Effect of Micro Constituents on Mechanical Behaviour and Corrosion Characteristics of Heat-Treated Alloved Ductile Cast Iron

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Abstract – The current research is focused on the investigation of response to static and dynamic loading condition and corrosive environment with respect to micro constituents of heat-treated alloyed ductile cast iron (DCI). DCI specimens with carbon equivalent (CE) 4.14 & 4.30 underwent annealing, normalizing, quench & tempering, austempering heat treatments processes by austenitization at 1000°C followed by subsequent cooling/quenching techniques. The dual matrix structure (DMS) heat-treatment process was carried out at austenitizing temperature of 800°C and then quenching into mineral oil maintained at 100°C. The mechanical properties viz. UTS, 0.2% YS, % elongation, Vickers hardness and impact strength was determined following respective ASTM standard and correlated with morphological aspects. To study the response to corrosive environment, respective as-cast and heat-treated specimens of alloys were immersed in sea water for 12 weeks, and at regular interval of 1 week the contaminated water was replaced by fresh sea water. The corrosion rate does not appear to follow a specific pattern, which was due to the replacement of fresh sea water with the contaminated one after every interval. The DMS-treated specimens were found to be more corrosion resistive as compared to other heat treated and as-cast specimens irrespective to the alloy composition. The morphological investigation revealed that graphitic corrosion is the primary phenomena that ultimately resulted in high rate of corrosion in specimens treated with normalizing, quench & tempering and austempering processes yielding to higher nodule count.

Keywords: DCI, nuclear fuel cask, corrosion rate, microstructure, fracture

1. Introduction

Ductile cast iron (DCI) also referred as nodular cast iron or spheroidal cast iron has gained popularity compared to other members of the cast iron family due to its superior strength with considerable amount of ductility. The ductile nature of DCI is because of the shape of graphite particle which are spherical in nature resulting in restricting the crack propagation under various loads. Whereas in case of white or grey cast iron due to the presence of flaky shaped graphite particles becomes difficult to restrict the crack propagation resulting lower ductility and impact strength. However, the physical and mechanical properties for DCI can be altered as per the requirement by addition of various alloying elements and/or performing desired heat treatment process. Ductile iron with fully ferritic matrix provides the highest amount of ductility & impact strength compared to any other matrix, whereas austempering treatment enhances strength & hardness along with fair amount of elasticity [1, 2]. Hardening & tempering treatment is applied to decrease the hardness & provide ductility coupled with significantly high strength, the latter being attained by tempering at temperatures ranging from 300°C to 450°C, depending on the chemical composition & the nodule count [3]. Metallographic aspects such as nodularity, nodule count (also referred as nodule density i.e., no. of graphite nodules/mm²) & area fraction of particular phases play a significant role in understanding the behavior under different loading conditions & system responses. The presence of exploded graphite nodules & higher nodule count leads to decrease in hardness & wear resistance irrespective of the matrix microstructure [4]. Yang et.al [5] have studied the effect two different types of austempering procedure on DI & reported the higher value of hardness & strength in case of two-step austempering process. This two-step austempering process had resulted in finer ferrite & austenite as well as higher austenitic carbon in the matrix. They also reported that the two-step austempering process has led to high wear resistance in austempered ductile iron (ADI). Heat treatment of DI through quenching followed by tempering involves delicate processing but leads to the formation of mixed matrix microstructure & presence of retained austenite which eventually improves the strength & toughness of the material [6]. Post-treatment/reheating after quenching gives rise to lower & upper bainitic, tempered martensitic structure depending upon the quenching medium & soaking/tempering time. Longer soaking/tempering time reduces the thermal stress developed during quenching & sometimes the martensite volume fraction as in the case of the studies performed by Wen et.al [7], who observed a decrease in tensile strength & increase in ductility & toughness induced by a reduction in martensite volume fraction. They also suggested that to achieve a better combination of strength & toughness tempering of the specimen
could opt which will eliminate the unfavorable effect of martensite volume fraction.

