(C)**	0.33612 **(B)**	0.562907 **(C)**	0.89009 **(C)**
10.	50% Nitric acid	B.P.	48 h	0.0603478 **(A)**	0.093776 **(A)**	0.07853 **(A)**	0.067186 **(A)**	0.137957 **(B)**	0.120811 **(B)**	0.103496 **(B)**
11.	50% Orthophosphoric acid	B.P.	48 h	0.0105403 **(A^{+})**	0.007925 **(A^{+})**	0.028403 **(A)**	0.006048 **(A^{+})**	0.026798 **(A)**	0.037784 **(A)**	0.035649 **(A)**
12.	25% Citric acid	B.P.	48 h	0.0032991 **(A^{+})**	0.000181 **(A^{+})**	0.000574 **(A^{+})**	0.001987 **(A^{+})**	0.00415 **(A^{+})**	0.006984 **(A^{+})**	0.006421 **(A^{+})**

Table 4.4c: Comparison among rate of corrosion duplex (Ni free) with duplex (low Ni), 316N, 304N, 304, 304L and 316L in different mediums

S. No	**Medium**	**Temp.**	**Time**	**Duplex (Ni free)**	**Duplex (Low Ni)**	**316N**	**304N**	**304**	**304L**	**316L**
13.	5% H_2SO_4 + 20% $(NH_4)_2SO_4$	B.P.	48 h	0.3235309 **(B)**	0.32614 **(B)**	5.793836 **(E)**	16.8451 **(E)**	19.69179 **(E)**	6.353126 **(E)**	4.539686 **(E)**
14.	3% H_2SO_4	B.P.	48 h	0.8347706 **(C)**	7.580529 **(E)**	14.46191 **(E)**	23.98698 **(E)**	56.05911 **(E)**	8.085674 **(E)**	6.926853 **(E)**
15.	5% H_2SO_4	B.P.	48 h	1.5961416 **(D)**	51.27619 **(E)**	34.17077 **(E)**	48.8891 **(E)**	Dissolve **(E)**	21.64539 **(E)**	17.56698 **(E)**
16.	White liquor	B.P.	48 h	0.0036593 **(A^+)**	-------------	-----------	------------	------------	0.005014 **(A^+)**	-----------
17.	Black liquor	B.P.	48 h	0.0005095 **(A^+)**	-------------	-----------	------------	------------	0.003873 **(A^+)**	----------

Where[31], < 0.02 → Outstanding → **A^+**
0.02 - 0.1 → Excellent → **A**
0.1 - 0.5 → Good → **B**
0.5 – 1 → Fair → C
1 – 5 → Poor → **D**
>5 → Unacceptable → **E**

4.4.1 Corrosion in inorganic media

In 50% Nitric acid (Figure 4.12) the duplex grades and high nitrogen grades have a slight edge near 304, 304L and 316L. Sedriks has pointed out that high chromium content has beneficial effect in nitric acid. From these results it appears that nitrogen may also have beneficial effect for protection from Nitric acid [1, 30, 34, 35].

In 3% and 5% sulfuric acid (Figure 4.13), duplex (Ni free) stainless steel exhibits far superior behavior as compared to 304, 304L, 304N, 316N and 316L. Sedriks has contended the higher Ni, Mo and Cu content of austenitic alloys increase corrosion resistance in sulfuric acid environment whereas chromium content of the alloy increases the corrosion rate. The present investigation reveals that the duplex (Ni free) stainless steel with high content of chromium, nitrogen and copper is more corrosion resistance in 3% and 5% sulfuric acid solutions as compared to 316L and 316N which have molybdenum in them. The comparison of duplex (Ni free) and duplex (low Ni) reveals beneficial effect of copper on corrosion in sulfuric acid [15, 30].

