

Atmospheric Corrosion Studies of Ductile Iron and Austenitic Stainless Steel in an Extreme Marine Environment

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ABSTRACT

This paper presents the corrosion characteristics and the accompanying changes in the microstructure of unalloyed ductile iron (DI) and austenitic stainless steel (ASS) in table salt medium representing an upper limit in an extreme marine environment. The individual corrosion rates of DI and ASS was evaluated for the maximum time period of 1200 hr. Using the immersion test technique, the corrosion rate of DI was evaluated and found to be four-orders of magnitude greater than that of ASS. The corrosion product morphologies of the DI showed that the nodular matrix was gradually covered up as immersion time progressed while the corrosion channels and volume of pits that initially formed in ASS respectively deepened and increased with increased exposure time. This work is important as a reference point for the quantification of the corrosion effectiveness of alloying DI. The microstructures of the corroded samples showed corrosion initiation and gradual accumulation of corrosion products.

Keywords: Atmospheric Corrosion; Ductile Iron; Austenitic Stainless Steel; Sodium Chloride and Microstructure

1. Introduction

The importance of austenitic stainless steel (ASS) in industrial applications and development cannot be over-emphasized. Its excellent properties which range from high tensile strength, good impact, corrosion and wear resistances have found various applications in many industries. This material is used in almost all environments that require an optimization of these properties, some of which are low and high pressure boilers and vessels, fossil-fired power plant, flue gas desulphurization equipment, evaporator tubing, super heater reheating tubing and steam headers and pipes to mention but a few [1-3]. ASS is known for its corrosion resistance principally due to the presence of chromium which is soluble in the austenitic matrix. Chromium adds to the overall corrosion resistance through a passivation process by forming a complex spinel-type $\{(Fe,Ni)O(Fe,Cr)_2O_3\}$ passive film [4-6]. This produces a coherent, adherent insulating and regenerating chromium oxide protective film on the

metal surface. The corrosion behavior of 18/8 stainless steel and nickel-plated low carbon steel in cassava fluid has been investigated [7]. Very large amounts of carbon steels are generally used in marine applications, such as construction, nuclear and fossil fuel power plants, chemical processing, mining and transportation. Carbon steels are primarily affected by general corrosion and they are prone to deleterious corrosion by seawater [8,9].

Ductile Iron (DI) consists of graphite in the form of nodules or spheroids in a matrix of either ferrite or pearlite [10,11]. DI is not a single material but part of a group of materials which can be produced to have a wide range of properties through control of the microstructure. The common defining characteristic of this group of materials is the morphological dominance of the graphite structure. In DIs, the graphite is in the form of spherical nodules rather than flakes (as in grey iron), thus inhibiting the creation of cracks and providing the enhanced ductility that gives the alloy its name. The formation of nodules is achieved by addition of nodularizing elements into the melt especially magnesium and less often, cerium [12]. Yttrium has also been studied as a possible nodularizer

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[12]. In contrast, the effect of chloride salts on the mechanical properties of gray cast iron has been recently reported [13]. The high temperature corrosion of two ductile cast irons (Si-Mo and Ni-Resist Alloys) in synthetic diesel and gasoline exhaust gases has also previously been reported [14]. Cast iron deterioration with time in various aqueous salt solutions has also been studied [15].

Seawater is a complex electrolytic solution, which has contributed to the corrosion of ocean oilrigs, water transport vessels (*i.e.* ships), tools, chemical plants, etc. It is a complex solution because it contains about 92 different chemical elements, the most common of which is NaCl. The salinity of water is 35 part per thousand in which 35 parts of salt is found in 1000 parts of seawater [16].

Corrosion studies of metallic structures remain a major area of interest for scientific investigation. Recent effort in the study of mild steel and AISI 304L stainless steel in the presence of dissolved ions in seawater was recently reported [17] in which the Copper ions were found to have pronounced effect on corrosion rate.

In this work, we compare the corrosion rates of DI and ASS as a measure of the suitability or otherwise of ductile iron for marine environment applications with reference to ASS, an established corrosion resistant material. It is also to develop necessary experimental data to serve as a reference point for the corrosion of alloyed DIs, a major ongoing research program. The medium used in this work is a replica of extreme and “upper limit” “sea-side” conditions. This is to allow us generate the highest possible corrosion response of the metallic structures under investigation in this type of high chloride profile environment.

2. Materials and Method

The plain DI used for this research work was produced with a uniform, well-graded and clean scrap following

processing procedure already optimized at the Engineering Materials Development Institute, Akure, Nigeria with EMR-100 Rotary Furnace developed at the institute and already in commercial production. An effort in this direction has been used for smelting white cast-iron and low alloy cast-carbon steels [18]. The DI test specimens were fabricated by sand casting while the ASS is the classic 18/8 type referred to as “A2” in accordance to ISO 3506. The materials were spectrometrically analyzed with a XRF Spectrometer. With the spectrometer, analysis of up to 41 elements is obtainable within 2 minutes except for light elements such as Al, Mg and Si. The comparative composition by weight percent of the two materials under investigation is as given in **Table 1**.