Use of ductile iron for spent nuclear fuel cask purpose came into picture towards the end of 20th century when the necessity to store & transport the spent nuclear fuel (SNF) away from the reactor site was realized. The benefit of using DI is that it can be cast to near final cask dimensions that reduce machining efforts/costs. The cask can be cast monolithically which eliminate welds in the containment boundary & serves both as the structural containment boundary & as the gamma shield. It also eliminates the needs for the “sandwich” type designs that includes welds & are harder to fabricate. Finally, the cheap material & fabrication costs compare favourably with the traditional sandwich stainless steel cask cost. According to the ASTM A874 Draft Specification Material Properties [8], the desired mechanical properties & microstructural aspects of DI material to be used for nuclear fuel transport cask is presented in Table 1. Mochizuki & Matsushita [9] conducted experiments to evaluate the structural integrity of spent nuclear fuel cask fabricated with an unalloyed ductile iron equivalent to FCD 37 in the JIS Standard. The fracture toughness value of ferritic ductile iron was found to be very low, but analytically it was confirmed that nodular cast iron containers are strong enough to withstand an impact load during drop tests if the applied stresses are less than the yield stress. Also, the critical flaw sizes associated with the yield stress were within the non-destructive inspection capabilities.

The current study is focused on correlating the mechanical properties with morphological aspects of DI specimen by varying the processing conditions viz. cooling rate through oil quenching & air-cooling after austenitization. The effect of alloying elements on promoting different microconstituents like ferrite, martensite & pearlite & effect of phase proportions on mechanical properties is also discussed.

Table 1: The desired mechanical properties & microstructural aspects of DI material to be used for nuclear fuel transport cask, according to ASTM A874 Draft Specification Material Properties.

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTS 45ksi (300MPa)</td>
<td>Essentially ferritic structure with no massive carbides.</td>
</tr>
<tr>
<td>YS 30ksi (200MPa)</td>
<td>&gt; 90% type I &amp; II graphite nodules.</td>
</tr>
<tr>
<td>Elongation 12%</td>
<td>&lt; 275/mm² graphite nodule count.</td>
</tr>
<tr>
<td>Static fracture toughness 50ksi-√inch (55MPa-√m)</td>
<td></td>
</tr>
</tbody>
</table>

II. Materials and Methods

The physical and mechanical properties of ductile iron have a direct relationship with morphological characteristics such as phase volume fraction, nodularity, and nodule count that can be controlled according to desired property requirement and application. In general, it is done by either addition of alloying elements like Cu, Cr, Ni, Mo, etc. or application of suitable heat treatment processes. DCI alloys of different composition determining the carbon equivalent (% CE) is shown in table 2.

Table 2: Chemical composition of alloys studied (in wt. %)

<table>
<thead>
<tr>
<th>Composition</th>
<th>SG - 2</th>
<th>SG - 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.61</td>
<td>3.45</td>
</tr>
<tr>
<td>Si</td>
<td>2.10</td>
<td>2.07</td>
</tr>
<tr>
<td>Mn</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>S</td>
<td>0.007</td>
<td>0.008</td>
</tr>
<tr>
<td>P</td>
<td>0.022</td>
<td>0.024</td>
</tr>
<tr>
<td>Cr</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>0.47</td>
<td>0.15</td>
</tr>
<tr>
<td>Mo</td>
<td>0.001</td>
<td>----</td>
</tr>
<tr>
<td>Cu</td>
<td>0.009</td>
<td>----</td>
</tr>
<tr>
<td>Mg</td>
<td>0.043</td>
<td>0.043</td>
</tr>
<tr>
<td>Ce</td>
<td>0.004</td>
<td>----</td>
</tr>
</tbody>
</table>

| % CE | 4.30 | 4.14 |

In present work five different heat treatment processes viz. annealing, normalizing, quenching & tempering, austempering and intercritical austenitizing followed by quenching are employed to get a range of microstructures. The heat treatments are carried out with the help of OKAY raising hearth furnace (Max. Temp. – 1700°C) for austenitizing. And a pit furnace (Make - Process Instrumentation & Engineering CO., Max. Temp. – 2000°C) for reheating after quenching in the case of respective heat treatment. For austempering, specimens were quenched in KNO3+NaNO3 (1:1 ratio) and in the event of quench & tempering as well as intercritical austenitizing process specimens are quenched in mineral oil maintained at 100°C. The respective heat treatment processes are illustrated in Fig. 1.

