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STRESS CORROSION RESISTANCE CAPACITY: AUSTEMPERED DUCTILE IRON AND HIGH STRENGTH ALLOY STEELS IN MARINE ENVIRONMENT

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Abstract: This paper presents the experimental study of Austempered Ductile Iron (ADI) and high strength alloy steels, mainly 316 Austenitic Stainless Steel (ASS), an established corrosion resistant material. The success of this work will increase the available options of material selections for structural engineers for application in marine industries. The experiment was carried out with ASTM A536 grade ductile iron, which was produced using a high frequency dual track induction furnace of 2500kg, followed by subjecting the ductile iron samples to a specific parameter of heat treatment – Austenitizing (930^{o}C for 140 minutes) and austempering (370^{o}C for 10 minutes) in potassium nitrate salt bath to give ADI. Stress corrosion cracking (SCC) characteristics of the ADI and the standard 316 ASS specimens were evaluated in marine environment for 15 and 30 days respectively at constant strain rate of 5mm/min at room temperature. The stress-strain characteristics of exposed and unexposed specimens were compared and parameters such as yield stress, ultimate tensile strength, elongation and fracture strength were used as benchmark to assess SCC susceptibility. The study reveals that ductile iron properties (mechanical) were significantly improved after heat treatment, elongation increased by 27.04% and tensile strength by 58.62%. SCC test results show loss of elongation in the range of 23.20 – 26.48% for ADI in 15 and 30 days exposure. In contrast, 316 ASS retains most of its ductility. Both alloys retain their tensile strength in 15 days, however, there was decrease in the tensile strength of ADI by 5.93% as compared to 4.40% for 316 ASS in 30 days exposure. The fracture stress for ADI nevertheless occurred at 611.35MPa higher than 394.25MPa for 316 ASS. This indicates that ADI is significantly more resistant to SCC by providing better protection under overload condition in marine environment.
Keywords: A536 Grade Ductile Iron, Austempered Ductile Iron, 316 Austenitic Stainless Steel, Stress Corrosion Cracking, Tensile Strength, Elongation, fracture strength, Metallography

1. INTRODUCTION

Austempered Ductile Iron castings or commonly called ADI castings, is produced by heat treating ductile iron to a temperature to produce austenite. The ductile iron is held at the selected austempering temperature until a microstructure known as ausferrite is developed. ADI is a unique material which possesses excellent combination of high strength, toughness, higher ductility, fatigue strength and wear resistance compared to standard grades of ductile iron meeting and often exceeding those of alloy steels. Typical uses are in automobile, agricultural, architecture, and mining industries. The effect of water and various automotive fluids such as mineral oil, motor oil, gear oil, brake fluids, power steering fluid and diesel fluid on the tensile properties of various low and high strength grades of ductile iron has been recently reported. The embrittlement characteristics of fracture toughness of several ductile iron samples with various kinds of matrix by contact with water has also previously been reported. The various ductile iron grades investigated for environmentally assisted embrittlement by various authors with a particular emphasis on austempered ductile iron has also been investigated.

High strength alloy steels such as austenitic stainless steels, duplex stainless steels, copper-nickel (18% nickel and 5% manganese) to mention but a few are developed primarily for high strength applications and better resistance to sea water. Austenitic stainless steel mainly 316 an established Corrosion resistant material was used as reference for this study. This grade of steel is widely used in highly corrosive environments, particularly in salt water. It is more corrosive resistant than type 304 due to added molybdenum. It is often iron based, low carbon stainless steel with alloying elements to promote corrosion resistance, stabilize the austenitic phase, and maintain adequate strength and ductility. Its importance in industrial applications and development cannot be overemphasis. Its excellent properties which range from high tensile strength, good impact, corrosion and wear resistance have found various applications in many industries. This material is used in almost all environments that requires an optimization of these properties, some of which are transportation equipment including aircrafts and railways, household items, marine hardware, chemical processing equipment, architectural applications, gas and oil production to mention but a few. The mechanical, metallurgical and electrochemical properties of the two types of stainless steels, austenitic stainless steel UNSS316603 and super duplex stainless steel UNSS32750 suggested by pumps manufacturer for evaluation to substitute Ni resist iron in manufacturing pump casing has been investigated. The comparative stress corrosion cracking and general corrosion resistance of Annealed and Hardened 440C stainless steel has also been studied.