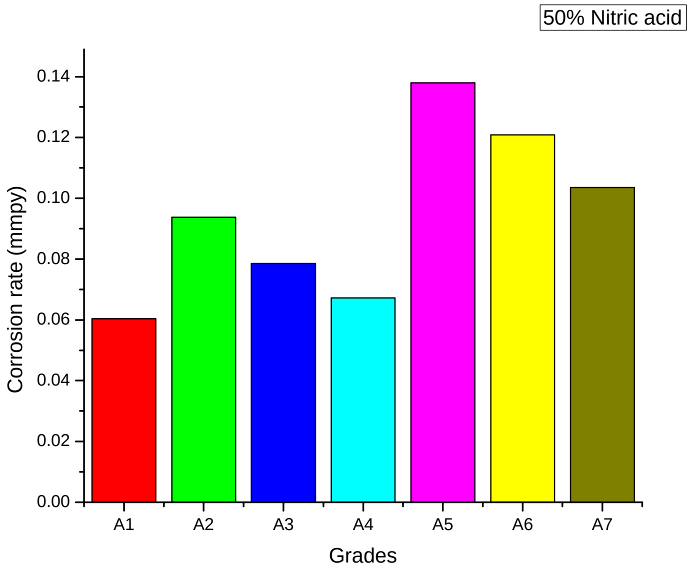


Figure 4.12: corrosion rate in 50% nitric acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

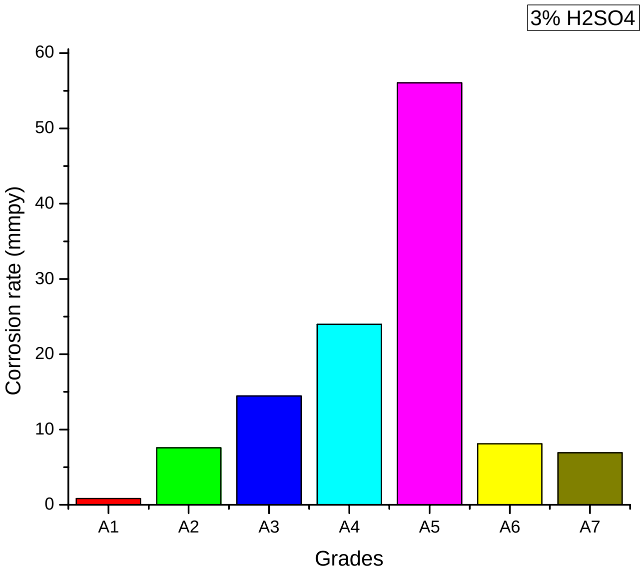


Figure 4.13: Corrosion rate in 3% sulfuric acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,
A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

4.4.2 Corrosion in organic media

Organic acids are generally weaker than inorganic acids because they are less ionized. Formic acid is the most corrosive of the common organic acids. In 2% Formic acid (Figure 4.14) all the alloys yielded outstanding results. In 5% formic acid (Figure 4.15), duplex (Ni free) is far superior as compared to 304, 304L, 304N, 316L and 316N [30].

Sedriks has stated that Mo and Ni play an important role in increasing corrosion resistance in formic acid media. Sedriks however compared 304L with 316L and 904L and 20Cb3 (20wt% Cr – 35wt% Ni – 2.5wt% Mo – 2wt% Mn – 1wt% Si). Since 904L, 20Cb3 and 316L have higher nickel and molybdenum content therefore he ascribed superior corrosion resistance of such grades as compared to 304L to their higher nickel and molybdenum content. However from our study it appears that higher chromium, nitrogen and copper also have beneficial effect. 20CB3 for example contains copper and higher chromium content [30].

In boiling 20% Acetic acid (Figure 4.16), the studied alloys (Ni free duplex, low Ni duplex, 304, 304L, 304N, 316L, 316N) performed well.

Similarly in “5% acetic acid + 5% formic acid” (Figure 4.17) also duplex (Ni free) is far superior compared to 304, 304L, 304N, 316L and 316N. From comparison between 304, 304L, 304N, 316L and 316N, it is evident that presence of molybdenum in 316L and 316N has a beneficial effect in “5% acetic acid + 5% formic acid”. However since duplex (Ni free) stainless steel has much higher Cr, Cu and nitrogen, it exhibits even superior behavior than 316L and 316N.

In 25% lactic acid (Figure 4.18) duplex (Ni free), duplex (low Ni), 304, 304L and 304N exhibits outstanding behavior which is superior to 316L and 316N. It appears that higher chromium content of duplex and 304 based grades is responsible for this better resistance.

In 1% oxalic acid (Figure 4.19) both duplex (nickel free) and duplex (low Ni) stainless steels exhibits excellent result and are far superior compared to 304, 304L, 304N, 316L and 316N.