![Diagram](image_url)
2.1 Optical Microscopic Analysis

The metallographic investigation is carried out using Metal Power image analyser incorporated with an optical microscope. Before the investigation, standard metallographic sample preparation technique was followed for each specimen and etched with 2% Nital etchant. All the unetched specimens were observed at 10X magnification and undergone for quantitative metallographic analysis for measuring graphite characteristics such as nodularity and nodule count following ASTM E2567-13a Standard. The specimens after etching were viewed at 10X magnification except the austempered specimens which were observed at 20X magnification. The quantitative metallographic technique was also applied to the etched specimens to determine the phase volume fractions in respective as-cast and heat treated specimens of each alloy.

2.2 X-Ray Diffraction Analysis

X-ray diffraction technique is employed to analyse the crystal structure of as-cast as well as heat treated specimens for every alloy studied. Rigaku Ultima – IV X-ray diffractometer with filtered Cu-Kα target (λ = 0.1542 nm) is used for getting the diffraction patterns by scanning specimens between 40°-90° at a rate of 10° per minute. Further, the patterns are analysed by Xpert Highscore and JCPDS tools to acquire the crystallographic planes. The volume fraction of austenite and ferrite in individual austempered specimens are calculated using the Direct Comparison Method, assuming only two phases, i.e., austenite & ferrite were present in the matrix.

The corrosion products were also subjected to X-ray diffraction analysis to investigate the role of alloying elements in corrosion process during subsequent weeks of immersion. The scanning was carried out from 20°-90° at a scanning rate of 10°/minute.

2.3 Mechanical Behaviour and Fracture Analysis

After demoulding the ingots were machined into tensile and Izod impact specimens according to ASTM E8 and E23 – 12c standards respectively. After heat treating the scales formed on the specimen surfaces were cleaned by grinding process and sharp edges were removed carefully. Tensile strength, 0.2% yield strength and %elongation were determined by conducting tension test on INSTRON 1195 universal testing machine incorporated with a computer, at a crosshead speed of 1mm/min. Vickers hardness (HV) was measured using Vickers hardness tester applying 20 kg load. VEEKAY - TL VS4 Izod impact tester was used for obtaining the impact energy, applying 50 J hammer blow at a striking angle of 150°.

To investigate the mode of failure under monotonic tensile and dynamic impact loading condition, fractured surfaces for each as-cast and heat treated specimens after tensile and impact test is investigated under JEOL - JSM 6480LV, Scanning Electron Microscope.
2.4 Corrosion Behaviour

Corrosion study was carried out by subjecting each specimen to sea water immersion under room temperature and pressure for twelve weeks following ASTM G52 – 00 (Reapproved 2011) standard. Weight loss of each specimen is noted down after a regular span of time, i.e., 173 hours with the help of Contec microbalance (0.001 gm. accuracy). The corrosion rate is calculated by equation 3.2, as stated in the Standard ASTM G1 – 03 (Reapproved 2011).

\[
\text{Corrosion rate} = \frac{K \times W}{A \times T \times D}
\]

Where:

- \(K = 8.76 \times 10^4\), A constant (decided on the basis of final unit i.e., mm/year in this case),
- \(T = 173\) hours, Time of exposure in hours,
- \(A = 0.66\) cm\(^2\), Area in cm\(^2\),
- \(W = \) Mass loss in grams, and
- \(D = \) Density in gm. /cm\(^3\).