Marine environment also known as sea water is h complex electrolitic solution which has contributed to the corrosion of ocean oil rigs, water transport vessels (i.e. ship), tools, chemical, plants and pumps in desalination plants to mention but a few. It is a complex solution because it contains about 92 different chemicals elements with high salt concentration mainly sodium chloride.

Stress corrosion cracking (SCC) is defined as a phenomenon by which ductile metals and alloys fail in a brittle manner through the initiation and propagation of cracks resulting from the combined action of sustained tensile stress (applied and/or residual) in a specific corrosive environment. The chemical environment causing SCC does not produce chemical corrosion of alloy and the species causing SCC need not be present in large concentration. It is widely believed that electrochemical dissolution plays a major role in the crack initiation and propagation. There is a possibility of the adsorption of damaging ions that weaken the atomic bonding at the crack tip. If hydrogen is generated as a result of corrosive species, it is then able to enter the metal, diffuse to the crack tip and cause crack propagation.

Most components and structures used in marine applications are made out of austenitic stainless steels and other high strength alloy steels. The rotating parts of brine circulation pumps (BCP) in desalination plants such as the shaft and impeller are examples of products made out of the above mentioned steels. These materials most especially the austenitic stainless steels have been reported to be highly susceptible to SCC.

Austempered Ductile Iron (ADI) having combination of exceptional strength and toughness, meeting an often exceeding those of alloyed steel may even be less susceptible to SCC than the austenitic stainless steel in marine environment. Hence the need to carry out an SCC evaluation of the two materials. In this work, we compare the SCC resistance of ADI and 316ASS as a measure of the suitability or otherwise of ADI for marine environment applications with reference to 316 ASS, an established corrosion resistant material. It is also to rate the SCC susceptibility of ADI and provides data that may be used by engineers and scientists in practical applications. Both alloys were studied principally by exposures to the aggressive sea water medium.

2. EXPERIMENTAL PROCEDURE

The ASTM A536 grade ductile iron was produced at the Nigeria Machine Tools (NMT), Oshogbo Nigeria. The metal was melted in 2.5 tons high frequency dual track induction furnace. Table 6 shows the summary of charged materials used for the iron production. Graphite and CRCA steel scraps were weighed and charged into the furnace and completely melted at 1550°C, slags were removed from the melt. Table 1 and 2 shows the composition of the graphite and CRCA steel scraps used for the investigation. Ferrosilicon 75% silicon grade was added as in the charge make up. A sample was taken for a chemical composition analysis using the optical emission spectrometry to ascertain the melt conformity as designated by ASTM A536 in Table 1. Two ladles were preheated such as the treatment and pouring ladle for about 40 minutes. The treatment ladle (1000kg) was taken to the treatment section which is closer to the moudling floor while the pouring ladle was taken to the furnace to tap out 600kg molten metal. The spheroidizing treatment was carried out with ferrosilicon magnesium alloy (analysis shown in Table 3) of 13kg using the sandwich method and it involves covering the alloy in a portion of the preheated treatment ladle with some mild steel fillings while the 600kg molten metal is poured unto the ladle and the reaction took place. Molten metal was inoculated with additional 3kg grounded ferrosilicon and then poured into an already prepared Y – block green sand mould (Fig. 1) using sand recipe mixed in a 500kg capacity sand mixer in accordance to ASTM A536. From the time the molten metal touches the ferrosilicon magnesium inside the treatment ladle until the end of casting into mould must be done within 7 minutes that is, after 7 minutes, the melt gradually returns to a grey cast iron.

The molten metal obtained was measured using the optical Pyrometer. The tapping temperature of the melts is within 1530°C to 1550°C while the pouring temperature obtained ranges from 1470°C to 1490°C. The casting was allowed to cool to room temperature before been removed out of mould, the Spectroanalysis of the ductile cast iron is shown in Table 7. From these Y – block castings, tensile specimens having 50mm total length, 19mm gauge length and 3mm gauge diameter were prepared.

