Effect of Microstructure on Contact Angle and Corrosion of Ductile Iron: Iron–Graphite Composite

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ABSTRACT: Ductile iron samples with similar compositions and varying microstructures were uniformly abraded, and the effects of phase fractions (ferrite, pearlite, and graphite) on the apparent contact angle (with water) and corrosion characteristics of ductile iron were investigated. We also investigated the effect of droplet volume on the apparent contact angle of ductile iron. Irrespective of the droplet size, the ductile iron system followed the Wenzel model of wetting, and the contact angle increased with increasing droplet volume. The Wenzel and Cassie–Baxter contact angles were calculated, and the calculated results agreed well with the experimental results. It was experimentally proven that pearlite is more susceptible to corrosion than ferrite and graphite, and a higher portion of pearlite in the microstructure can be detrimental to the corrosion resistance of the material. Understanding the relationship between the microstructure, contact angle, and corrosion can be used to develop materials with higher contact angle and corrosion-resistant microstructures. Using metal pipes that have high contact angles is desirable because artificial coatings on metal pipes can degrade over time leading to high cost of replacement and contamination to water systems.

INTRODUCTION

Ductile iron is widely used for piping and other components by the water industry due to its low cost, durability, and mechanical properties. However, these pipes often corrode and suffer from accumulation of unwanted buildup of deposits. With high volume of wastewater passing through sewerage systems combined with the increasing number of pipes, this buildup becomes costly and difficult to remove. Self-cleaning materials have been used to address these issues as they minimize water contact angle and therefore can potentially minimize crucial environmental degradation processes such as corrosion, scaling, biofouling, and accumulation of dirt on the components. Self-cleaning materials typically employ the lotus effect, which is the surface roughness-induced superhydrophobicity, common on the leaves of water-repellent plants. The wettability of surfaces is often characterized by water contact angle measurement and it depends upon the relation between interfacial energies of phases present at the triple solid–liquid–gas line, as well as on surface roughness, heterogeneity, and physical and chemical processes occurring at the solid–liquid interface. Therefore, microstructural parameters of metallic alloys such as phases, alloying elements, grain size, grain orientation, texture, state of strain, and state of oxidation can affect the contact angle by altering the interfacial energies of the solid surface with air and water. To date, little work has been done on studying the effect of these microstructural parameters of an alloy on its wetting and corrosion characteristics. The experimental data in the literature show that an increase in roughness increases the contact angle, while an increasing contact angle decreases corrosion.

Generally, internal coatings (e.g., polyurethane, cement-mortar, and glass) are used, which can protect metal pipes from fouling and corrosion. However, these coatings may be short-lived, expensive, or may even contaminate the water system by leaching. Therefore, it is imperative to develop and study alloy systems that have high water contact angles by virtue of their microstructure, eliminating the need for any coating or secondary surface treatment to reduce fouling and corrosion.

The theoretical value of the equilibrium contact angle of a liquid droplet on a flat solid surface is determined by Young’s equation, as given by eq 1. It shows a geometrical relation between the cosine of the intrinsic contact angle (i.e., the contact angle that a liquid would make with a rigid, flat, chemically homogeneous, insoluble, and nonreactive solid surface) as a function of the interfacial energies of the solid–vapor (γsv), solid–liquid (γsl), and liquid–vapor (γlv) interfaces.

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$ (1)

Two classical models, Wenzel and Cassie–Baxter, describe the wetting conditions of the surface in contact with the liquid forming either a homogeneous (solid–liquid) or inhomoge-
neous (solid–liquid–vapor) interface. Figure 1 shows a schematic of these two models. The contact angle that is observed on a rough surface (i.e., measured macroscopically on a given surface) is called the apparent contact angle ($\theta^*$) to differentiate it from the Young’s contact angle. Therefore, the apparent contact angle can either be the Wenzel contact angle (eq 2) or the Cassie–Baxter contact angle (eq 3), depending on the respective model that is followed.

$$\cos \theta_w = r \cos \theta_y$$

(2)

where $\theta_w$ is the Wenzel contact angle, $r$ is a roughness parameter, and $\theta_y$ is the Young’s contact angle. The Cassie–Baxter contact angle of a liquid droplet with a rough surface, $\theta_{CB}$, is described by

$$\cos \theta_{CB} = F_s (1 + \cos \theta_y) - 1$$

(3)

where $F_s$ is the solid fraction in contact with the liquid droplet and $\theta_y$ is the Young’s contact angle.