In 50% orthophosphoric acid (Figure 4.20) duplex grades and 304N are in outstanding category, whereas other grades are in excellent category. Higher chromium and nitrogen appear to have beneficial impact. In 25% citric acid (Figure 4.21) all alloys exhibits high resistance to corrosion.

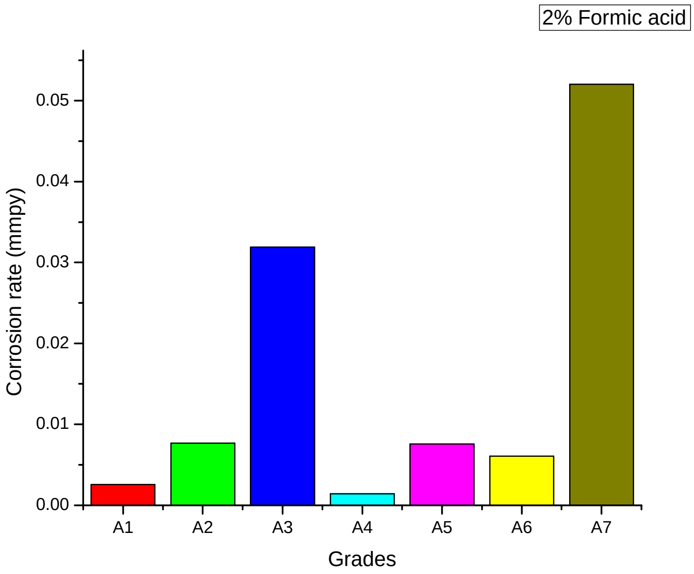


Figure 4.14: Corrosion rate in 2% formic acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

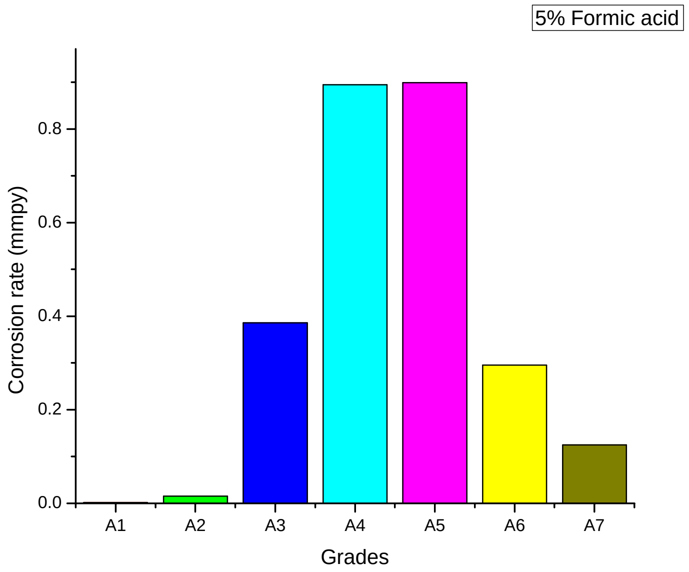


Figure 4.15: Corrosion rate in 5% formic acid.

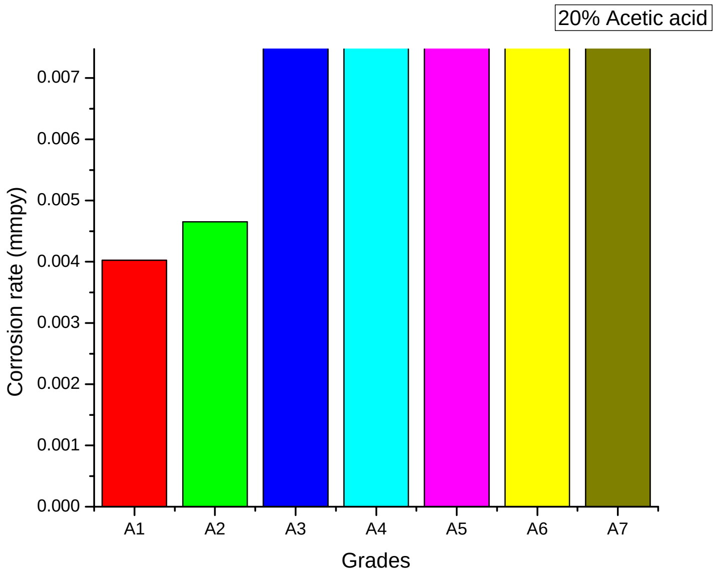


Figure 4.16: Corrosion rate in 20% acetic acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