The austempering was carried out at the foundry shop of National Metallurgical Development Centre (NMDC) Jos, Plateau State, Nigeria. The samples were charged into the 2804 Bremen Naberindustrieofenbau tubular heat treatment furnace and set to the austenitizing temperature 930°C for 140 minutes and autempering 370°C for 10 minutes in a potassium nitrate salt bath which was set up and positioned close to the furnace. After final heat treatment, ADI and 316 ASS having same dimensions were tensile tested in dry and wet condition. Figures 2a and 2b presents the ADI and 316 ASS samples, while Figures 3a and 3b shows SCC test preparation and fractured samples after the experiment. The tested dry condition specimens serve as a control, while in the wet condition both alloys were exposed to the aggressive sea water medium (unstressed) for 15 and 30 days respectively under ambient conditions of laboratory atmosphere. Subsequent tension testing was carried out to evaluate the materials resistance to SCC using a Universal Testing Machine (Instron – series 3369) according to ASTM E8/E8M – 09. Experimental techniques such as tensile test with constant strain rate (5mm/min), loading the sample uniaxially till fracture was adopted in the experimental process. Parameters such as yield strength, ultimate tensile strength, elongation to failure and fracture strength were used as benchmark to analyze the SCC resistance of the materials.

Microstructure observations were carried out using Olympus GX 51 paxit metallurgical microscope on metallurgraphic specimens prepared using conventional grinding and polishing. For etching, Nital solution (2% nitric acid in 98% water) was used for the ADI, while acid solution of the following composition 10ml HNO_3, 10ml acetic acid, 15mlHCL and 2 – 5 drops of glycerin was used for the 316 ASS to reveal microstructure.

Table 1: Composition of CRCA Steel Scraps used for the Production of the Ductile Cast Iron by weight %

Carbon	Sulphur	Phosphorus	Manganese
0.05	Max 0.03	Max 0.03	0.3

Table 2: The Composition of Graphite used

Carbon %	Ash %	Volatiles %	Sulphur %	Moisture %
69	30	<0.5	0.27	0.10

Table 3: Analysis of the Nodulizer, MgFeSi

Si%	Ca%	Mg%	RE%	Al%	Fe%
44.5	2.02	10%	0.8	<0.7	Bal.

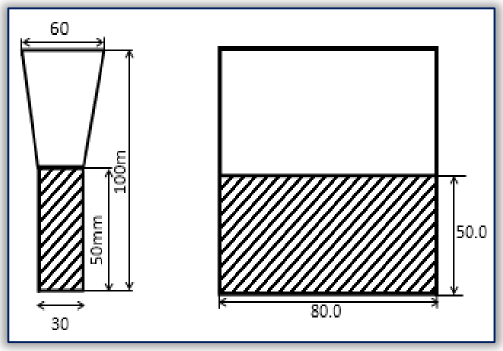

Figure 1: Y – block mould for the Ductile Iron Melts

Figure 2a: 316 ASS Sample

Figure 2b: ADI Sample

Figure 3a: SCC Test Preparation

Figure 3b: ADI Fractured Sample

3. CHARGE CALCULATION

The furnace was charged with metallic materials to give base iron with the following composition shown in table 4. The charge consisted of CRCA steel scraps, graphite and ferrosilicon. Spectrometric determination of the composition is given above.

Table 4: Permissible Range of Ductile Cast Iron Composition as per the ASTM A536-77 [65-45-12]

Grade	C	Si	Mn	S	P	Mg
ASTM A 536- 77 (65-45-12)	3.40 – 3.85	2.30 – 3.10	0.1 – 0.3	Max 0.03	Max 0.04	0.015 – 0.05

Table 5: Charge Calculation for 2.5 Metric Tons Metals

Charge material	Charge Mass kg	Carbon % / kg	Silicon % / kg	Manganese % / kg
CRCA steel scraps	2325	0.05 / 1.1625	- / -	0.30 / 6.975
Graphite	129.84	69 / 89.7	- / -	- / -
(FeSi)	45.16	- / -	75 / 33.75	- / -
Total	2500	- / 90.8625	- / 33.75	- / 6.975
Charge %		$\left(\frac{90.8625}{2500} \times 100 = 3.6345\right)$	1.35	0.279