A solid–liquid system can follow either of the two states, Wenzel or Cassie–Baxter or a mixed regime. Therefore, it is important to understand which model is followed. This knowledge is a prerequisite to design hydrophobic and superhydrophobic surfaces for research and other applications. Moreover, the Cassie and Wenzel models do not exhaust all of the possible wetting regimes. Also, the pure Cassie and Wenzel regimes are rare in their occurrence. The so-called “mixed wetting” is often observed. Shibuchi et al. conducted experiments with fractal surfaces and showed how the solid area fraction that is in contact with the water affects its apparent contact angle. A fractal surface is a kind of rough surface with very high roughness values. They have shown that a water droplet on a rough superhydrophobic material (alkylketene dimer) follows the Cassie–Baxter model, and the apparent contact angle is 174°, that is, the droplet does not wet the cavities and sits on the surface and air spaces. However, when the drop is pushed onto the surface by applying an external pressure, it wets the asperities, that is, switches from the Cassie–Baxter model to Wenzel model and the apparent contact angle changes to 128°. It should be noted that each state of the drop is a local minimum of its energy state and the drop is considered to be in equilibrium. In both the cases, the apparent contact angle found experimentally was in close agreement with the values predicted by each respective model. Building on this work, Patankar showed that it is possible for a droplet to transition from one equilibrium state to another provided it can overcome the energy barrier between two states. He proposed that both the equations used for predicting apparent contact angles in Wenzel and Cassie–Baxter models should be obeyed successively as the apparent contact angle increases. Therefore, the apparent contact angle where this transition takes place can be determined by equating the contact angles predicted by the two models, and it is named as the threshold contact angle $\theta_c$. Lafuma and Quéré have compared the interfacial energies associated with Wenzel and Cassie–Baxter models and confirmed that the trapping of air is favored only if $\theta$ is larger than $\theta_c$. They have plotted the apparent contact angle ($\theta^*$) as a function of the Young’s contact angle ($\theta$), as shown in Figure 2. Here, the expected behavior is shown as a solid line while the metastability of the Cassie–Baxter model is shown as a dotted line.

In addition, some researchers have reported that the size of water droplets can affect the apparent contact angle. The dependence of apparent contact angle on droplet size is mainly due to the scale effect and gravity. Scale effect suggests that as the droplet grows larger, it encompasses larger regions of heterogeneity, which can affect the contact angle of the droplet. It is interesting to note that it has been reported in the literature that the apparent contact angle is affected more by the phases on which the three-phase contact line (line where the solid, liquid, and gas meet at the periphery of the drop) is placed than the phases entirely below the drop. Gravity effects are miniscule for droplets smaller than the capillary length. Capillary length can be defined as the characteristic length of the interface between two fluids. It is given by $L = \sqrt{\frac{\gamma}{\rho g}}$, where $\kappa^{-1}$ is the capillary length, $\gamma$ is the surface tension, and $\rho$ is the density of the droplet.
tension, \( \rho \) is the density of the fluid, and \( g \) is the acceleration due to gravity. The capillary length for pure water and air at standard pressure and temperature is 2.7 mm. As we increase the droplet size, however, the spherical shape of the drop can be influenced by gravity. It can change the radius of curvature of the drop and, consequently, the apparent contact angle of the droplet.

The effects of the droplet size on the apparent contact angle have been studied for rough polyethylene surfaces,\(^{35}\) and it was found that the apparent contact angle increases with an increase in the droplet volume. Thus, for a droplet of 0.024 \( \mu \text{L} \), the measured contact angle was \( 55^\circ \). However, when the droplet volume was increased to 2 \( \mu \text{L} \), the apparent contact angle rose to \( 93^\circ \). Good and Koo\(^{36}\) also reported an increase in the apparent contact angle with increasing water droplet size for Teflon FEP and polymethyl methacrylate.