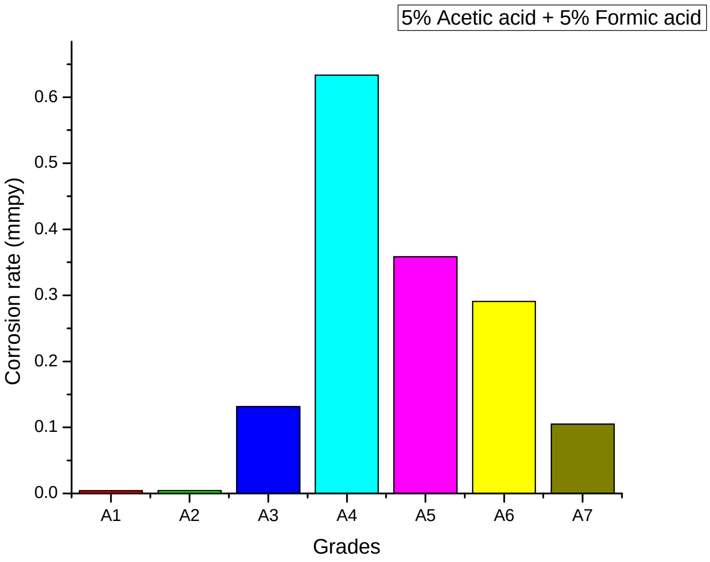


Figure 4.17: Corrosion rate in 5% acetic acid and 5% formic acid.

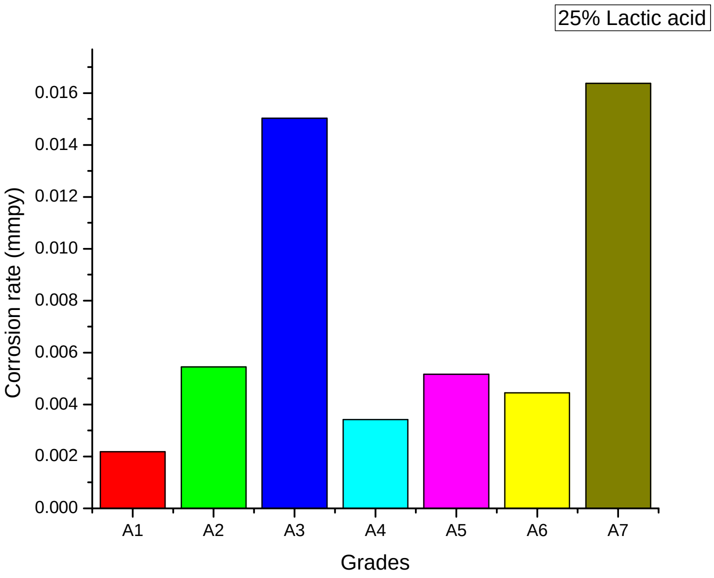


Figure 4.18: Corrosion rate in 25% lactic acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

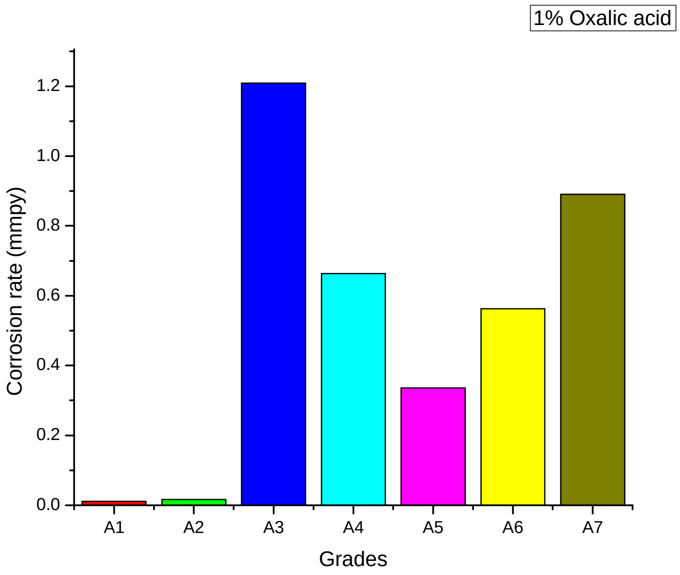


Figure 4.19: Corrosion rate in 1% oxalic acid.