Silicon content increased during the batch treatment of 600 kg melt (weight of ladle). Si in FeSiMg is 44.5%, the weight of FeSiMg being 13 kg. Thus % Si is 44.5 x 13kg = 0.964%, in 600 kg. Having in view that the total Si after treatment = 0.964

+ 1.35 = 2.314%, 3kg Ferrosilicon (FeSi75) was used for inoculation which is required to give 75% x 3kg FeSi = 0.32% Si, in 613 kg. Therefore gross % of Si in melt is (0.32 + 2.314)% = 2.634%

4. RESULTS

— Test Materials

The chemical composition of the ADI and 316 ASS is presented in table 7 and 8 below.

Table 6: Summary of Charge Materials

Charged materials	Quantity (kg)
CRCA steel scraps	2,325
Graphite	129.84
FeSi in furnace charge	45.16
Nodulizer (MgFeSi)	13
FeSi used as inoculants	3
TOTAL	2,516

Table 7: Chemical composition in Percentage of the DCI in relation to permissible range of composition as per the ASTM A536 – 77

Grade	C	Si	Mn	S	P	Mg	Mo	Al	Cu	Ti	Nb	Fe
ASTM A536 – 77(65-45-12)	3.40-3.85	2.30-3.10	0.1- 0.3	Max. 0.03	Max. 0.04	0.015 – 0.05	-	-	-	-	-	-
Sample Composition	3.65	2.04	0.096	0.006	0.015	0.028	0.026	0.013	0.077	0.023	0.01	Bal.

Table 8: Chemical composition in Percentage of the As-received 316 Austenitic Stainless Steel in relation to the permissible range of composition as per the SAE and ASTM UNS

Material	C	Cr	Ni	Mo	Mn	P	S	Si	Cu	Mg	Va	Ti	Al	Nb	Fe
UNS S31600	0.10 Max	16–18	10- 14	2 - 3	-	-	-	-	-	-	-	-	-	-	-
As-Received 316 ASS	0.082	18.83	11.95	2.45	1.94	0.005	0.002	0.752	0.201	0.073	0.234	0.001	0.001	0.323	Bal.

— Structural Investigation Metallography

Figures 4a and 4c illustrate typical microstructure of ASTMA536 grade DCI and the 316 ASS while 4b presents the microstructure of the ADI after 10 minutes austempering at 379°C.

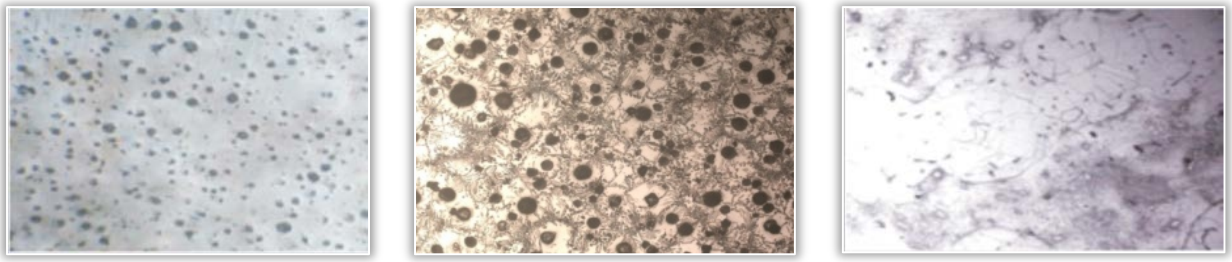

Figure 4: a. Microstructure of the DCI; b. Microstructure of the ADI (X400) ASS (X400); c. Microstructure of the 316 (X200)

— Test Environment

The chemical composition of the sea water in mg/L in relation to the International Council for the Exploration of the Sea (ICES) is shown in Table 9 below. The relationship between the parameters and the standard is represented in the Chart (Figure 5). Calcium (Ca) and Potassium (K) shows very significant distance from the standard values, all other parameters (I believe) conform with the standard values.