The contact angle of a material depends on its surface energy.\(^{37}\) Metals and, consequently, metal matrix composites tend to have higher surface energies than polymers, which makes it difficult to achieve high contact angles especially superhydrophobicity on their surfaces. However, some advances have been made in this area.\(^{30,31} - 33\) Different phases coexist simultaneously within a given alloy system. A phase is a domain within a material in which the relevant physical properties are uniform, and each phase will have its own intrinsic contact angle. Ductile iron has three distinct phases, namely, ferrite, pearlite, and graphite. The apparent amount of each phase in the material is determined by the area it occupies in a given microstructure. This is denoted as the phase fraction of that phase. We have studied the effect of varying the phase fractions on the wetting and corrosion characteristics of ductile iron.

It is hypothesized by virtue of Cassie’s Law (explanation provided further, see eq 13) that as the phase fraction of graphite increases on the surface, its influence on the water droplet increases as well. It has been shown by Drelich et al.\(^{27}\) that on a heterogeneous surface, the three-phase line of a drop is contorted, which indicates the existence of energy barriers. In another work by the same group,\(^{34}\) the authors have shown that in a heterogeneous surface with alternating hydrophobic/hydrophilic micron-sized strips, the macroscopic contact angle varied depending on the direction of the contact angle measurement (normal/parallel to the strips). It is reported that the water contact angle of flat graphite is \( 90 - 95^\circ \),\(^{35,36}\) and the contact angle of water on mild steel (ferrite and pearlite) is \( 64^\circ \).\(^{36}\) As a result, the contact angle of water on the surface should increase with the increase in phase fraction of graphite. This follows from the fact that different phases have different surface energies.\(^{37}\) Also, since the contact angle can be calculated as a function of surface energy, controlling the microstructure can lead to a control of contact angle as well.

These effects are compounded by the addition of surface roughness on the surface. There has been significant reported work on the effect of roughness on the contact angle,\(^{38 - 43}\) but the effect of varying phase fractions on wetting has been very limited. We have therefore focused on finding the effect of variation of phase fractions in ductile iron on contact angle and corrosion rate. A theoretical model is developed, and the trends derived from this model are compared with the experimental results.

### WETTING MODEL FOR AN ABRATED COMPOSITE MATERIAL

#### Theoretical Roughness Factor of Composite Due to Abrasion.

The mechanical abrasion of the composite surface creates a roughness on its surface. The apparent contact angle of water that is seen can be predicted by either Cassie–Baxter or Wenzel model. However, since we also have reinforcement particles, their effects need to be decoupled from that of roughness. A model discussed by Nickelsen et al.\(^{44}\) is used to describe the effect of abrasion on the roughness factor. It is assumed that the roughness factor of the reinforcement particles is negligible in affecting the apparent contact angle of water as compared to that of the matrix. Therefore, we assume the roughness factor of the entire composite to be equal to the roughness factor of the matrix, which is calculated below. It is also assumed that the symmetric packing of the sand particles in the sandpaper creates semi cylindrical parallel scratches on the surface of the samples. Figure 3 shows a simplified model of the abraded surface, where \( D \) is the diameter of sand particles, \( a \) and \( a_t \) are geometrical parameters depending on the depth of scratch, and \( 2R_a \) is the average depth of scratch. \( D \) values for each sandpaper grit are available in ISO 6344-3. The average depth of the scratches is assumed to be \( R_a \) such that the actual depth is \( 2R_a \). It is also assumed that the distance between two scratches (\( \lambda \)) is equal to the diameter of the abrasive particles (\( D \)).

**Wenzel Model.** Using the Pythagoras theorem and the length of chord of a circle, we formulate eq 4.

\[
h^2 + \left( \frac{D - 2a}{2} \right)^2 = \left( \frac{D}{2} \right)^2
\]

\(2R_a\) is termed as the sagitta of a circle, and the following relation is noted.

\[
\frac{D}{2} = h + 2R_a
\]

From eqs 4 and 5, eq 6 can be developed between all the different variables that are associated with abrasion of the composite surface.

\[
\left( \frac{D}{2} - 2R_a \right)^2 + \left( \frac{D - 2a}{2} \right)^2 = \left( \frac{D}{2} \right)^2
\]

\( D \) is a known property of sandpaper; \( R_a \) was measured, so the flat portion of the substrate, \( a \), can be determined by rearranging eq 4, as shown below.

\[
a = \frac{D}{2} - \sqrt{2R_a \left( D - 2R_a \right)}
\]
The angle $\alpha$ in the figure can be calculated by eq 8.

$$\alpha = 2 \sin^{-1} \left(1 - \frac{2a}{D}\right)$$  \hspace{1cm} (8)