To investigate the corrosion mechanism as well as role of chemical composition, corrosion products were investigated under SEM/EDAX elemental mapping. Two different type of products were analysed i.e., the corrosion scale over the surface of specimens and the porous product collected after 1st and 12th week of immersion.

III. Results and Discussion

3.1 Morphological Characterization

3.2.1 Optical Microscopy Analysis

The microstructure of as-cast and heat-treated specimens are shown in Fig. 2. It can be clearly seen that all the specimens have graphite nodules lodged into the respective matrices. There was no difference in the microstructure was observed after subsequent heat treatment processes for both the alloys. However, the difference in as-cast microstructure can clearly be observed that alloy SG-2 has ferritic matrix whereas that for alloy SG-9 is pearlitic/ ferritic in nature. This can be attributed to the higher amount of Si and Cr present in alloy SG-2, that promotes ferrite formation and suppresses the initiation of pearlite in the matrix. The two stage annealing process comprises of a slow cooling rate resulting slower transformation of the parent matrix from the austenite stage, consequently achieving fully ferritic matrix as can be observed in Fig. 2 (c). The full annealing treatment resulted in a significant reduction in cooling rate (close to equilibrium eutectoid transformation temperature), which significantly increased the ferrite fraction in the matrix. The volume fraction of ferrite was found to be higher for alloy SG-2 than that of SG-9, which can further be attributed to the difference in amount of Si and Cr in respective alloys. The normalized heat treatment resulted in a pearlitic-ferritic matrix, due to increased rate of cooling as compared to annealing process. A higher transformation temperature leads to the lower driving force resulting less growth rate about the diffusion speed giving rise to large pearlite spacing, whereas lower temperature results in finer spacing.

The dominance of Si and Cr was also observed in this case as complete perlitic transformation was not achieved and the volume fraction of ferrite in case of alloy SG-2 was found to be higher. The quenching in paraffin oil at 100°C and subsequent reheating at 500°C resulted in tempered martensitic matrix with graphite nodules lodged into it, for both alloys as can be seen in Fig. 2(e). The tempering of oil quenched specimens at 500°C resulted in breaking of large martensite into tempered martensite [13]. On the other hand following similar heat treatment process by quenching in salt bath solution at 500°C and maintaining there for 5hr30mins resulted in coarse upper bainitic matrix with graphite nodules embedded within, in case of both the alloys that can be accredited to two facts. One is the high austenitizing temperature and longer austenitizing time, leading to increased stable austenite and less ferrite formation [14] and secondly high austempering temperature and time that results in coarsening the ferrite [15]. Austempering involves a two-step reaction process consisting transformation of primary austenite into acicular ferrite and carbon enriched austenite in 1st stage reaction, and the 2nd stage reaction comprises a decomposition of carbon enriched austenite in ferrite-carbide aggregate depending on the temperature and time. The austempered specimens were observed to free from carbide and martensite due to the higher austenitizing temperature that resulted in complete austenitization and higher austempering temperature and time, i.e., 500°C and 240 minutes respectively that suppresses the carbide precipitation and martensite formation [16–19]. The higher amount of Ni and addition of Cu into alloy SG-2 resulted in higher volume fraction of bainite compared to that for alloy SG-9. The results are in agreement with that observed by [20]. The inter-critical austenitization followed by quenching in mineral oil to room temperature resulted the transformation of as-cast matrix into a matrix combining ferrite and martensite with graphite nodules surrounded by ferrite, for both the alloys. Intercritical heat treatment commences with partial austenitization that depends on the alloy composition and temperature. The partial austenite transforms to martensite upon quenching in oil resulting in a final matrix of graphite nodules embedded in ferrite + martensite [21]. It was observed that most of the alloys have the large graphite spheroids surrounded by ferrite phase, which is further localized by martensite. Such arrangement of phases can be explained by the nucleation and growth of martensite at the intercellular boundaries [22]. It was noticed that the martensite was continuous and distributed uniformly in both the alloys. All of the specimens was observed to undergone a complete transformation without any precipitation of carbides or retained austenite after respective heat treatment.
processes, which is good enough for obtaining higher ductility in respective materials. Again the increased amount of Ni and addition of Cu resulted in increased amount of martensite in case of alloy SG-2, as both the elements are good promoter of austenite [23].

