Metallurgical investigations on corrosion behavior of simple and heat treated duplex stainless steel 2205 exposed to corrosive media

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Abstract: Duplex stainless steel 2205 has proven to be the most acceptable material for marine and saline applications because of its superior corrosion resistance with good erosion and wear resistance. However, the disadvantage of stainless steel is its sensitivity to local corrosion in a solution containing chloride, which limits their use in seawater systems. The effect of heat treatment on corrosion properties of stainless steels can be studied in marine or chloride environments and investigation of changes in microstructure and corrosive property. This study presents the consequence of heat treatment on the microstructure and corrosion resistance and systematic approach to examine the corrosion behaviour of plain DSS 2205. Precipitation of secondary parts in DSS 2205 led to an extreme reduction in its corrosion resistance and another factor contributing to changes in ferrite and austenite ratios where preferential corrosion occurred in the DSS 2205 ferrite phase. The austenite phase shows better corrosion resistance than the ferrite phase due to maximum Ni content than ferrite. Cr is the most active element in the passive film to develop the resistance of DSS 2205 to localized corrosion. The heat treatment about 1080°C to DSS 2205 improves the corrosion resistance of steel comparatively.

1. Introduction
The degradation of materials due to chemical reactions with their environment is term as corrosion [1]. Corrosion of a material malfunction causes a gradual deterioration of its properties until it fails to meet its objectives and necessities to be replaced. Moreover, corrosion causes aesthetic problems and increasing costs of repair and rebuilding [2]. In order to succeed in corrosion protection it is important to know the fundamentals of corrosion reactions and what are their main causes. The most naturally occurring state of a material is its lowest energy states and for metals this is usually an oxide. This means that naturally all metals exist as oxides and extensive processing is required to convert the metal oxides of pure metals. Therefore, corrosion of a material can be simply defined as the driving force towards its natural, lowest energy state. If not protected properly, any metal will oxidize, resulting in rust formation or paint defects on the surface of the material.

DSS 2205 exhibits higher resistance to stress corrosion cracking and it has higher strength than austenitic stainless steel [3]. Taking advantages of these positive factors, DSS 2205 is widely used in the marine applications, tubing for heat exchanger, oil and gas, petrochemical, pulp and paper, and pollution control industries. It is well known that the DSS 2205 exhibit good weld ability, but the melting and solidification associated with fusion welding processes destroys the favourable duplex microstructure of this stainless steel. The heat treatment process is often used for the refinement of grain structure of the steels to improve the corrosion and wear resistance properties of the base material e.g. vessels, valve cone, spindle and valve seat, valves collar and pipes used in marine and other application where the material exposes to severe atmospheric conditions to improve the mechanical and tribological properties of the key element like pressure vessels, valve seat and sleeve which is made up of DSS 2205 or Inconel for chemical, petrochemical, oil/gas, marine and nuclear...
industries, for economic reasons. DSS has equal phase balance of about identical quantities of ferrite and austenite. It has an assorted microstructure consisting of ferrite (BCC) and austenite (FCC) phases. The corrosion properties of stainless steels can be studied in marine or chloride environments with the effect of heat treatment and investigation of changes in microstructure and corrosive property.

2. DSSs 2205
DSS 2205 is an intermediate grade between ferritic and austenitic stainless steels. DSS 2205 is more resistant to stress corrosion than austenitic types, but worse than ferritic types. They have better toughness than ferritic steels but are not as good as austenite [4]. On the other hand, the strength of DSS 2205 is greater than that of austenite. As a result of extensive research and development recently, a number of new forged alloys have been developed and relevant technical data obtained to verify the treatment of dual-phase steels as other types of steel [5]. DSSs 2205 have a structure of austenite and ferrite phases. Chromium and nickel are the principle alloying elements, the chromium is between 18-28% and the nickel is between 4.5-8%. Copper, molybdenum, tungsten, nitrogen, manganese, and silicon may be added to control structural balance and to provide certain corrosion resistance [6]. Molybdenum is typically added to also enhance crevice corrosion and pitting corrosion resistance [7]. The amount of the two phases is controlled by the composition of the alloy and its heat treatment. The ratio of the phases plays a significant role in defining their properties.