The DI and ASS were cut into 20 mm × 20 mm × 10 mm and 20 mm × 20 mm × 1 mm coupons respectively (**Figures 1(a)** and **(b)**). The coupons surfaces polished to 600 grit, thoroughly washed under tap, swabbed with acetone and then dried. Subsequently, the initial weight of the coupons was measured on a metler balance to 0.001 g accuracy. Each coupon was weighed and the dimensions carefully taken and recorded before exposure to the test media for a period of 1200 hr. Ten coupons each of both materials was fully immersed in table salt placed in separate containers. On the completion of each exposure test, the coupons were cleaned with wire brush, rinsed under tap and air dried prior to second weighing of samples to determine weight losses due to corrosion. This procedure is in consonance with ASTM G1-90 [19]. The corrosion rate of each coupon was calculated and the coupon examined under a software-driven optical microscope.

A small piece was cut from each coupon before the corrosion test to serve as a control specimen. It was mounted and mechanically ground progressively on grades of SiC impregnated emery paper (120 - 1200 grits) with water as the coolant. The ground coupon was then

Table 1. Comparative chemical composition of DI and ASS.

Element	% composition of alloying elements										
	Fe	C	Cr	Ni	Mo	Si	Mn	P	S	Nb	Mg
DI (wt%)	82.242	3.600			0.014	2.000	0.300	0.007	0.010		0.050
ASS (wt%)	68.495	0.080	18.000	8.000	2.500	0.750	2.000	0.045	0.030	0.100	



(a)



(b)

Figure 1. (a) DI coupons; (b) ASS coupons after the experiment.

polished with 1.0 microns diamond polishing paste followed by 0.5 microns paste. The micrograph of each polished coupon showing the respective microstructural feature was also obtained.

3. Results and Discussion

The corrosion rate was computed in mils per year (mpy) with the standard expression [20-22].

$$R = \frac{534W}{\rho AT}$$

where W is weight loss in mg, ρ is the density of the coupons in g/cm^3 , A is the exposed area in square inch and T is the exposure time in hours [20]. This shows that corrosion rate is linearly proportional to the weight loss.

Figure 2 shows the plots of weight loss of DI and ASS with time after immersion in table salt for 1200 hr. However, it can be observed that the weight loss in ductile iron increased progressively whereas the opposite effect is observed for ASS as it progressively decreased. This response can be attributed to increased anodic dissolution of the DI coupon in NaCl. This is in contrast to the anodic passivation in ASS due to the presence of chromium in the austenitic matrix [4-6]. From the chemical composition of DI, (Table 1), molybdenum is in traces and chromium which could have enhanced corrosion resistance is conspicuously absent in the matrix of plain DI. When the ASS and DI coupons were physically

inspected, no significant change in appearance was observed in ASS coupons (**Figure 1(b)**). However, the DI coupons (**Figure 1(a)**) were observed to be substantially corroded during the respective immersion time periods.

Figure 3 shows the comparative plots of the corrosion rates of DI and ASS in sodium chloride as time changes. A decrease in corrosion rate of for ASS with increasing immersion time was also observed following similar pattern when compared to the loss in weight. This effect could be attributed to the adherent thin passive film of chromium oxide formed on the metal surface [4-6]. This prevents the solution from contacting the metal itself.

The observations made in respect of the weight loss (**Figure 2**) is in agreement with that made for the corrosion rate (**Figure 3**) which is consistent with previously reported works [4-6]. It has previously been observed that that the presence of chromium alloying element adds to the overall resistance through a passivation process by forming a complex spinel-type $\{(Fe,Ni)O(Fe,Cr)_2O_3\}$ passive film. This complex produces a coherent, adherent insulating and regenerating chromium oxide protective film on the metal surface; while molybdenum increases the ability of stainless steel to resist the localized corrosion in aggressive ion environments [7].

Figure 4 shows the microstructures of DI before and after immersion in NaCl at immersion times of 120 hr, 720 hr and 1200 hr depicting the corrosion product morphologies at the onset, middle and end of the experiment.

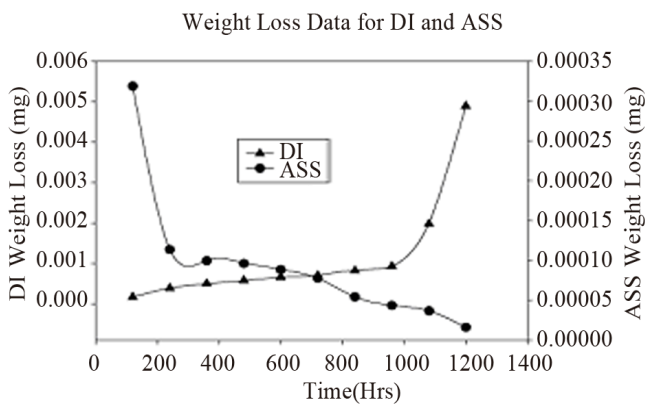


Figure 2. Weight loss of DI and ASS in NaCl.