The nodularity and nodule count for as-cast and heat treated specimens of both the alloys are presented in Table 2, and can be noticed that there was not much difference in nodularity in respective cased. However the increased nodule count for alloy SG-2 in as-cast as well as heat treated specimens, was due to the addition of Ce that act as a graphite accumulator during the solidification process [24]. It can also be noticed that the nodule count value was higher for the heat treatment processes with increased rate of cooling than that of as-cast and annealed specimens where specimens undergone a slow cooling rate, for both the alloys. This can be attributed to the fact that increased rate of cooling that restricts the movement of carbon atoms from getting accumulated at nearby sites, resulting increased nodule count and potential secondary graphite particles which cannot be considered as nodules, at final microstructure [25-28].
Fig. 2: Microstructure of As-cast and heat treated specimens after etching (Nital 2%).

F - Ferrite, G - Graphite, P - Pearlite, M - Martensite

Table 2: Morphological parameters for the respective alloys in as-cast and heat treated conditions

<table>
<thead>
<tr>
<th>Heat treatment Process</th>
<th>Nodularity (%)</th>
<th>Nodule Count (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SG - 2</td>
<td>SG - 9</td>
</tr>
<tr>
<td>As-cast</td>
<td>95</td>
<td>97.5</td>
</tr>
<tr>
<td>Annealed</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Normalized</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>Quench &amp; Tempered</td>
<td>99</td>
<td>92</td>
</tr>
<tr>
<td>Austempered</td>
<td>93</td>
<td>87.5</td>
</tr>
<tr>
<td>DMS</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

3.2.2 X-Ray Diffraction Analysis

The X-Ray diffraction pattern for as cast and heat-treated specimens is shown in Fig. 3. It can be noticed that there were only three major crystallographic planes found for every state i.e., plane (1 1 0) at 43°, 2θ position with d-spacing of 2.02, plane (2 0 0) at 65° with d-spacing of 1.43 and plane (2 1 1) at 82° with d-spacing of 1.17. All of these planes belong to BCC crystal structure which confirms the ferritic, pearlitic-ferritic, tempered martensitic, and ferritic + martensitic matrix for as-cast, annealed, normalized, quench & tempered, and DMS treated specimens, as obtained from metallographic investigation. However, for specimens underwent austempering heat treatment a plane of (3 1 1) was obtained at 65° with d-spacing of 1.43. The plane (3 1 1) belongs to the FCC crystal structure and thus confirms the presence of retained austenite in the matrix microstructure of austempered specimens. Quantitative XRD analysis was carried out for austempered specimens to determine the volume fraction of ferrite and austenite in individual alloys, following the Direct Comparison Method and assuming only ferrite and austenite was present in the matrix. The austenite and ferrite volume fraction and carbon content in the retained austenite was calculated from the equation stated in equation 2 and 3 respectively. It was observed that the carbon content in the retained austenite was increased with increase in the carbon content of the alloy. The phase volume fractions in respective alloys are presented in Table 3. The volume fraction of retained austenite was observed to increase with the increase in Ni content as was observed from the quantitative metallographic investigation.

\[ X_\gamma = \frac{I_\gamma/R_\gamma}{(I_\gamma/R_\gamma) + (I_a/R_a)} \quad - - - - - - (2) \]

\[ a_\gamma = 0.3548 + 0.0044C_\gamma \quad - - - - - - (3) \]

Where \( I_\gamma \) and \( I_o \) are the integrated intensities and \( R_\gamma \) and \( R_a \) are the theoretical relative intensity for the austenite and the ferrite, respectively. And \( a_\gamma \) is the lattice parameter of austenite in nanometre and \( C_\gamma \) is the carbon content of austenite in wt.%.  