Table 9: Chemical Composition of the Sea Water (Mg/L)

Environment PH	Ca	Mg	Na	K	Cl^-	SO_4^{2-}
Sea Water – 7.2)	4.51 ± 0013	1.27 ± 0.0013	6.475 ± 0.0020	3.96 ± 0.005	18.20	2.68
ICES (STANDARD)	0.409	1.30	10.77	0.338	19.37	2.71

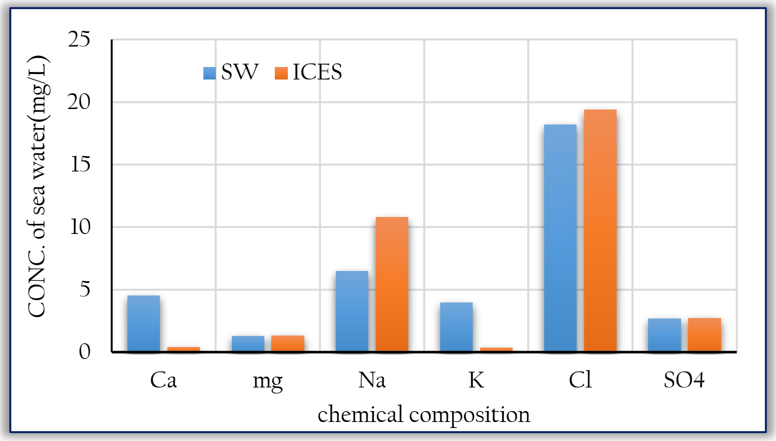

Figure 5: Chart Showing the Relationship between the Values and ICES Standards

— Mechanical Testing

Stress-Strain Curves of Unexposed Materials

The results of the flow curves (stress-strain) obtained from the tension test conducted on the dry specimens – DCI, ADI and ASS are shown in figures 6a, b and c below Table 10 presents the percentage increase in tensile properties for the ADI, while Table 11 show the mechanical properties of the 316 ASS.

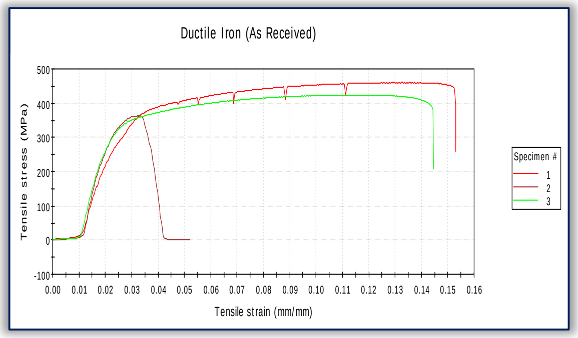

Figure 6a: Stress Strain Curve for DCI

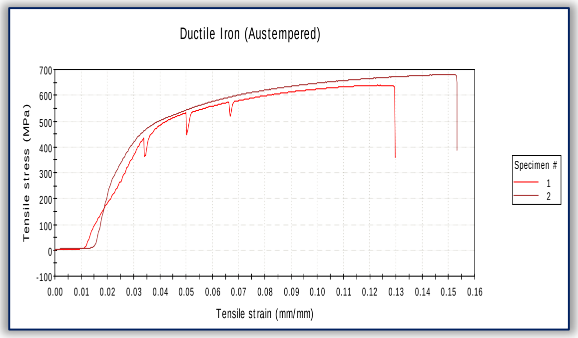

Figure 6b: Stress- Strain curve for ADI

Table 10: Percentage Increase in Tensile Properties for the ADI

Sample/Property	UTS (MPa)	Yield Stress (MPa)	Elongation (%)
Ductile Cast Iron	415.98	363.12	11.65
Austempered Ductile Iron	659.84	478.14	14.80
% Increase in Property	58.62	31.68	27.04

