On the Corrosion behavior of 4A and 5A cast duplex stainless steel under different heat treatment conditions

E Edward Anand¹, C Gopi², N Moorthy³, J Prince Richard⁴

¹, ², ³ & ⁴ Department of Science & Humanities, E.G.S. Pillay Engineering College, Nagapattinam, India

E-mail: alphsedward@gmail.com

Abstract. In this analysis, corrosion efficiency and mechanical properties of duplex stainless steel castings (DSS-4A and DSS-5A) were compared to their wrought counterparts. Cast duplex stainless steel DSS-4A and DSS-5A are characterized in two separate solution treated settings, while their wrought counterparts are characterized in both solution treated and forged form. Optical microscopy and X-ray diffractometry were employed to perform the metallurgical characterization. Electrochemical techniques such as Tafel extrapolation and electrochemical impedance spectroscopy were used to investigate corrosion activity. An electrochemical workstation was used to perform the corrosion studies. To compare the stability and changes in corrosion properties of both grades, an ASTM standard B117 salt spray test was performed in a 3.5 percent NaCl medium. Without any intermetallic phases, the XRD showed austenite and ferrite phases. The elements were partitioned further into the phases that they promoted, according to the elemental study of the phases. The ultimate tensile strength and hardness values of DSS-5A are higher than those of DSS-4A. DSS-5A had a higher corrosion resistance than DSS-4A. When comparing the two media used (H₂SO₄ and NaCl), DSS-5A demonstrated superior corrosion resistance.

Keywords: Aluminium – DSS, EIS, XRD, Corrosion, EDS

1. INTRODUCTION

Owing to their improved pitting and stress corrosion cracking resistance, duplex stainless steels (DSS) are being specified for chloride-containing environments. They outperform austenitic stainless steels in terms of corrosion resistance. Duplex stainless steels have better strength properties and come in a variety of wrought and cast forms. Duplex stainless steels (DSS) have two phases in almost equal proportions: ferrite and austenite. The arrangement of the two phases is highly dependent on their composition and thermal background. Because of its excellent mechanical and corrosion resistance, duplex stainless steel is used in the pharmaceutical, petrochemical, nuclear, marine, and paper industries¹,². It has a unique combination of properties, including high corrosion resistance in chloride-ion-rich settings, mechanical strength and ductility, abrasion resistance, and weldability³-⁵. Around 1937, the commercial development of duplex stain-free steels began⁶-⁸.
These alloys outperform austenitic stainless steel in terms of weldability and mechanical properties. Duplex stainless steel has twice the strength of normal austenitic or ferritic stainless steel. They are, however, more vulnerable to phase precipitation and embrittlement than austenitic steels. They have higher durability and ductility than ferritic grades, but not to the same extent as austenitic grades. Duplex stainless steels solidify from a liquid phase to a fully ferritic structure after melting. Around half of the ferritic grains turn to austenitic grains as the materials cool. Decomposition of the ferritic phase in the solution treated condition (at around 1000°C) can result in higher hardness, yield stress, and ultimate tensile strength, but at the cost of ductility and toughness.

Even though duplex stainless steels have become increasingly common in recent years, their availability in cast form has lagged behind that of the wrought form. Duplex stainless steel castings are widely used in pumps and valves in several applications, and they are critical components in systems where unexpected service failures can cause major operational problems and costs.

The quality of the performance is crucial. Variability and insufficient performance characteristics of duplex stainless steels in all types, which can be linked to severe in-service issues, are therefore a source of concern. It is also important to have readily available, appropriate methods and procedures for determining performance characteristics of duplex stainless steel cast materials before the operation.

In this analysis, corrosion performance and mechanical properties of selected grades of duplex stainless steel castings (4A and 5A) were assessed. Since there is little literature on the topic, this article aims to compare the performance of cast versus forged DSS. The effect of composition and microstructure on the corrosion behaviour of the samples in 3.5% NaCl and 1.0 N sulphuric acid is discussed in this article.

2. EXPERIMENTAL PROCEDURE
The research was done on cast duplex stainless steel alloys of Grade 4A and 5A. For comparison, forged DSS 4A and 5A samples were used. Tables 1 and 2 show the chemical compositions and pitting resistance equivalent (PRE) numbers of the cast 4A and 5A samples.

| Elements | C% | Mn% | Si% | P% | S% | Cu% | Ni% | Cr% | Mo% | V% |
|----------|----|-----|-----|----|----|-----|-----|-----|-----|----|
| Weight % | 0.026 | 1.02 | 1.12 | 0.022 | 0.006 | 0.03 | 63.3 | 23.12 | 2.92 | 0.064 |
| Elements | W% | Nb% | N% | Al% | Ti% | Sn% | Pb% | B% | Sb% | As% |
| Weight % | 0.016 | 0.004 | 0.190 | 0.007 | 0.020 | 0.004 | 0.002 | 0.003 | 0.004 | 0.014 |
| Elements | Bi% | Ta% | Ca% | Se% | Co% | Fe% | PRE* |
| Weight % | 0.001 | 0.010 | 0.001 | 0.124 | 0.035 | 64.90 | 35.796 |