The proportion of α-ferrite and γ-austenite varies with temperature and at high temperatures the structure becomes more ferrite, less Ni and more Cr equivalents. The relationship between both phases is usually about 50% (by volume) although it can vary between 40% and 60% and even between 30% and 70%. The duplex grades are not hardened with heat treatment but are stronger than either of these two grades in the annealed condition and have approximately double the yield strength of the common austenitic grades [8]. Like the ferritic, they are ferro-magnetic, but have the good formability and weldability of the austenitics (although larger forces are required in forming due to their higher strength), and have lower thermal expansion and higher heat conductivity than austenitic grades. The duplex grades are known to be resistant to chloride SCC, pitting and crevice corrosion. In cast duplex, a structure of austenite is lands in a ferrite matrix can be observed. For wrought alloys, the morphology of the microstructure has laths of austenite in a ferrite matrix. The presence of ferrite with austenite not only provides better inter-granular corrosion resistance but also improves SCC resistance compared to fully austenitic stainless steels.

Also, the presence of austenite in the structure could enhance the mechanical properties and improve the localized corrosion resistance due to the availability of austenite stabilizing elements (N and Ni). Moreover, DSSs 2205 become increasingly ferritic as they are heated to high temperatures. However, the presence of ferrite in austenite may cause complex metallurgical reactions that include the formation of a variety of secondary phases, which have unpleasant effects on both corrosion resistance and mechanical properties. The precipitation is usually caused by decomposition of the ferrite phase, which contains large amounts of Cr and Mo, and has low solubility of N and C. Since toughness and corrosion resistance are the criteria of interest, the composition of DSS 2205 and their processing, including fabrication practice, must ensure sufficient formation of austenite and prevention of intermetallic compounds. Figure 1 shows the precipitates in DSS and it is evident that most of these precipitates concern ferrite and ferrite promoting elements such as Cr, Mo and W. The Figure also illustrates that almost all these reactions take place over the temperature range of 300° - 1000°C [9].
The higher composition of alloying elements in DSS 2205 grades makes them vulnerable to creation of intermetallic and intermediate phases with inevitable form after prolonged service at high temperatures or due to incorrect heat treatment. In addition, these inter-metallic phases could be formed in DSS 2205 during isothermal ageing or quenching. The unwanted creation of secondary phases decreases the overall corrosion resistance and makes the alloy more susceptible to localized corrosion attack. Moreover, such precipitations may also affect the tribo-mechanical properties, mainly the toughness and corrosion resistance. Due to this, service temperatures are usually restricted to be less than about 300°C [10].

3. Literature review
Considering the applications of DSS and the said objectives of research a detailed literature review is carried out to understand the applicable testing methods and systematic approach for investigations. The literature studied for the investigation is summarized as follows. Mesquita et al. [11] studied the corrosion and metallurgical investigation of two super martensitic stainless steels for oil and gas environments in that, the corrosion properties of two super martensitic stainless steels were studied in chloride and H2S environments. Comparison between 1.4542 and 1.4418 SS grades was made considering the effects of microstructure, different steps of the heat treatment on the pitting and sulfide stress cracking SSC properties. Mundhenk et al. [12] in their investigation of corrosion and scaling as interrelated phenomena in an operating geothermal power plant the study refers to an experimental research and contributes to a better understanding of corrosion and scaling in an operating geothermal power plant (Soultz-sous-Forêts, France).

An in situ physicochemical monitoring program has been performed in order to characterise the processed brine. In situ and laboratory corrosion experiments were performed using conventional and candidate metals. Similar or some modified studies were also reported in the literature which includes, Pohrelyuk et al. [13] investigated the resistance offered against corrosion in case of Ti–6Al–4V alloy with nitride coatings in Ringer’s solution. Gastaldi & Bertolini [14] investigated the effect of temperature on the corrosion behavior of low-nickel DSS bars in concrete.

