CORROSION BEHAVIOUR OF ANTIMONY MODIFIED CARBIDIC AUSTEMPERED DUCTILE IRON (CADI) IN NEUTRAL ENVIRONMENT

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Abstract

In this work, effects of antimony on the corrosion behaviour of antimony modified carbidic austempered ductile iron were studied. Rod-like samples (CADI) were produced by sand casting technique in which sandwich method were used to evaluate the influence of austempering temperatures on corrosion behaviour of antimony modified carbidic austempered ductile iron. Six different alloys with equivalent carbon of hyper-eutectic composition (carbon equivalent of 4.44) were used in order to evaluate the effect of antimony contents ranging from 0.096 to 0.48% at austenitic temperature of 910°C and austempering temperatures of 300 °C and 325 °C for period of 3hrs. Studying particularly effects of carbide content and graphite shape, besides their stability during the heat treatment with respect to corrosion behaviour of the CADIs. The results show that the microstructures of the as-cast samples mainly consist of few nodular graphite, pearlite and carbides. While the heat- treated samples contain graphite nodules, carbides of varying sizes, ausferrite and retained austenite. As the antimony content increases, corrosion resistance of the carbidic austempered ductile iron increase until critical antimony content is attained. With increase in antimony content, the amount of nodular graphite decreases, pearlite and carbides present increase. As antimony content increases, the acicular ferrite becomes finer, corrosion resistance increased. At austempering temperature of 300°C, CADI sample with antimony content of 0.192 wt.% Sb has the best corrosion resistance in neutral environment at austempering time of 1hour with the least corrosion rate of 6.0234E-07 mmpy. While at austempering temperature of 325°C, the best corrosion resistance was obtained with the CADI having 0.096 wt. % antimony content held for austempering time of 2hours (least corrosion rate of 6.6108E-4 mmpy). From the corrosion results obtained, it was observed that the electrochemical behaviour of these CADIs in neutral environment was influenced by antimony content, austempering temperature, and austempering time.

Keywords: Carbidic austempered ductile iron; Microstructure; Carbides; Antimony; corrosion, Austempering temperatures of 300°C and 325 °C; neutral environment.

Introduction

(CADI) is a new class of Austempered Ductile Iron (ADI) containing carbides in the ausferrite matrix. CADI is produced by austempering the carbidic ductile iron at different temperatures and time. It is an economical substitute for wrought or forged steel and has been used more and more in automobile, mining, railway and agricultural machinery sectors (Seshan, 1998). Due to its superior properties over other materials it can also be used in applications like piston rings in internal combustion (IC) engines, dies, gears, navy ship boards, and rollers (Panditl and Patil, 2015). Metallic materials are precious resources of any country, someday there will be an acute shortage of these materials. An impending metal crisis does not seem anywhere to be a remote possibility but a reality. To preserve these valuable resources, we need to understand how these resources are destroyed by corrosion and how they must be preserved by modifying the microstructure of the material for corrosion protection. Corrosion has been a very important factor in these disasters. Applying the knowledge of corrosion protection can minimize such disasters. Prevention would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment. For example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes, and electrochemical potential. The study of corrosion of cast irons is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest (Bouklah, *et al.*, 2005). The problem of metallic corrosion is one of significant proportions: in economic terms, it has been estimated that approximately 5% of an industrialized nation's income is spent on corrosion prevention, maintenance, replacement, products lost or contaminated as a result of corrosion reactions (Callister, 2001). The aim of this work is to investigate the corrosion behaviour of antimony (Sb) modified CADI in neutral environment as an agricultural implement.

Experimental procedure

2.1. Sample preparation

The material used in this study was obtained in a metal casting laboratory, using a 3 kg capacity electric arc furnace. Cast iron scrap and foundry returns were used as charge materials.

In all cases the melts were nodulized with Fe Si Mg (9 wt. % Mg) and inoculated with Fe-Si (75 wt. % Si). Six alloys of ductile iron were obtained, with approximately 0, 0.096, 0.192, 0.288, 0.384 and 0.48wt. % Sb. The dimension of each sample cast is 20mm by 20mm by 200mm.

The rods were cut longitudinal into 20mm x 30mm long for the microstructural characterisation, 10mm thick x 50mm long for impact and 20mm x 40mm for wear test samples. Hardness measurements were also performed on all the samples of dimensions 20mm x 25mm.

The samples obtained from the five alloys were then heat-treated by austenitizing at 910 °C and held for 1hour in a muffle furnace followed by an austempering step in a sodium nitrate - potassium nitrate salt bath at temperature 300°C and 325°C at different time of 1-3hrs. The

unalloyed samples without antimony (conventional CADI) were used as reference material for wear and impact tests together with the CADI variants (having different antimony contents).