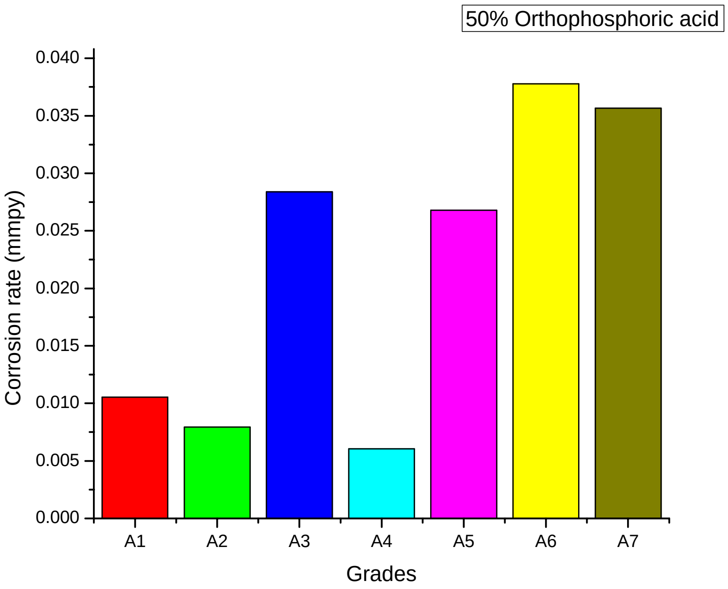


Figure 4.20: Corrosion rate in 50% orthophosphoric acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

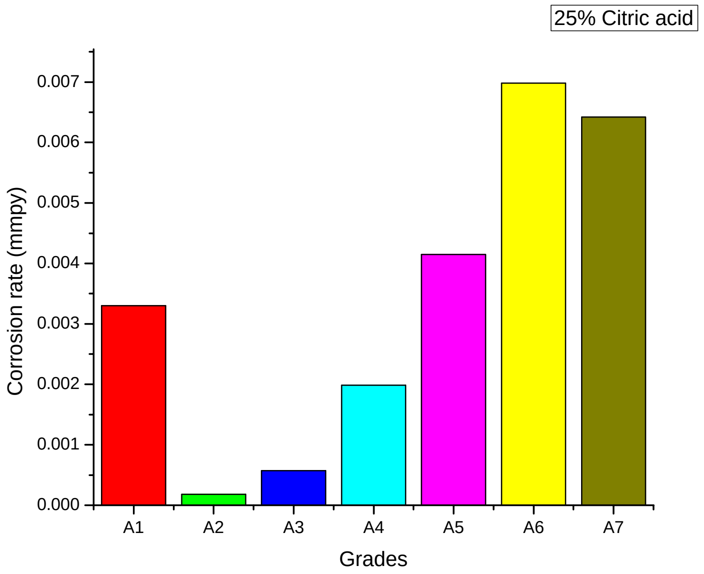


Figure 4.21: Corrosion rate in 25% citric acid.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,
A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

4.4.3 Corrosion in other media

In organic acids containing NaCl salt were also compared. In “1% Acetic acid + 1% NaCl” (Figure 4.22) all grades exhibits outstanding behavior. However in “10% Acetic acid + 5% NaCl” (Figure 4.23) duplex (Ni free) and duplex (low Ni) are slightly better than other grades. In 3.5% NaCl (Figure 4.24) all the studied alloys exhibited similar behavior.

In mixture of 5% sulfuric acid and 20% ammonium sulphate (Figure 4.25), the duplex alloys are far superior to 304 and 316 based alloys.