Hua et al. [15] investigated the hot corrosion behavior of TC11 titanium alloy treated by laser shock processing. Alvarez et al. [16] studied the Corrosion behavior of corrugated lean DSS in simulated concrete pore solutions. Machnikova et al. [17] studied the Corrosion inhibition of carbon steel in hydrochloric acid by furan derivatives. Tan et al. [18] had investigated the pitting corrosion resistance of 2304 DSS after autogenously PAW and subsequent short-time post-weld heat treatment at different temperatures, determined by critical pitting temperature in 1.0 M NaCl solution, etc.
4. Experimental procedure

4.1 Material and heat treatment:
In the present work, plates DSS 2205, 18 mm thick are used. The chemical % compositions of the DSS 2205 material is indicated in Table 1. The heat treatment is initially carried out at 880°C and 1080°C in the muffle furnace, followed by quenching with water in accordance with the ASTM A182. This is necessary to eliminate second phase of treatment, balancing the phase fractions and release the residual stresses during the manufacturing practice. Specimens are heat treated at 880°C and 1080°C and then water cleaned.

| Alloy  | Cr    | Ni   | Mo  | C    | N    | Mn   | Fe       |
|-------|-------|------|-----|------|------|------|----------|
| SS 2205 | 22.37% | 5.48% | 3.49% | 0.021% | 0.20% | 1.370% | Balance  |

4.2 Optical microscopy:
Specimen for the micro structural examination is prepared by following conventional metallographic procedures. The steps for preparation involves mountings and polishing the specimen using 120, 220, 320, 600, 1000, 1200, 2000 and 2500 grit silicon carbide paper.
These specimens are then cleaned with distilled water and then polished with 0.9, 0.3 µm diamond paste to obtain a surface like a mirror finish. After polishing, the specimens are cleaned with ethanol media for 10 min. Light microscopy is used to reveal the changes in ferrite and austenite phases and detect the presence of third phases. Following Figure 2 shows the microstructure of DSS 2205 (i) simple DSS (ii) 880°C (iii) 1080°C, where specimens annealed at different conditions, the dark part represents ferrite while the light representing austenite.

![Figure 2](image_url)

**Figure 2.** Optical microstructure of DSS 2205 specimens annealed at different conditions, the dark part represents ferrite while the light representing austenite (i) Simple DSS (ii) 880°C (iii) 1080°C

4.3 Scanning electron microscopy (SEM):
SEM is applied to recognize microstructural structures related to austenite, ferrite and intermediate stages. Also, specimens are checked by energy dispersive spectroscopy (EDS) to analyze the chemical composition of specimen. Figure 3 shows SEM images of 2205, indicating dark part associated with ferrite while the light representing austenite (i) Simple DSS (ii) 880°C (iii) 1080°C
2.1080°C in potentiodynamic polarization tests require a distilled water electrolyte which contains artificial seawater which is prepared by addition of 5% NaCl to the 95% of distilled water. A conventional metallographic procedure is adopted for the preparation of specimens and before being tested, all specimens are ground with SiC paper up to 3000 grit and polished. After polishing, the specimens are cleaned with ethyl alcohol and dried in air. As per the requirements, all specimens are immersed in the electrolytes and the cell is left to stabilize the open circuit potential (OCP) before the actual conduction of tests on each specimen. The potential sweep rate is 1 mV/s and the sweep rate is -300 to 200 mV with respect to a saturated Calomel electrode. Corrosion tests are performed with artificial seawater (5% NaCl). The first is potentiodynamic polarization using a three-electrode electrochemical cell, with a platinum counter-electrode and a saturated calomel reference electrode (SCE) and the working electrode (DSS). Figure 4 shows potentiodynamic polarization curves of 2205 DSS specimen and heat treated at 880°C in artificial sea water and Figure 5 Potentiodynamic polarization curves of 2205 DSS specimen and heat treated at 1080°C in artificial sea water. The current density and corrosion rate of specimens are shown in Table 2.

4.4 Vickers micro-hardness test:
Vickers micro hardness test is carried out using micro hardness machine (Made Mitutoyo available with Nashik Engg. Cluster), with an attached microscope, at 10-400X total magnification according to ASTM E 384 – 99 and 1000 gram load. The microhardness of simple DSS is 242 HV1.0, for specimen heat treated with 880°C microhardness is 254 HV1.0 and for the specimen 1080°C microhardness is 258 HV1.0.