2.2. Chemical and microstructural examination

The chemical composition of the alloys was determined by means of a Spark Emission Optic Spectrometer with a DV6 excitation source. The chemical composition of the carbides was evaluated by using a FESEM Scanning Electron Microscope with an EDX module, in order to analyse the micro-segregation effects and its influence on the carbide dissolution during heat treatment. The values reported are the average of five determinations.

Metallographic sample preparation for optical microscopy examination was carried out by using standard techniques for cutting, grinding and polishing before etching with 2% Nital.

Corrosion test was conducted using potentiodynamic polarization electrochemical methods in accordance with ASTM G57-97 (2014) standard. The experiment was carried out using Versa Potentiostat. Corrosion behaviour of the samples was investigated in neutral and chloride environment at ambient temperature (25 °C). Potentiodynamic polarization measurement was carried out using a scan rate of 0.1666 mV/s at a potential initiated at -200 mV to +250 mV. Two repeat tests were carried out for all compositions of the alloys, and the reproducibility and repeatability were observed to be reasonably good as there were no significant differences between results from duplicates. Corrosion rate was calculated using both penetration rate (C.R) and mass loss rate (M.R) of Faraday's law of corrosion (Barnartt, 1977). The equations stated below according to Mansfeld, 1972 were used to calculate both the penetration rate (C.R) and mass reduction rates (M.R) as in expressions 1 and 2.

$$C.R = \frac{K_i \times I_{corr} \times E_w}{d} \quad (1)$$

$$M.R = (K_2 \times I_{cor} \times E_w) \quad (2)$$

C.R is given in mm / yr, I_{corr} ($\mu A/cm^2$)

$K_i = 3.27 \times 10^{-3}$ (mmg/ μA cm yr)

$K_2 = 0.008954$

M.R is given in g / m²d, EW is equivalent weight of 27.9

Electrochemical Investigation

Electrochemical experiments were performed on the samples in a neutral environment by means of Versa-Stat interfaced with computer using potentio-dynamic technique. The cell contained a platinum disc as counter electrode, a saturated calomel electrode as reference and the working electrode (with and without antimony modified carbidic austempered ductile iron). Before every run, the surface of the specimens of area 1cm² was polished using emery paper of 60 and

400grits. The potential scanning rate was 1mV/min at -250mV to 250mV. All potentials are reported with respect to the saturated calomel electrode. The experiment was done at ambient temperature. The polarization curves were performed on the cast samples and heat treated samples in neutral environment.

3. Results and discussion

3.1. Chemical and microstructural characterization

Table 1: Chemical Composition of the produced Alloys (wt. %)

	Fe	C	Si	Mn	Cr	Ni	Cu	Mg	Sb	S	P	C.E
No												
1	89.39	3.62	2.42	0.58	2.6	0.60	0.69	0.06	-	0.004	0.040	4.43
2	89.33	3.62	2.40	0.57	2.61	0.61	0.65	0.07	0.096	0.005	0.041	4.43
3	89.24	3.62	2.41	0.57	2.62	0.62	0.61	0.07	0.192	0.005	0.042	4.44
4	89.19	3.63	2.40	0.56	2.60	0.60	0.62	0.07	0.288	0.005	0.042	4.44
5	89.10	3.62	2.41	0.56	2.63	0.61	0.62	0.06	0.384	0.005	0.040	4.44
6	88.97	3.62	2.40	0.58	2.62	0.60	0.63	0.06	0.480	0.004	0.041	4.43

Sterographs of the Corroded Surfaces of the Produced Samples

Plate 1: unmodified CADI

Plate 2: modified CADI

Plate 3: modified CADI

SEM (S.E) Photographs of the Corroded Surfaces of the Produced Samples

Plate 4: unmodified CADI

Plate 5: modified CADI

Plate 6: modified CADI

Stereographic View of the Corroded Surfaces of the Produced CADI

Changes in the appearance and colour of the corrosion products formed on the surface of the produced cast samples were examined using stereo microscope (Plates 1 - 3). As seen from Plates (4 - 6), the general appearance of the surface corrosion products was similar for all the produced CADI samples, the specimen exposed in static water formed on adhering corrosion produced without sign of delamination from the surface (Plates 4 - 6).

The produced CADI samples exposed to static water, show an initial layer of adherent, red oxide formed on the surface and covered substantial portion of the surface.

From Plates 4 - 6, it can be seen that the general corrosion is the primary type of degradation that took place, localized corrosion seems to be minor form of surface degradation on the samples.