The Wenzel roughness factor, $R_{\text{W}}$, can be calculated from eq 7 for parallel scratches of length $L$.

$$R_{\text{W}} = \frac{\text{true area}}{\text{projected area}} = \frac{(2a + \frac{aL}{2})L}{DL} = \frac{2a}{D} + \frac{\alpha}{2}$$  \hspace{1cm} (9)

**Cassie–Baxter Model.** In this model, only the top horizontal part of the surface comes into contact with water. So, the true area of contact is equal to the projected area.

$$R_{\text{CB}} = \frac{\text{true area}}{\text{projected area}} = 1$$  \hspace{1cm} (10)

**Theoretical Contact Angle Due to Phase Fraction.**

The contact angle of graphite can vary significantly depending on the orientation as graphite has a very anisotropic structure. Extensive studies have been conducted since the mid-1900s on the wetting characteristics of graphite. Fowkes and Harkins\textsuperscript{45} concluded from their tilting plate method experiment on mined Ceylon graphite that the water contact angle (WCA) was 86°. Adamson and Gast\textsuperscript{46} reported the same WCA on pyrolytic graphite. A similar result of 83.9° was reported by Morcos\textsuperscript{47} on pyrolytic graphite. Wang et al.\textsuperscript{48} have reported a WCA value of 98.3° for graphite films prepared from natural flake graphite using a filtration process. Kozbial et al.\textsuperscript{49} and Wei and Jia\textsuperscript{50} have shown that graphite is intrinsically hydrophobic. However, when contamination occurs due to the adsorption of hydrocarbon monolayer from the ambient atmosphere, the contact angle goes up to 90°. Li et al.\textsuperscript{51} showed that graphite is very sensitive to airborne contaminants and that the contact angle can increase very quickly when exposed to air. Based on experiments by Taherian et al.\textsuperscript{52} on static WCA on graphite, a value of 90°–95° seems acceptable.\textsuperscript{52} For this study, we are using a value of $\theta_i = 90°$.

As discussed in the above section, the theoretical roughness factor that is calculated above is the roughness factor of the matrix. This factor can be termed as $R_{\text{mat}}$ for both models. The effect of the phase fraction on contact angle has been discussed by Nosonovsky et al.\textsuperscript{53} and the following equations have been derived for each model. Note that in these ductile iron samples, the graphite nodules are spherical. For such particles, the surface roughness is equal to the ratio of the half of the total surface area to the cross-sectional area of the nodule. Therefore, $R_{\text{fr}} = 2$.

**Wenzel Model.** For a composite material, having a reinforcement fraction of $f_i$, using a simple rule of mixtures

$$\cos \theta = R_{\text{mat}} \left(1 - f_i\right) \cos \theta_{\text{mat}} + R_{\text{fr}} f_i \cos \theta_i$$  \hspace{1cm} (11)

**Cassie–Baxter Model.**

$$\cos \theta = R_{\text{mat}} \left(1 - f_i\right) \cos \theta_{\text{mat}} + R_{\text{fr}} f_i \cos \theta_i - 1$$

$$+ f_i \cos \theta_{\text{fr}} + (1 - f_i) \cos \theta_{\text{fr}}$$  \hspace{1cm} (12)

Using the model calculated above (eqs 11 and 12), graphs are plotted (Figure 4), which show the variation of contact angles with respect to increasing graphite percentage (up to 50%). It can be seen that in the Wenzel model, the water contact angle increases while in Cassie–Baxter, the contact angle decreases. From Table 1, it can be seen that the experimental values of contact angle follow the trends as the values calculated using the Wenzel model. As predicted by Lafuma and Quère\textsuperscript{16} (see Figure 2), the Young’s contact angle is less than the critical contact angle in this system, and therefore, it obeys the Wenzel model. As a result, the contact angle increases with an increase in the phase percent of graphite. One reason for a larger experimental contact angle than predicted could be the heterogeneity on the surface due to contamination by hydrocarbons, dust, large droplet size, high roughness, and so forth.