4.5 Electrochemical corrosion tests:
The specimens required for the potentiodynamic polarization test are prepared as per the requirements, these are prepared in discs shape with an area of 1 cm2 and a height of 2 mm. Three specimens are prepared for the test as mentioned earlier sections which consist of simple DSS and two heat treated DSS. The polarization tests are carried out by the potentiostat made by Gamry®, the cell contains an electrolyte which contains artificial seawater which is prepared by addition of 5% NaCl to the 95% of distilled water. A conventional metallographic procedure is adopted for the preparation of specimen and before being tested, all specimens are ground with SiC paper up to 3000 grit and polished.

Figure 3. SEM images of 2205, indicating dark part associated with ferrite while the light representing austenite (i) Simple DSS (ii) 880°C (iii) 1080°C

Figure 4. Potentiodynamic polarization curves of 2205 DSS specimen and heat treated at 880°C in artificial sea water
Figure 5. Potentiodynamic polarization curves of 2205 DSS specimen and heat treated at 1080°C in artificial sea water

Table 2. Current density and corrosion rate for 2205 DSS alloys specimens

| Specimens  | Current density (µA/cm²) | Corrosion rate (mpy) |
|------------|--------------------------|----------------------|
| Simple DSS | 1.96                     | 0.872                |
| 880°C      | 0.98                     | 0.416                |
| 1080°C     | 0.67                     | 0.318                |

5. Results, discussion and analysis

The microstructure of DSS 2205, as in Figure 2 shows that the optical microstructure of the simple DSS specimen also SEM image Figure 3(i) contains only ferrite and austenite with no secondary phases. In those microstructural images ferrite phases appears darker than austenite phases, after heat treatment, the evolution of secondary phases influences the corrosion and mechanical properties of the DSS 2205. The temperature of the treatment shows effects on the microstructure, secondary phases also on the volume fraction of these all phases. Moreover, the effects of these change in temperature and heat treatment of DSS 2205 can be observed in Figure 2 (i-iii) and Figure 3 (i-iii). When the DSS 2205 is the heat treated the decomposition of thermodynamic balance occurs causing the material to endeavor a more stable thermodynamic state by precipitation and formation of secondary phases. The sigma phase is preferentially nucleated at α / γ or α / α interfaces and grows through the adjacent ferrite, since the ferrite phase is unstable at elevated temperatures. Indeed, diffusion rates of alloying elements such as Cr and Mo are 100 times faster than diffusion rate values in austenite [19]. The simple DSS specimen treated contained ferrite and austenite only but secondary phases did not appear, as shown in Figure 2 and Figure 3 (i). The substantial consequences of heat treatment on microstructural morphology and distribution of phases is observed in the present investigation. Likewise, to justify the effects of the heat treatment on the constituent phase's morphology, specimens are characterized by the SEM. SEM micrographs of the specimen are shown in Figure 3 (i-iii), from these figures it can be clearly observed that the darker region represents the ferrite phase and the brighter region represents the austenite phase with differences in microstructure with the temperature of treatment. The heat treatment has an effect on the volume fraction of ferrite and austenite and on the size of its grains. The volume fraction of the ferrite phase increased with increasing aging temperature and the aging time directly affected the volumetric concentrations of the ferrite and austenite phases. The other effect of the heat treatment that appeared with the increase in the aging temperature is the increase in the size of the ferrite grains. The EDS analysis of the specimen is also carried out to analyze the % contribution of alloying elements in the material. Table 3 shows the analysis of specimens with % of composition of ferrite and austenite. The chemical composition of each phase does not vary much with the composition of the base alloys where it is shown that the ferrite phase is rich in chromium and molybdenum with regard to nickel, while the austenite phase enriches in nickel.
and content chromium and molybdenum lower than the ferrite phase. Moreover, Figure 6-8 shows the % distribution of alloying element in simple DSS 2205, 880°C DSS 2205 and 1080°C DSS 2205. Where, the % composition of Ni and Cr in the ferrite and austenite can be seen clearly. Ferrite phases are richer in Cr and Mo with veneration to Ni, while austenite phase enhanced in Ni with Cr and Mo lower than the ferrite.