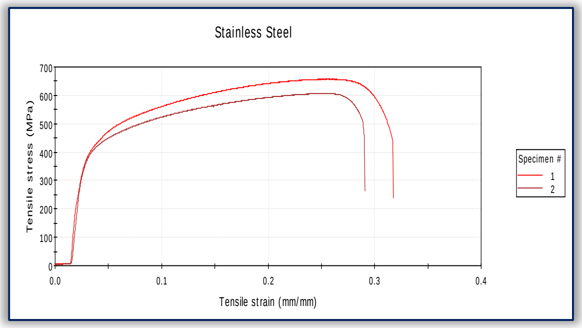

Figure 6c: Stress – Strain curve 316 ASS

Table 11: Mechanical Properties of the 316 ASS in Relation to the Permissible Property as per ASTM A240/A240M

Material	UTS (MPa)	Yield Stress (MPa)	Elongation (%)
ASTM A240/A240M	515 (Mini)	205 (Mini)	40
As Received 316 ASS	632.22	435.14	30.39

Stress – Strain Curves of Exposed Materials

The data on the ADI and 316 ASS in contact with sea water for 15 and 30 days respectively are presented in figures 7 and 8 below. The SCC test results and percentage decrease in properties on both materials are listed in table 12. Both materials are sensitive to the phenomenon by interaction with the sea water.

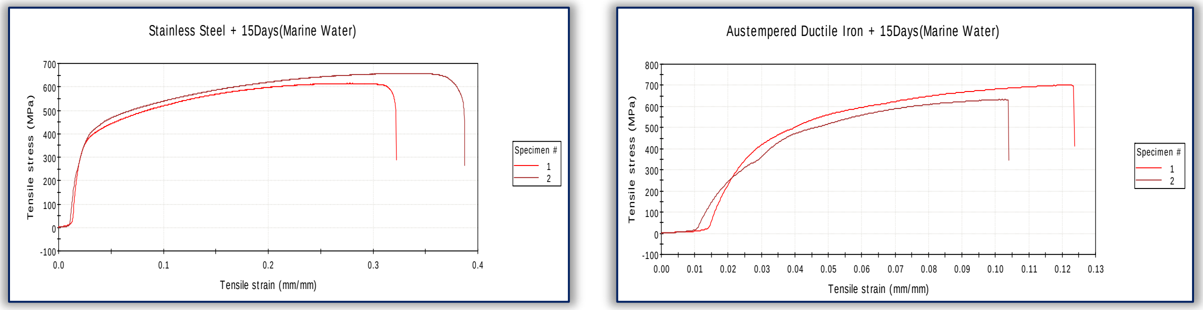

Figure 7: Comparison of Stress-Strain curves for ADI and 316 ASS subjected to 15 days SCC test in sea water.

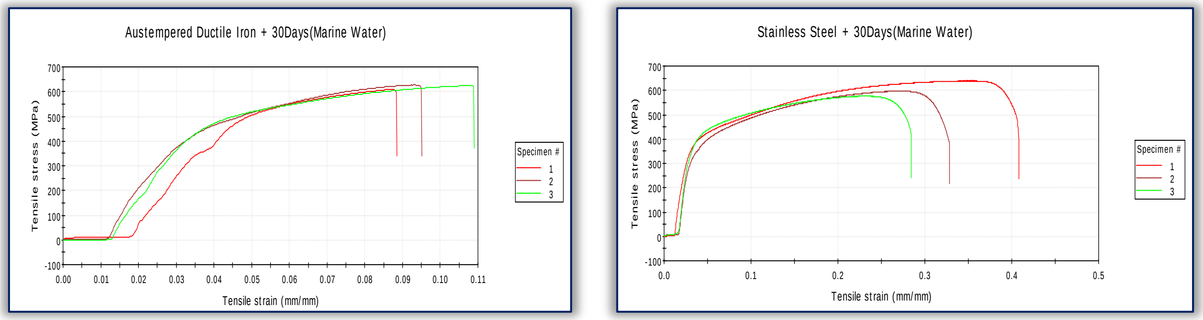

Figure 8: Comparison of Stress – Strain Curve for ADI and ASS subjected to 30days SCC test in sea water

Table 12: SCC test results and percentage decrease in properties on the ADI and 316ASS