### EXPERIMENTAL PROCEDURE

In this study, four types of ductile iron samples with varying percentages of graphite nodules were used. The chemical composition of these samples is shown in Table 2. These samples are named as DI 1, DI 2, DI 3, and DI 4 for experiments. The DI 1 and DI 2 samples were obtained from Dr. Hugo Lopez, University of Wisconsin–Milwaukee; the DI 3 sample was collected from Applied Process, and the DI 4 sample was obtained from Willman Industries. DI 1 and DI 2 samples were cast by Fras et al.\textsuperscript{54} in a 2 mm-thick mold, which gives a very high nodule count of graphite in the matrix while significantly reducing the size of individual nodules. The other ductile iron samples were commercially available. These ductile iron samples were mounted in epoxy and fully polished using a MetaServ 3000 variable speed grinder/polisher; imaging was done on a Zeiss AxioVert.A1 optical microscope on unetched samples. The micrographs of each sample are shown in Figure 5, which depicts the distribution of the graphite nodules in them.
Contact Angle Measurements. For the contact angle measurements, the samples were mechanically abraded using 400 grit sandpaper. After abrasion, the samples were washed in water and ethanol to prevent any contamination from the air. The water contact angle (WCA) was measured using a Rame-Hart 250 goniometer. The goniometer consists of a horizontal stage to mount the sample, a high-precision microsyringe to form a water droplet, a light source, and a camera equipped with a macro lens. A water droplet of the required size is created, and the sample is slowly moved upward to bring it in contact with the droplet. The sample is then moved down with the droplet on it. This method is called a sessile drop test. A picture of the droplet profile is taken, and the measurement was achieved by aligning the tangent of the sessile drop profile at the contact point with the surface and finding the angle. It is suggested that the lens be tilted down slightly off the horizon so that the near edge of the sample stage is out of the line of sight, and a portion of the drop profile is reflected by the substrate surface and is brought into focus, which prevents forming a fuzzy liquid–substrate contact line in the profile, as shown in Figure 6.

Roughness Measurements. The roughness profile of the samples was also measured after abrading with 400 grit sandpaper using an Olympus LEXT OLS4100 3D laser confocal microscope. The measured values of roughness for 400 grit sandpaper were used as inputs in the model that is discussed to predict the WCA for various samples.

Corrosion Measurements. Electrochemical corrosion tests were carried out using Bio-Logic Science Instruments’ SP-200 potentiostat using an EC lab software to measure the electrochemical behavior. A conventional three-electrode glass cell consisting of a ductile iron coupon with an exposed surface area of 0.920 cm² as the working electrode and graphite rod and saturated calomel electrode (SCE) as auxiliary and reference electrodes, respectively. All potentials were measured against the SCE reference electrode. Prior to all electrochemical measurements, the working electrode was immersed in G61 solution (34 g of NaCl in 920 g of distilled water) for 3 days to attain a stable open corrosion potential (OCP). Tests were performed in an aerated but unstirred G61 solution at 25 °C. Linear polarization resistance experiments were done from −250 to +250 mV versus $E_{\text{corr}}$ at the scan rate of 0.166 mV/s. The slope of the I versus $E_{\text{corr}}$ at I = 0 was determined and used to obtain the corrosion current densities ($I_{\text{corr}}$).

# RESULTS AND DISCUSSION

Effect of Microstructure on Contact Angle. Optical micrographs of unetched samples are shown in Figure 5 and Table 3 shows the average volume percent of graphite nodules in the samples. The area fraction gradually increases from sample to sample, from 10.13% in DI 1 to 25.84% in DI 4. The size and distribution of the graphite nodules also vary in the samples. Most nodules are spherical, and therefore, it is assumed that the reinforcement particles are perfectly spherical for the models that were earlier discussed.

Figure 7 demonstrates the combined effect of volume percentage of graphite nodules and the droplet volume on apparent contact angle of all tested samples. It has been observed that the apparent contact angle increased from 56.41° to 79.9° for 2 μL of droplet volume and $59.83^\circ$ to $86.93^\circ$ for 8 μL of droplet volume at 400 grit. Cassie’s law for calculating the contact angle of a liquid on the composite surface is given by

$$
\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2
$$

where $f_1$ is the fraction of component 1 in the composite, $\theta_1$ is the theoretical contact angle of component 1, $f_2$ is the fraction of component 2 in the composite, and $\theta_2$ is the theoretical contact angle of component 2.4,5 Ductile iron is composed of
dispersion of graphite nodules and a mild steel matrix. The measured contact angles of graphite and mild steel are 90 and 64°, respectively.\textsuperscript{36} So, by Cassie’s law (eq 13)