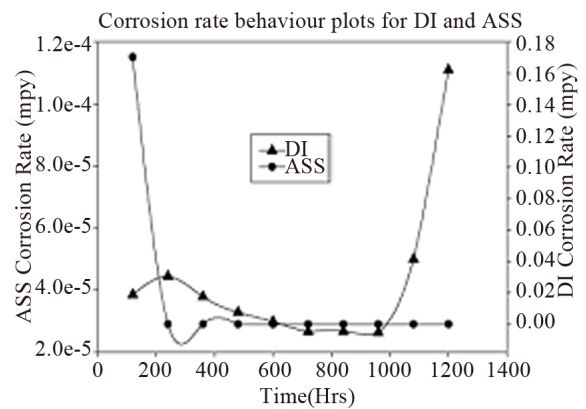


Figure 3. Corrosion rate of DI and ASS in NaCl.

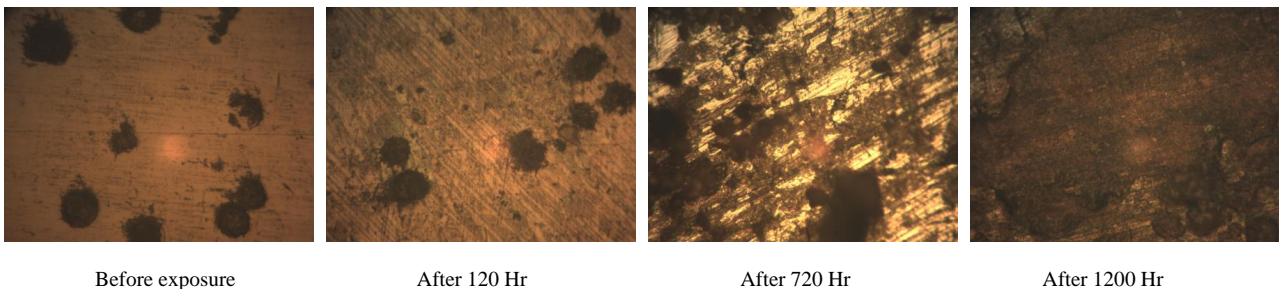


Figure 4. Microstructures of DI before and after immersion in sodium chloride (400x).

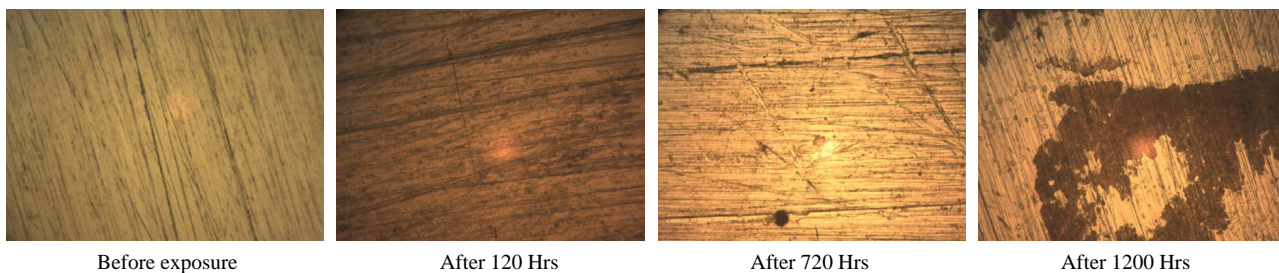


Figure 5. Microstructures of ASS before and after immersion in sodium chloride (400×).

The microstructures of DI (**Figure 5**) showed that the corrosion products gradually covered up the nodular matrix as the immersion time increased. Initially, the coupons revealed evenly distributed nodules in the pearlite/ferrite matrix of ductile iron.

Figure 5 shows the microstructures of ASS before and after immersion in NaCl at times 0 hr, 120 hr, 720 hr and 1200 hr. It shows the morphologies of the surface corrosion product in which points of possible initial pitting corrosion are revealed. The volume of pits formed on each ASS coupon also increased progressively with time.

4. Conclusion

This paper has reported the study of corrosion behavior of DI and ASS in table salt representing an extreme marine environment as the media. After 1200 hr, the corrosion rate of DI was 1.1×10^{-4} mpy compared to that of ASS which was 6.8×10^{-7} mpy. The fact that ASS outperformed DI has been established but what this work has established is an almost 4 orders of magnitude difference in corrosion rate between the two materials. This is not unconnected with the presence of chromium in ASS coupons which greatly adds to the overall corrosion resistance through a passivation process by forming a complex spinel-type $\{(Fe,Ni)O(Fe,Cr)_2O_3\}$ passive film. While corrosion rate of DI increased progressively with immersion time that of ASS decreased at comparable immersion time periods.

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