Table 3: Volume fraction of austenite and ferrite and carbon content in austenite of respective austempered specimens.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Carbon content in austenite (Cγ)</th>
<th>Austenite volume fraction</th>
<th>Ferrite volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG-2</td>
<td>2.6393</td>
<td>87.95%</td>
<td>12.05%</td>
</tr>
<tr>
<td>SG-9</td>
<td>2.5941</td>
<td>70.00%</td>
<td>30.00%</td>
</tr>
</tbody>
</table>
3.2 Mechanical Properties

3.2.1 Vickers Hardness

The interesting fact observed in hardness values for as-cast and heat-treated specimen was that the standard deviation was minuscule, that indicates uniform and homogeneous matrix, achieved during casting and heat treatment processes as well. The hardness values were observed to be increasing with the rate of cooling from the austenitization stage. The reason was quite clear that increased rate of cooling resulted in formation of harder matrices. The Vickers hardness for alloy SG – 2 in case of as-cast and annealed specimen was close to each other due to the presence of pearlite content. However in case of alloy SG – 9 the hardness of as-cast specimen is higher than that of annealed specimen due to the presence of pearlite in the former case. It was observed that the hardness of annealed specimen in case of alloy SG – 2 was higher than that of SG – 9 although for both the alloys the matrix fully ferritic. The reason behind this was the higher amount of Ni content that results in increasing hardess by solid solution strengthening for ferritic matrix[29]. The hardness values in case of normalizing, quench & tempering, austempering and DMS treatment appeared to be higher for alloy SG – 2 than that of SG – 9, that can be attributed to the the higher Ni content resulting higher austenite at the eutectic stage resulting subsequent presence of pearlite, and martensite at the final microstructure leading to higher hardness. However the additional alloying elements viz. Cu and Mo are also responsible for increased hardness even though it is present in smaller amount.

3.2.2 Strength & Elongation Characteristics

Specimens underwent full annealing treatment resulted with the lowest strength values and highest ductility, and that of greatest strength and lowest ductility was obtained for alloys in quench and tempered specimens. The strength and elongation values of the as-cast and annealed specimens were pretty close to each other without any significant difference, which may be due to the presence of similar matrix microstructure. The large transformation window and the slow cooling process of annealing treatment led to lower hardness value; a similar effect was observed for decreased tensile strength and a favorable effect for improved ductility [27]. The strength values in case of as-cast specimen was observed to be higher for alloy SG – 9 due to the presence of pearlite content. The normalized treatment resulted pearlitic /ferritic matrix showed strength higher than that of as-cast and annealed specimens for respective alloys. Whereas on comparison for both the alloys, alloy SG – 2 had higher strength with lower ductility and impact energy than that of SG – 9, that can be accredited to the effect of higher Ni content and presence of Cu in promoting austenite at upper critical region consequentially resulting higher amount of perlite volume fraction. The effect of higher Ni content was also observed for quench & tempering, austempering and DMS treated specimens in similar fashion. The tempered martensitic specimens appeared to have highest strength and hardness value with lowest ductility and impact energy, whereas fully ferritic specimens had lowest strength and hardness with highest ductility and impact energy. The pearlitic, bainitic and ferritic + martensitic matrices have properties intermediate to that of annealed and tempered martensitic specimens. The influence of ferrite promoting elements viz. Si and Cr was also observed in both the case, resulting proeutectoid ferrite content in all the matrices leading to considerable amount of ductility and impact energy, for both the alloys.
Table 3: Mechanical properties of respective alloys in as-cast and heat treated condition