Corrosion current and rates results obtained from open circuit potential (OCP) monitoring of the specimens are shown in Figure 1. From which it can be seen that the OCP for specimens exposed to static well water experiment, it moves toward less positive (more anodic),

Electrochemical Behavior

Figure 1: Open Circuit potential of the Produced Samples against Elapsed Time

Figure 2: Corrosion Potential of the Unheated Treated Produced Samples against Elapsed Time

Figure 3: Corrosion Potential of the Heat Treated Samples against Elapsed Time

Figure 4: Corrosion Potential of the Produced Samples against Elapsed Time

Among the carbidic ductile irons (CDI) containing antimony content ranging from 0.096 wt. %, 0.192 wt. %, 0.288 wt. %, 0.384 wt. % and 0.48 wt. % produced without heat treatment, CDI with antimony content of 0.384 wt. % has the highest open circuit potential value and consequently the least corrosion rate value, signifying the positive influence of antimony on the produced CDI (Venkatesan *et al.*, 2002).

Figures (1 - 4) show that the CADI generally displayed similar polarization curves and passivity characteristics. It was observed that CADIs with 0.384 wt. % Sb has the lowest corrosion rate of 0.00068907 mmpy compare with CADIs with 0.096 wt. % Sb (0.015782 mmpy), 0.288 wt. % Sb (0.002735 mmpy), and 0.48 wt.% Sb (0.62568 mmpy). Correspondingly, the produced CADI with 0.384 wt. % Sb has the least corrosion current density of -59.383 nA and the highest corrosion potential of -518.205mV compared with samples with 0.096 wt.% Sb (1.36 μ A and -728.002 mV), 0.288 wt.% Sb (-235.707 nA and -530.657 mV), and 0.48 wt.% Sb (-53.921 μ A and -532.496mV). From the above corrosion parameters obtained from the electrochemical test, it was discovered that CADI sample with 0.384 wt. % Sb has the best corrosion resistance hence it has the least corrosion current density, lowest corrosion rate and the highest corrosion potential. It was also observed that there was a progressive increase in corrosion resistance with increase in the antimony content until a critical content of 0.384 wt.% was reached beyond which the corrosion resistance reduced significantly. It is observed that there was an appreciable increase in the corrosion resistance of the samples subjected to austempering heat-treatment

operations compared with the as-cast samples. Among the samples subjected to austempering temperature of 300 °C with austempering time of 1 hour, the least corrosion rate of 0.0000060234 mmpy for CADI with 0.192 wt. % Sb was obtained, suggesting that at austempering time of 1 hour, CADI with 0.192 wt. % has the best corrosion resistance. At austempering time of 2 hours, CADI sample with 0.192 wt. % still has the best corrosion resistance. For the austempering time of 3 hours, CADI with 0.384 wt. % Sb has the least corrosion rate of 0.0014806 mmpy, current density of -127.595 nA and corrosion potential of -369.563 mV at the austempering temperature of 300 °C. Graphitic corrosion normally observed in grey cast iron as a result of selective leaching of the cast iron in water that leave graphite network was not observed in this case.

The surface of the samples was uniformly covered with corrosion products and no fouling was seen (Schumacher, 1979 and Shreir, 1984). The severe corrosion usually experienced by austempered ductile iron as result of carbide was reduced by the antimony element judging from the corrosion rate values (Beccaria, 1995). It was very clear that for most of the CADI, use of micro - quantity of antimony element does not degrade the corrosion properties of the CADI in well water.

CONCLUSION

1. Electrochemical behaviour of antimony modified CADI in neutral environment has been studied.
2. Stereo – micrographs of the corroded surface of the produced samples was taken which revealed that similar general corrosion appearance was formed on the samples
3. Reddish and adherent oxide was seen on the substantial portion of the stereo-graphs of the samples
4. Open Circuit Potential of the CADI immersed in well water moves towards less positive potential.
5. Among the produced Carbodic Ductile Iron (CDI) samples immersed in well water, the sample with antimony content of 0.384 wt.% has the lowest current density, corrosion rate and the highest corrosion resistance.
6. CADI sample (heat treated CDI) with antimony content of 0.192 wt.% has the least corrosion rate and consequently the best corrosion resistance.
7. No graphitic corrosion was observed in the samples
8. Generally, it can be summarized that the CADI samples with antimony additions displayed better corrosion resistance compared to CADI without antimony additions. This shows that antimony element has been able to modify to CADI samples to the extent of reducing the susceptibility carbide induce corrosion usually experienced in cast irons with high carbide content.

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