In craft solutions (white and black liquor) the performance of duplex (Ni free) stainless steel and 304L are equally good and both grades gives the outstanding performance. The result shows that white liquor is more aggressive than black liquor (Figure 4.26) [36]

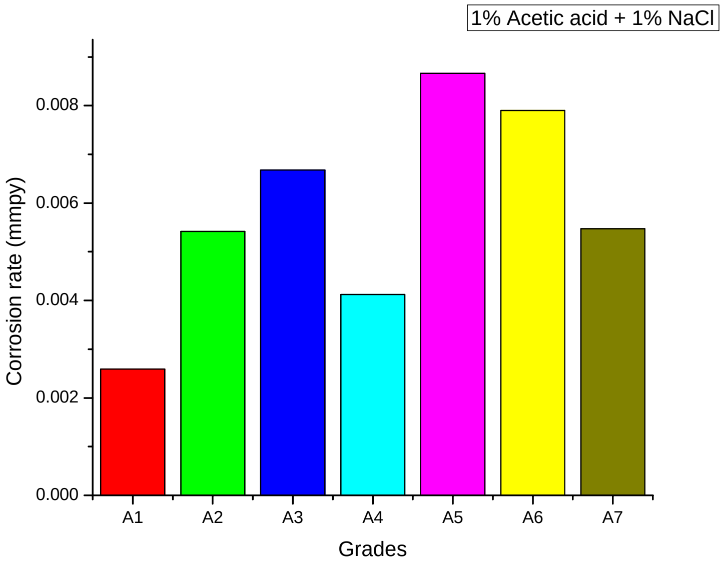


Figure 4.22: Corrosion rate in 1% acetic acid+ 1% NaCl.

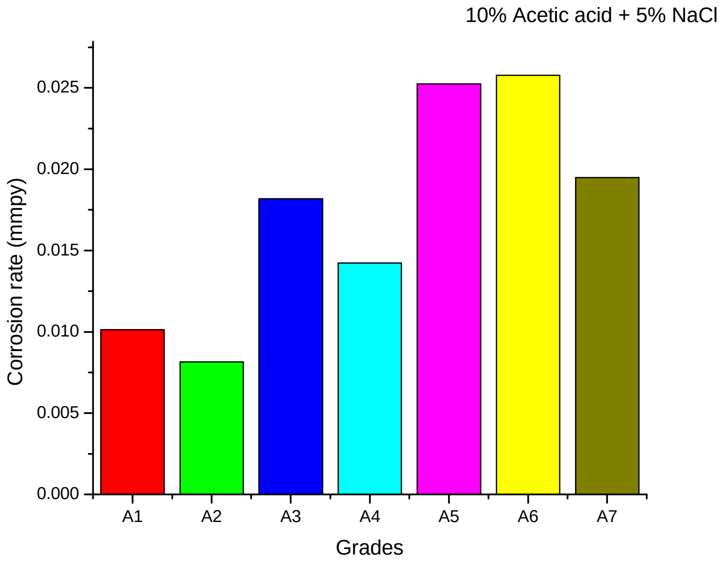


Figure 4.23: Corrosion rate in 10% acetic acid+ 5% NaCl.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

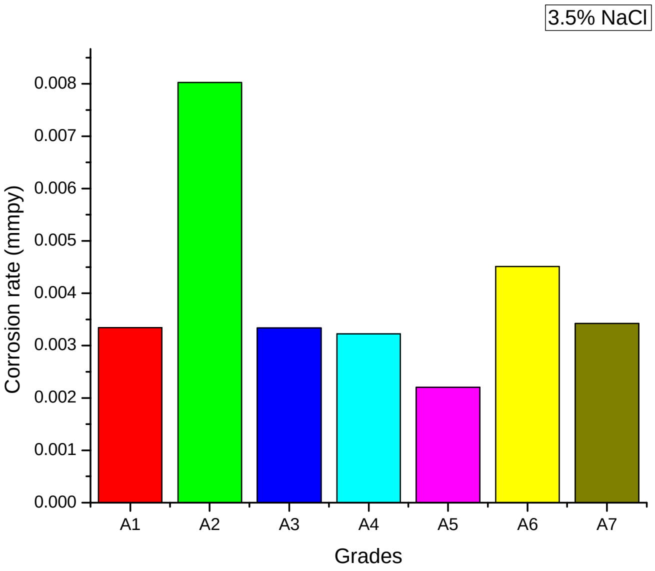


Figure 4.24: Corrosion rate in 3.5% NaCl.