<table>
<thead>
<tr>
<th>Heat-treatment</th>
<th>Tensile strength (in MPa)</th>
<th>0.2% Yield strength (in MPa)</th>
<th>Elongation at Fracture (in %)</th>
<th>Impact Energy (in J)</th>
<th>Vickers Hardness (HV20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cast</td>
<td>334.5</td>
<td>522</td>
<td>160.63</td>
<td>192.57</td>
<td>31.2</td>
</tr>
<tr>
<td>Annealed</td>
<td>328.7</td>
<td>349.7</td>
<td>159.7</td>
<td>199.4</td>
<td>32.8</td>
</tr>
<tr>
<td>Normalized</td>
<td>847.7</td>
<td>722.4</td>
<td>245.6</td>
<td>371.1</td>
<td>14.1</td>
</tr>
<tr>
<td>Quench &amp; Tempered</td>
<td>1099</td>
<td>1039.6</td>
<td>722.9</td>
<td>269.7</td>
<td>11.2</td>
</tr>
<tr>
<td>Austempered</td>
<td>990.4</td>
<td>783.9</td>
<td>356.7</td>
<td>434.3</td>
<td>14.4</td>
</tr>
<tr>
<td>DMS</td>
<td>504.4</td>
<td>400.1</td>
<td>312.4</td>
<td>288.65</td>
<td>19.01</td>
</tr>
</tbody>
</table>

3.2.3 Fractographic analysis.

The Fractographic images of as-cast and heat treated specimens after tensile, and impact fracture is shown in Fig. 4.1 and Fig. 4.2 respectively. The as-cast and annealed specimens with ferritic matrix observed to have dimples around the graphite nodule and on the matrix as well, Fig. 4.11 (a) & (b) respectively. Due to decohesion at the ferrite graphite interface the micro-voids nucleates at the naked region and grows at the grain boundary; suggesting that extensive deformation has occurred for ferrite prior to the fracture and the material is highly ductile. The deformation of ferrite matrix during the end period of straining before the fracture was evident from the dimples around graphite nodule [30]. On the other hand, the pearlitic, tempered martensitic and bainitic specimens had river markings and cleavage facets over the matrix justifying the brittle nature of the fracture. Martensite characterizes lower strain leading to a low rate of deformation mechanism culminating brittle fracture. The quenching process results in segregation of sulphur and phosphorus impurities before the austenite grain boundaries that result in the favorable growth of transgranular paths, thereby reducing the cohesive strength [30]. The transgranular cracks were initiated at graphite/matrix interface and start to propagate where there is an atomic mismatch between the phases such as ferrite/austenite interface in case of austempered specimens. The austenite being soft tends to deform whereas ferrite starts cracking and the crack propagates along the length of ferrite sheaves [30, 31]. The cleavage facets appeared due to the plastic deformation of the matrix, and the growth of deformation was because of the presence of secondary phase particles [22]. The transgranular, low energy stress paths (river markings) that signify cleavage fracture are derived from the separation of atomic bonding and change direction when passes through the sub-grain boundaries graphite nodules [32], [33]. The DMS-treated specimen had both dimples around the graphite nodules and river markings which are an indication of the mixed mode of fracture that justifies the semi-ductile nature of the specimen. The voids nucleate at the ferrite-martensite interface associated with decohesion from the adjacent martensite [22]. The continuous martensite along the intercellular boundaries is a vital factor that determines the deformation extent of ferrite around graphite nodules. Alloys with higher martensite fraction were observed to have zero deformation of ferrite under tensile loading, suggesting decreased ductility with martensite continuity in the matrix. All the specimens showed similar kind of behaviour under impact loading condition that observed under monotonic uniaxial tensile loading and is shown in Fig. 4.2.

Fig. 4.1: Fracture surfaces of as-cast and heat treated specimens after tensile failure.
3.3 Corrosion behaviour