Sample	Property	Initial (dry)	15 days (Wet)	% Decrease	30 Days (Wet)	% Decrease
ADI	UTS (MPa)	659.84	667.61	-1.18	620.69	5.93
	Yield Stress (MPa)	478.14	455.43	4.75	415.95	13.00
	Elongation (%)	14.80	11.36	23.20	10.88	26.48
316 ASS	UTS (MPa)	632.22	636.42	-0.66	604.38	4.40
	Yield Stress (MPa)	435.14	429.12	1.38	404.71	6.99
	Elongation (%)	30.40	36.38	-19.67	34.03	-11.94

5. DISCUSSIONS

In the austempering transformation as demonstrated by Kovac (1987), consists of full austenitization of the casting in the temperature range of 815 – 950°C followed by quenching to an intermediate (austempering temperature) range of 235 – 400°C to avoid formation of pearlite. It was evident in this work that the as-cast ductile iron was austenitized at 930°C for 140 minutes and the transformation was formed at the upper end austempering temperature (370°C for 10 minutes).
Typical microstructure of ADI as described by Polishetty (2011) consists of ferrite needles distributed in the autenite phase. According to Plate 4b on microstructure of the ADI, the structure over the whole cross-section consisted of fine feathery ferrite and graphite nodules distributed in the austenite phase. It is seen that, white background represents the austenite phase, dark feathery like structure constitute the ferrite and spherical nodules represent the graphite.
The Mechanical properties of the as cast ductile iron was significantly improved after the heat treatment as presented in Table 10. It is shown that tensile strength and ductility of the ADI is more enhanced. The elongation increased by 27.04% and tensile strength by 58.62%.
The SCC data of ADI and 316 ASS is presented in table 12. It is seen that, ADI is embrittled when in contact with sea water as compared to 316 ASS in 15 and 30 days SCC test.
Data for the ADI shows consistent decreased in elongation in the range of 14.80 – 10.88%. Such a decreased is believed to be due to the gradual depletion of the nodule counts caused by the hydrogen generation during corrosion reaction. On the other hand, 316 ASS retain its ductility. This has been clearly shown in the data reviewed by Gagne and Hayrynen on the environmental embrittlement of ductile iron, which reveals the embrittlement of ASTM A897/897M ADI grades 1 – 4 when tested in liquid (Grade 1, 11.2% dry and 3.4% wet, Grade 3, 8.3% dry and 4.0% wet)
Both alloys retains their tensile strength in 15 days exposure, however, there was decrease in tensile strength of ADI by 5.93% as compared to 4.40% for 316 ASS in 30 days. This loss indicates a possibility of the absorption of the environmental species that lowers inter-atomic bond strength.
The ADI failed in a brittle manner when in contact with sea water as shown in figure 5 and 6 respectively, while 316 ASS enjoys low yield prior to failure.
It is worth noting that the ADI is favoured by high fractured stress 611.35MPa as compared to 394.25MPa for 316 ASS. This indicates that the ADI is significantly more resistant to SCC than the 316 ASS by providing better protection under overload condition in sea water environment.

6. CONCLUSIONS

On the basis of the experimental results, the following conclusions can be proposed:
- Microstructure of the DCI consists of nodular graphite in ferritic – pearlitic matrix, while the ADI contains nodular graphite in a matrix of feathery ferrite and carbon enriched austenite called ausferrite and this explains its superiority in strength.
- The ADI has higher mechanical properties as compared to the conventional ASTM A536 DCI (65 – 45 – 12). ADI – yield strength 478MPa, UTS 660MPa and elongation 14.8%.
- The ADI lost its ductility while under SCC test, results to failure in a brittle manner. On the other hand, 316 ASS enjoys low yield after the ultimate load.
- The ADI has higher fracture stress (611.35MPa) as compared to 394.25MPa for 316 ASS.
- The ADI exhibit superior SCC resistance to 316 ASS in terms of load bearing application in sea water environment.
- Three factors have to be present to impact SCC
  - # presence of liquid in contact with the material
  - # applied tensile stress
  - # low strain rate.

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ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665