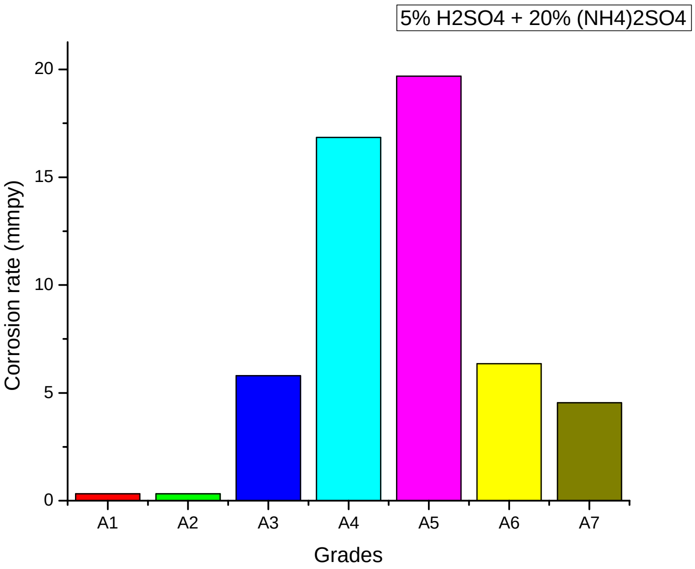


Figure 4.25: Corrosion rate in 5% H2SO4 + 20% $(NH_4)_2SO_4$.

Where,

A1 = duplex (Ni free), A2 = duplex (low Ni), A3 = 316N,

A4 = 304N, A5 = 304, A6 = 304L, A7 = 316L

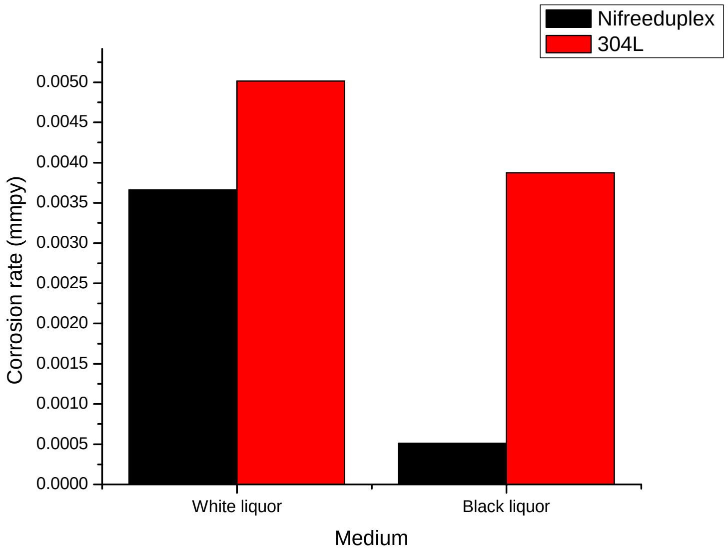


Figure 4.26: Comparison of corrosion of duplex (Ni free) and 304L in craft solutions: white & black liquor.

CHAPTER-5

CONCLUSION AND SCOPE FOR FUTURE WORK

5.1 Conclusions

From current investigation following conclusion has drawn:

1. Duplex (Ni free) stainless steel containing 21wt% Cr, 1.6wt% Cu, 5wt% Mn, and 0.2wt% N is characterized with high strength and toughness with excellent corrosion resistance property.
2. In comparison with commercial duplex stainless steels like 2304 and 2205, duplex (Ni free) stainless steel has higher yield strength.
3. As compared to 304, 304L, 304N, 316L and 316N, duplex (Ni free) stainless steel has much higher corrosion resistance property.
4. Because of the absence of costly nickel and molybdenum, duplex (Ni free) stainless steel can be cost effective solution where austenitic stainless steel grades with high nickel content are currently used.
5. Duplex (Ni free) stainless steel can be used in chemical, pulp and paper industry where high strength with good corrosion resistance property required.

5.2 Scope for future work

Following are the works, suggested for future:

1. To study the stress corrosion cracking in hot NaCl and other media.
2. To find the suitability in pulp and paper industry for specific application.
3. Study of mechanical and chemical properties after hot and cold rolling.
4. Study of sigma phase with variation in heat treatment cycle.