Table 3. EDS analysis of specimens with % of composition of ferrite and austenite

| Specimen details | Phases Identified | Cr Avg. % | Ni Avg. % | Mn Avg. % | Mo Avg. % | Fe Avg. % |
|------------------|-------------------|-----------|-----------|-----------|-----------|-----------|
| Simple DSS       | Ferrite           | 22.83     | 3.25      | 0.82      | 5.21      | Balance   |
|                  | Austenite         | 15.26     | 5.51      | 0.6       | 3.22      | Balance   |
| 880 (°C)         | Ferrite           | 21.17     | 3.42      | 0.68      | 5.65      | Balance   |
|                  | Austenite         | 19.07     | 5.49      | 0.66      | 3.28      | Balance   |
| 1080 (°C)        | Ferrite           | 20.17     | 3.64      | 0.6       | 5.33      | Balance   |
|                  | Austenite         | 19.64     | 5.53      | 0.5       | 3.78      | Balance   |

Figure 6. % Distribution of alloying element in simple DSS 2205

Figure 7. % Distribution of alloying element in heat treated at 880°C DSS 2205

Figure 8. % Distribution of alloying element in heat treated at 1080°C DSS 2205
The ferrite / austenite ratio in which corrosion occurs preferentially in the ferrite phase of DSS affects the corrosion resistance of the steel. The austenitic phase has superior corrosion resistance compared to ferrite phase for a variety of reasons, including higher nickel content than ferrite, and in general, Cr improves the resistance of DSS to local corrosion in the existence of ferrite phase. Among the most effective elements maximum amount of Cr plays vital role in improving resistance of steel against corrosion.

However, the main alloying element in the austenitic phase is Ni, whereas in the ferrite phase it is Cr. The ferrite phase is active electrochemically than austenite phase, whereas the probability of Cr to act as an anode is more. Though, the corrosion prospective of Ni is higher than that of Cr which concludes that the main responsible element for the improving the corrosion resistance is % of Ni in the phase. Also in austenite, higher solubility of N than ferrite is observed due to maximum availability of Mn % which enhances the corrosion resistance of austenite. Also this can be evidences from Figure 6 and Figure 7, which shows potentiodynamic polarization curves of specimens for simple 2205 DSS, heat treated at 1080°C and 880°C in artificial sea water. The results show that the best ferrite/austenite ratio for the studied specimens is obtained after treated the specimen at 1080°C. This specimen shows minimum current density compared to other specimen as shown in Table 2 and lower corrosion rate showing highest corrosion resistance.

6. Conclusions
In the present investigations an attempt has been made to investigate the behaviour of DSS 2205 under the action of corrosive media. Also, the effect of heat treatment on the microstructure and corrosion resistance has been evaluated. From the investigation it can be clearly seen that simple DSS can be protected from corrosion if treated well. Looking towards the various industrial applications of DSS 2205 this research is important for the development in materials and methodologies applied for the various steels. It is envisaged from the current analysis that the heat treatment changes the morphology of the material as well as microstructure of the steels. Not only the microstructure but also the chemical composition of the steel in phases such as austenite and ferrite changes due to heat treatment which ultimately improves the corrosion resistance of the steel. Following are the major conclusions drawn from present research.

1. The change in microstructure, due to heat treatment and secondary phase precipitation, shows a significant part in the corrosion performance of the DSS 2205.
2. Precipitation of secondary parts in DSS led to a drastic reduction in its corrosion resistance.
3. Another factor which is responsible for the change in the ferrite/austenite ratio where the corrosion occurred preferentially in the ferrite phase of DSS 2205.
4. The austenite phase shows better corrosion resistance than the ferrite phase due to maximum Ni content than ferrite.
5. Cr is the most active element in the passive film to develop the resistance of DSS 2205 to localized corrosion.
6. The heat treatment about 1080°C to DSS 2205 improves the corrosion resistance of steel comparatively.

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