\[
\theta_{\text{DI1}} = \arccos[(0.89) \cdot \cos 64^\circ + (0.10) \cdot \cos 90^\circ] = 67.03^\circ
\]
\[
\theta_{\text{DI2}} = \arccos[(0.86) \cdot \cos 64^\circ + (0.13) \cdot \cos 90^\circ] = 67.85^\circ
\]
\[
\theta_{\text{DI3}} = \arccos[(0.85) \cdot \cos 64^\circ + (0.15) \cdot \cos 90^\circ] = 68.12^\circ
\]
\[
\theta_{\text{DI4}} = \arccos[(0.82) \cdot \cos 64^\circ + (0.18) \cdot \cos 90^\circ] = 68.93^\circ
\]

Apparent contact angles measured in the experiments tended to be larger than the theoretical calculations because the samples were abraded to a higher roughness, which generally increases the contact angle. However, the theory predicts an increase in contact angle as graphite amounts increase, as observed.

Table 2. Composition of Ductile Iron Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Mg</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
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<tbody>
<tr>
<td>DI 1</td>
<td>3.7</td>
<td>2.7</td>
<td>0.1</td>
<td>0.03</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>DI 2</td>
<td>3.7</td>
<td>2.7</td>
<td>0.1</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>balance</td>
</tr>
<tr>
<td>DI 3</td>
<td>3.55</td>
<td>2.55</td>
<td>0.48</td>
<td>0.55</td>
<td>0.048</td>
<td>0.07</td>
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<tr>
<td>DI 4</td>
<td>3.68</td>
<td>2.65</td>
<td>0.5</td>
<td></td>
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<td>balance</td>
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</table>

Table 3. Phase Percentage of Graphite Nodules

<table>
<thead>
<tr>
<th>sample</th>
<th>% of graphite nodules</th>
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<tbody>
<tr>
<td>DI 1</td>
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</tr>
<tr>
<td>DI 2</td>
<td>12.68</td>
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<tr>
<td>DI 3</td>
<td>15.60</td>
</tr>
<tr>
<td>DI 4</td>
<td>18.46</td>
</tr>
</tbody>
</table>

Figure 5. Micrographs of unetched samples showing the distribution of graphite nodules: (a) DI1, (b) DI2, (c) DI3, and (d) DI4.

Figure 6. Example of contact angle measurement showing both the droplet and the reflected profile.

If the size of nodules were to decrease for these same given area percentages, the apparent contact angle produced for the composite would remain constant, as the drop would occupy a space consisting of the same ratio of graphite to mild steel.\textsuperscript{55}

Effect of Droplet Volume on Contact Angle. The effect of droplet volume on contact angle is shown in Figure 8. It is observed that the apparent contact angle has a direct relationship with the droplet volume in all the samples studied. These effects have been extensively studied by Drelich et al.\textsuperscript{25,27,56−59} The shape and size of a liquid drop placed at a homogenous, rigid solid surface are controlled by the free energy of three interfaces, solid/liquid, solid/vapor, and liquid/vapor.
vapor, and by the solid topography. However, the samples in this study have heterogeneous and rough surfaces, which are nonideal surfaces. For such surfaces, Drellich et al. have proposed that several phenomena cause the contact angle dependence on droplet volume. These are (1) contourtions of three-phase contact line, (2) mechanical barriers of roughness features, and (3) surface heterogeneity.

**Effect of Surface Energy on Contact Angle.** The relationship between surface energy and wetting can be explained such that a low surface energy liquid can spontaneously wet a surface that has a higher surface energy. Water has a surface energy of 72 mJ/m². Thus, materials with surface energies greater than 72 mJ/m² will easily adhere to water and will have contact angles lower than 90°. However, materials with surface energies lower than 72 mJ/m² will not easily adhere to water and will have contact angles greater than 90°. Ductile iron is composed of pearlite, ferrite, and graphite. The surface energy of ferrite is 2482 mJ/m². Cementite, an iron compound (Fe₃C) that layers with alpha ferrite to form pearlite, has a surface energy of 2050 mJ/m². Since pearlite is composed of ferrite and cementite and cementite has a surface energy lower than ferrite, pearlite also has a lower surface energy than ferrite. It was shown by Kozbial et al. that the surface energy of graphite is 54.8 mJ/m², which is far lower than that of ferrite. In our experiments, water has a lower surface energy than all the phases in the iron microstructures with ferrite can lead to an increase in corrosion. It was shown by Ramachandran and Nosonovsky that change in contact angle could potentially change the corrosion rate. Change in contact angle can affect the fractional area of the surface in contact with water (Fₜₐₘ) as the water repels and minimizes contact with the surface. Fₜₐₘ was shown to be the main factor in corrosion, and a decrease in this was shown to decrease the corrosion rate. Reducing the space that water is occupying on the material creates a smaller medium for a redox reaction. Thus, an increase in contact angle reduces Fₜₐₘ and high contact angles decrease corrosion rates. Materials with higher surface energies are easily wet and corroded as the chemical instability on the surface attracts oxygen, showing why samples containing more ferrite had more corrosion rate and lower contact angles.