References

1. J. H. Qiu, Surface and Interface Analysis 33(2002) 830-833
2. P. R. Beely, P. J. Beely; Steel-makes and knotted string, Harry Breareley, The Institute of Materials, 221-227
3. J. R. Davis; Alloy digest, source book, stainless steel, Americon Society for Metals (ASM), 1-338
4. S. Lamb, J. E. Bringas; Hand book of stainless steel and nickel alloys (Second edition), ASM International, 102-142
5. Australian Stainless Steel Development Association ASSDA Technical Bulletin 200 Series Stainless Steels Cr-Mn Grades (First edition), (October 2006) 1
6. http://www.atlasmetals.com.au/
7. D. Schino, J. M. Kenny; Journal of Material Science, 38 (2003) 3257 – 3262
8. H. Sieurin; Doctoral thesis (Fracture toughness properties of duplex stainless steel), Department of Material Science and Engineering, Royal Institute of Technology, Sweden, 2006
9. J. Charles ; Duplex Stainless Steels 97-5th world conference, Stainless Steel World, 29-42
10. J. Olsson, M. Snis, Desalination, 205 (2007) 104-113
11. E. I. Kivineva, N. E. Hannerz; Proceedings of the Fourth International Conference on Duplex Stainless Steels, 2 (1994), 13-16 November
12. I. Calliari, M. Zanesco, E. Ramous, P. Bassani; JMEPEG, 16 (2007) 109-112
13. V. Muthupandi , P. Bala Srinivasan , S.K. Seshadri, S. Sundaresan; Materials Science and Engineering, A358 (2003) 9- 16,
14. L. F. Garfias, J. M. Sykes, C. D. S. Tuck; Corosion Sciene, 38(1996), 1319-1330,
15. S. S. M. Tavares, J. M. Pardal, L. D. Lima, I. N. Bastos, A. M. Nascimento, J. A. de Souza; Materials Characterization, 58 (2007) 610-616
16. Ihsan-ul-Haq Toor, P. J. Hyun, H. S. Kwon; Corrosion Science, 50(2008), 404-410
17. Hyuk-Sang Kwon and H. S. Kim; Material Science and Engineering, A172 (1993) 159-166

18. J. Wang, P. J. Uggowitzer, R. Magdowski, M.O. Speidel; Scripta Materialia, 40 (1999) 123–129,
19. R. N Gun; Duplex stainless steels; Microstructure, Properties and Application, Abington Publishing, Cambridge, England, page: 14-21
20. A. D. Schino, J. M. Kenny, M. G. Mecozzi, M. Barteri; Journal of Material Science, 35 (2000) 4803
21. Y. H. Jang, S. S. Kim, J. H. Lee; Materials Science and Engineering, A 396 (2005) 302-310
22. C. D. Van Lelyveld, A. V. Bennekom; Materials Science and Engineering, A205 (1996) 229-238
23. H. Sieurin, R. Sandstrom; Materials Science and Engineering, A 444 (2007) 271–276
24. Chi-Shang Huang, Chia-Chang Shih; Materials Science and Engineering, A 402 (2005) 66–75
25. Pohl, O. Storz, T. Glogowski; Microsc Microanal, 11, 2005
26. H. M. Ezuber, A. El-Houd, F. El-Shawesh; Desalination, 207 (2007) 268–275
27. Z. Cvijovic, G. Radenkovic; Corrosion Science, 48 (2006) 3887-3906
28. R. Merello, F. J. Botana, J. Botella, M. V. Matres, M. Marcos; Corrosion Science, 45 (2003) 909-921
29. L. F. Garfias- Mesias, J. M. Sykes and C. D. S. Tuck; Corrosion Science, 38 (1996) 1319-1330
30. A. John Sedriks; Corrosion of Stainless Steels, Second edition, Wiley-International Publication, John Wiley & Sons, INC (1996) 2- 385
31. R. L. Klueh, P. J. Maziasz, E. H. Lee; Materials science and engineering A, 102 (1988) 115- 124
32. M. Martins, S. M. Rossitti, M. Ritoni, L. C. Casteletti; Materials Characterization, 58 (2007) 909-916
33. M. G. Fontana; Corrosion Engineering, Third edition, Mc Graw Hill, New York (1986) 172
34. C. T. Kwok, S. L. Fong, F. T. Cheng, H. C. Man; Journal of Material Processing Technology, 176 (2006) 168-178

35. G. Lothongkum, P. Wongpanya, S. Morito, T. Furuhara, T. Maki; Corrosion Science, 48 (2006) 137-153
36. Jean- Pierre Audouard; Duplex Stainless Steels 97-5th world conference, Stainless Steel World, 565