Table 2: Chemical composition of Cast 5A (obtained from Spectro analysis)

| Elements | C% | Mn% | Si% | P% | S% | Cu% | Ni% | Cr% | Mo% | V% |
|----------|----|-----|-----|----|----|-----|-----|-----|-----|----|
| Weight % | 0.028 | 0.77 | 0.860 | 0.023 | 0.002 | 0.13 | 7.25 | 25.30 | 4.08 | 0.047 |
| Elements | W% | Nb% | N% | Al% | Ti% | Sn% | Pb% | B% | Sb% | As% |
| Weight % | 0.028 | 0.004 | 0.145 | 0.006 | 0.014 | 0.005 | 0.002 | 0.003 | 0.002 | 0.020 |
| Elements | Bi% | Ta% | Ca% | Se% | Co% | Fe% | PRE* |
| Weight % | 0.001 | 0.010 | 0.001 | 0.104 | 0.073 | 61.10 | 41.084 |

3. MATERIALS AND METHODS

3.1 Melting and Casting
An induction melting furnace was used to melt and cast Duplex stainless steel. The constituent elements were charged in the crucible after being washed with acetone. When all of the elements have melted completely, the melt is poured into the die.
3.2 Hot forging
Cast samples were heated to 1100°C in an oil-fired furnace with a 100 kg capacity and two HP blowers. Three thermocouples are lined with fire brick and fire clay on the three sidewalls. In the pneumatic press, the heated samples were taken one by one and subjected to upset forging. Solution treatment was carried out after hot welding to a reduction of 32 percent.

3.3 Heat treatment
Two different types of heat treatments are applied to the samples. 1) Solution treatment at 1010°C for 1 hour, followed by water quenching; 2) Solution treatment at 1130°C for 1 hour, followed by water quenching.

3.4 Microstructural Analysis
The microstructure of samples is examined using a high-resolution LEICA DM2500M DIC microscope. Optical metallography was performed on samples that had been manually cut out. The specimen was polished using traditional metallographic techniques, which included belt grinding and polishing with emery papers of grades 600, 800, 1000, 1200, 1500, and 2000. Finally, with a legated alumina abrasive on a polishing wheel to achieve a mirror finish. Before testing, the polished specimen was cleaned with double distilled water, degreased with acetone, and dried. Keller's reagent was used to etch the specimen to expose the microstructure.

3.5 X-ray Diffraction Analysis
Rigaku Ultima III XRD equipment was used for the X-ray diffraction study. Cu K radiation with a wavelength of 1.54 Åwas used in the study, with a step size of 0.05 between the values of 20° and 100°.

3.6 Corrosion Test
Corrosion tests are carried out in two types of medium. 1) In 3.5 % NaCl and 2) 1.0 N H₂SO₄.

3.6.1 Electrochemical Measurements. Gill AC ACM instrument is used to perform electrochemical measurements. With a platinum counter electrode and a saturated calomel electrode (SCE) as a reference, a three-electrode compartment with a pyrex glass cell was used. The SCE is referred to for all possible values mentioned. The working electrode was a specimen of Duplex Steel alloy. Polarization experiments are carried out on the same exposed electrode surface as the electrochemical impedance spectroscopy (EIS) experiments, with no additional surface treatment.

3.6.2 Potentiodynamic Polarization Studies. The corrosion media were exposed to a well-polished Duplex Stainless Steel specimen coupon, which was allowed to create a steady-state open circuit potential (OCP). At a scan rate of 1 mVs–1, the Tafel plots were recorded by polarising the specimen to 250 mV cathodically and +2000 mV anodically relative to the OCP.

3.6.3 Electrochemical Impedance Spectroscopy (EIS) Studies. The application of a periodic small amplitude (10 mV) ac voltage signal with a broad frequency range ranging from 100 kHz to 0.01 Hz was used to calculate impedance at the open circuit potential (OCP). Nyquist plots were used to analyze the impedance data.

3.7 Salt Spray Test
In a chamber temperature of 35°C, test specimens are put in an enclosed chamber and exposed to a continuous indirect spray of salt water (3.5 % NaCl) solution (also known as fog or mist) that falls-out on the specimen at a rate of 1.0 to 2.0 ml/80cm²/hour. The chamber environment is held at a constant steady-state temperature. The duration of the test is variable, and it is carried out in compliance with the ASTM B1117 standard.
4. RESULTS
4.1 Microstructural analysis

Figures 1a - 1d display the microstructures of the as-cast 4A and 5A after solutionizing treatments. Delta ferrite, austenite, and sigma are the three major phases shown by the microstructures. Secondary austenite is more visible when solutionizing at 1010°C. In DSS-4A, solutionizing at 1130°C shows less secondary austenite and the sigma phase is absent. However, austenite is found within the ferrite in the case of DSS-5A, and the sigma phase is also present.