The linear polarization curves for the ductile iron samples in G61 solution at 25 °C are shown in Figure 9. Eₜₐₘ for the ductile iron is affected by the type of matrix and the amount of graphite phase percent. The slope of the curve when it crosses the zero current gives the Iₜₐₘ. It should be noted that graphitic carbon and iron carbides have more corrosion resistance to sea water than iron. However, their appearance in heterogeneous microstructures with ferrite can lead to an increase in the corrosion rate. 

with a total surface energy of 72 mJ/m². Thus, the calculated contact angle of mild steel can be found using eq 15, as shown below in Table 4.

\[
\theta = \arccos \left( \frac{1}{2} \left( \frac{\gamma_{lv}}{\gamma_{ss}} \right)^{1/2} + \frac{\gamma_{lp}}{\gamma_{ss}} \right) - 1 \right) = 57.66°
\]

<table>
<thead>
<tr>
<th>phase</th>
<th>calculated from surface energy</th>
<th>measured through experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>mild steel</td>
<td>57.66°</td>
<td>64°</td>
</tr>
<tr>
<td>graphite</td>
<td>80.89°</td>
<td>90°</td>
</tr>
</tbody>
</table>

**Effect of Microstructure on Corrosion.** In the electrochemical reaction between water and iron, water acts as the electrolyte and the corrosion current depends on the area of contact between the electrode and the electrolyte. Thus, more water on a metal will cause a rapid reaction and more corrosion. It was shown by Ramachandran and Nosonovsky that change in contact angle could potentially change the corrosion rate. Change in contact angle can affect the fractional area of the surface in contact with water (Fₜₐₘ) as the water repels and minimizes contact with the surface. Fₜₐₘ was shown to be the main factor in corrosion, and a decrease in this was shown to decrease the corrosion rate. Reducing the space that water is occupying on the material creates a smaller medium for a redox reaction. Thus, an increase in contact angle reduces Fₜₐₘ and high contact angles decrease corrosion rates. Materials with higher surface energies are easily wet and corroded as the chemical instability on the surface attracts oxygen, showing why samples containing more ferrite had more corrosion rate and lower contact angles.

![Figure 9. Linear polarization curves of the four ductile iron samples.](image)
corrosion rate, as a result of formation of localized galvanic cells.

Figure 10 shows the micrographs of the samples. Three phases can be seen, namely, ferrite, pearlite, and graphite. The percentages of each respective phase are shown in Table 5. Ferrite is composed of mostly iron as very little carbon can diffuse into its matrix. Pearlite is composed of ferrite and cementite, arranged in a lamellar structure. Cementite is essentially iron carbide with a chemical formula of Fe₃C; thus, it has almost 25 atom % C. On an average, pearlite comprises 88 wt % ferrite and 12 wt % cementite. From the micrographs, it can be seen that DI 1 is mostly ferritic while DI 2 is mostly pearlitic. DI 3 and DI 4 have a ferritic/pearlitic microstructure with DI 4 having a slightly larger pearlite/ferrite ratio than DI 3.

Table 5 summaries the microstructural features shown in Figure 10 and the data acquired from the corrosion experiments. It shows that the DI 2 sample has the noblest corrosion behavior among all samples. It is so because the matrix is mostly composed of pearlite, which has a lower surface energy than ferrite. However, DI 2 also shows the highest corrosion current density. This implies that the rate of corrosion is highest in the pearlitic matrix. It agrees with the findings of Clover et al. which proposes that a microstructure with segregated distribution of cementite (Fe₃C) such as in banded ferrite/pearlite performs poorly in corrosive environments and shows higher corrosion rate. Hao et al. have reported in their study that the banded structures of pearlite lead to accelerated galvanic effects between the lamellar cementite and the exposed ferrite phase. This galvanic effect leads to a higher corrosion rate than uniform corrosion in ferrite matrices. Similar results have been reported by Al-rubaiey et al. and Mora-Mendoza and Turgoose where it is shown that the corrosion rate increases with the presence of cementite residue on the surface caused by the preferential dissolution of the ferrite phase. DI 3 and DI 4 have some pearlite content but are predominantly ferritic. Thus, they have comparable corrosion results. However, DI 4 has a higher corrosion rate than DI 3 as the volume percent of pearlite is higher in DI 4 than in DI 3. It should be noted that the phase percent of graphite is higher in DI 4 than in DI 3. This would suggest that the corrosion rate is influenced more by the type and phase fraction of matrix than the phase percent of graphite. DI 1 shows a lower corrosion current because its matrix is mainly ferritic and the corrosion on the matrix is mostly uniform. An important thing to note is that since all the samples contain graphite nodules, localized galvanic corrosion between the ferrite and graphite cannot be avoided. However, after an initial fast corrosion rate, graphitic residue is left over the surface, which is adherent and corrosion-resistant, in a process called graphitization. This helps in slowing down the rate of corrosion in cast/ductile irons.

Table 5. Phase Percentage of Ferrite, Pearlite, and Graphite Nodules

<table>
<thead>
<tr>
<th>sample</th>
<th>ferrite %</th>
<th>pearlite %</th>
<th>graphite %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI 1</td>
<td>97.87</td>
<td>1.00</td>
<td>10.13</td>
</tr>
<tr>
<td>DI 2</td>
<td>1.98</td>
<td>85.34</td>
<td>12.68</td>
</tr>
<tr>
<td>DI 3</td>
<td>76.22</td>
<td>8.18</td>
<td>15.60</td>
</tr>
<tr>
<td>DI 4</td>
<td>59.45</td>
<td>22.08</td>
<td>18.47</td>
</tr>
</tbody>
</table>

Table 6. Corrosion Current Density, Corrosion Potential, and the Matrix of the Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>matrix type</th>
<th>$E_{cor}$ (mV)</th>
<th>$i_{cor}$ (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI 1</td>
<td>ferritic (F)</td>
<td>−648.5</td>
<td>17.3</td>
</tr>
<tr>
<td>DI 2</td>
<td>pearlitic (P)</td>
<td>−616.0</td>
<td>26.4</td>
</tr>
<tr>
<td>DI 3</td>
<td>F/P</td>
<td>−636.5</td>
<td>20.9</td>
</tr>
<tr>
<td>DI 4</td>
<td>F/P</td>
<td>−646.3</td>
<td>21.8</td>
</tr>
</tbody>
</table>

In this study, the effects of phase fractions, droplet volume, and surface energy on apparent contact angle were investigated on ductile iron. It was found that an increase in graphite fraction increases the apparent contact angle in ductile iron on account of its lower surface energy than the matrix. An increasing droplet volume also led to an increase in the WCA due to contortion of the liquid droplet base. The effects of phase fractions on corrosion characteristics were investigated, and it was concluded that corrosion behavior is affected more strongly by pearlite fraction than by graphite fraction. Therefore, while pearlite is detrimental and graphite is beneficial to corrosion characteristics, an increase in pearlite fraction causes increased corrosion, irrespective of the amount of graphite present in the microstructure.

CONCLUSIONS

In this study, the effects of phase fractions, droplet volume, and surface energy on apparent contact angle were investigated on ductile iron. It was found that an increase in graphite fraction increases the apparent contact angle in ductile iron on account of its lower surface energy than the matrix. An increasing droplet volume also led to an increase in the WCA due to contortion of the liquid droplet base. The effects of phase fractions on corrosion characteristics were investigated, and it was concluded that corrosion behavior is affected more strongly by pearlite fraction than by graphite fraction. Therefore, while pearlite is detrimental and graphite is beneficial to corrosion characteristics, an increase in pearlite fraction causes increased corrosion, irrespective of the amount of graphite present in the microstructure.

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Notes
The authors declare no competing financial interest.

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