Figure 1a: Microstructure of DSS-4A after Solutionizing at 1010°C

Figure 1b: Microstructure of DSS-5A after Solutionizing at 1010°C
Figure 1c: Microstructure of DSS-4A after Solutionizing at 1030°C

Figure 1d: Microstructure of DSS-5A after Solutionizing at 1030°C

4.2 X-ray analysis

The XRD patterns of as-cast DSS-4A and DSS-5A solutions treated in 1010°C and 1030°C are shown in Figure 2(a-d). The peaks corresponding to austenite and ferrite can be seen in the X-ray diffraction patterns of duplex stainless steel samples. Ferrite and austenite make up the sequence in the DSS-4A and DSS-5A samples. The peak corresponding to ferrite has the highest peak strength in both 4A and 5A. In the case of a solutionizing temperature of 1130°C, the peak density of ferrite increases more than that of austenite.
Figure 2a: XRD pattern of as-cast DSS - 4A solutionized at 1010°C

Figure 2b: XRD pattern of as-cast DSS - 5A solutionized at 1010°C
4.3 Potentiodynamic Polarization Measurements

Figures 3a-b display potentiodynamic polarization curves for 4A and 5A in 3.5% NaCl solution and 1.0N H2SO4. The polarisation curves for the two specimens are identical, implying similar corrosion mechanisms. Only at cathodic branches of polarisation curves did the linear Tafel actions appear, which are thought to reflect cathodic hydrogen evolution through water reduction.
Since the anodic polarisation curves did not show Tafel activity, they are thought to reflect anodic oxidation. The chemical composition of samples has a major impact on corrosion properties, as shown by a comparison of polarization curves. DSS-4A and DSS-5A have identical potentiodynamic curves for as-cast duplex stainless steels. There were active dissolutions found in the samples. DSS-5A had a higher corrosion potential at first. However, after 120 hours of accelerated corrosion, the corrosion potential values of both specimens are virtually identical. The polarisation curves for both samples initially showed strong passivation, but after 120 hours, no passivation is visible. Both samples have pitting potentials greater than 0.8 V vs SCE. Pseudo-passivity can be seen in the graphs. Because the corrosion potential is a mixed potential in which the absolute values of the anodic and cathodic currents are identical, and because the cathodic phase corresponds to hydrogen evolution, the corrosion potential is expected to reflect the samples' corrosive propensity. The amount of chromium and molybdenum in the material determined how resistant it was to pitting attacks. The corrosion resistance was unchanged by the volume fraction. All of the steels used in the study were duplex, with austenite to ferrite ratio of 70:30, which is appropriate.

![Figure 3a: Polarization curves for 4A & 5A in 3.5% NaCl](image-url)
Figure 3b: Polarization curves for 4A and 5A in 1.0N H$_2$SO$_4$

Figure 3c: Nyquist plots for 4A & 5A in 1.0N H$_2$SO$_4$
Table 3. EIS parameters obtained from Nyquist plots for 4A & 5A

| Parameter  | 4A          | 5A          |
|------------|-------------|-------------|
| $R_{\text{sol}}$ (ohm.cm$^2$) | 1.839       | 1.839       |
| $R_{\text{ct}}$ (ohm.cm$^2$)   | $3.721 \times 10^4$ | $5.983 \times 10^4$ |
| $C_{\text{dl}}$ (F)        | $5.172 \times 10^{-5}$ | $9.332 \times 10^{-5}$ |

4.4 Electrochemical Impedance measurements
In 1.0N H$_2$SO$_4$ solution, electrochemical impedance spectra for 4A and 5A were calculated at the open circuit potential. Figure 3c shows the obtained impedance response as a Nyquist plot, and table 3 shows the parameters extracted from it. Both 4A and 5A have three impedance characteristics in common: a single semi-circle with a real axis intercept that is: at high frequencies, the solution resistance; at low frequencies, the charge transfer resistance.

4.5 Salt Spray Test
According to ASTM specifications, both samples 4A and 5A passed the salt spray inspection. Figures 4a and 4b represent the samples before and after the test. After 120 hours of exposure to 3.5 percent NaCl at a chamber temperature of 35.6°C and an air saturator temperature of 45°C, no weight loss was reported.

The sample is checked for PDP after the salt spray test on the same surface to see if any surface changes have occurred, and the polarization curve is shown in figure 4c. The corrosion resistance of DSS-4A is found to be lower after a 120-hour salt spray test. The corrosion potentials are nearly similar, and both samples have shown pseudo passivation. Passivation is slightly more in the case of DSS – 5A.
5. CONCLUSIONS
1. When solutionizing at 1010°C, cast DSS 5A is more corrosion resistant.
2. Corrosion activity in 4A and 5A is similar, and pitting potential is virtually identical in both samples.
3. DSS-5A has low corrosion resistance when solutionized at 1130°C, indicating more sigma phase.
4. DSS-5A’s supremacy is confirmed by salt spray samples. Both the 4A and 5A steels exhibit equal corrosion resistance in a 3.5 percent NaCl solution when hot forged.

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