The nuclear spent fuel casks often disposed under the sea at distance of 30m deep from the sea level. The purpose is twofold; first, if in any case the containment fails to serve its purpose, nuclear radiations won’t scatter into the environment and consequentially do not pose a threat neither to the environment nor to the living being. And the second is to cool the container, from the liberating heat of spent nuclear fuel. The response of SGCI samples of alloys SG – 2 and SG – 9, in as-cast and heat treated conditions, with sea water environment are illustrated in Fig. 5.1 and Fig. 5.2 respectively in terms of corrosion rate vs. time plot. It can be noted that there was no significant pattern obtained for any of the as-cast or heat treated specimens over the time. This unusual corrosion behaviour in as-cast and heat treated conditions can only be attributed to the fact that after every regular time interval the specimens had been subjected to fresh sea water, resulting variation in the reactivity level of sea water that was exposed to the specimens. The reactivity level of sea water was evident from the pH value noted at the end of every 173 hours. The highest rate of corrosion was obtained for austempered specimens with coarse upper bainitic matrix and that of lowest for the DMS treated specimens having ferrite and martensite in matrix microstructure. The corrosion rate follows DMS-treated < annealed < as-cast < normalized < quench & tempered < austempered, pattern for all the alloys. The large corrosion exhibition of normalizing, austempered and Quench & tempered specimens can be attributed to the fact that, increased rate of cooling resulted in increased nodule count leading to increased potential sites for graphitic corrosion. Although in many observations some values are higher than 50µm/year, but some values below 50µm/year is also observed in some cases. Moreover, these data are acceptable and also not yet objected after the sample tests conducted by Bhaba Atomic Research Centre (The purpose of the BRNS sponsored project).

The resistance to corrosion can be improved by the addition of Ni, Cu, and Cr. It was clear that the austempering treatment exhibited highest corrosion rate and that of annealed, and DMS are the lowest for every alloy composition. In this case, the difference of Cr content in respective alloys is very minor and hence its effect was not significant or negligible. On the other hand, the corrosion resistance was observed to decrease with increase in Ni and Cu content. Copper addition reduces the nodule count and additionally forms a compact Cu2O passive oxide film over the alloy surface in chloride solution which is mainly responsible for better corrosion resistance [34]. Additionally, Nickel and Copper shifts the open circuit potential to more positive values resulting the alloy to enter into the passive region under natural immersion in solutions with high pH like seawater [34]. Furthermore, the addition of Nickel results in reduced nodule count and consequentially reduces the graphitic corrosion potential of the concerned alloy [35]. The formation of Cu2O has not been observed on the corroded surface but found in the porous product. Also, the sea water contains ions of other than Na+ & Cl−, so it was quite possible that during the reaction other ions might have led to the formation similar potential that was repellent to each other and leading to removal of scale from the surface. Hence the Cu2O compound was only observed in the porous product, and not on the corroded surface.
3.3.1 Morphology of Corroded Surfaces

Two different type of products were analysed i.e., the corroded surfaces of specimens and the porous product collected after 1st and 12th week of immersion. The surface micrographs of as-cast and heat treated specimens as well as porous product, after 1st week of immersion are presented in Fig. 6.1. It was observed that, the specimens were experienced with localized attack at the boundaries of the spherical nodules and at the grain boundaries. The localized attack resulted in fine network of cracks near the grain boundaries covered with non-homogeneous lose scale like layer. The results observed were quite in agreement with the observation made by Zeng et.al [36], who studied the corrosion response of SGCI and laser surface alloyed SGCI in HCl solution. Similar results were also observed by Venkatesan et.al [37] for austempered specimens treated in still deep sea water. Pitting corrosion was observed over the specimen surfaces, with porous layers allowing to the water to impinge through the scale and react with base material resulting increased rate of corrosion, which may be the reason of highest rate of corrosion in present case. The pitting corrosion mechanism was attributed to the reaction of SGCI samples with sea water under physico-chemical condition. The surface micrographs of as-cast and heat treated specimens as well as porous product, after 12th week of immersion are presented in Fig. 6.2. The surfaces after 12th week of immersion were observed to be covered fully with corroded layer and no graphite particle was found. The EDAX spectra revels the presence of Fe, O, and C in major quantity whereas other alloying elements were found in traces. The absence of Ni, Cr, Mn was the evidence of iron oxide layers over the surface which can due to the reaction between sea water and the base material. As compared to the 1st week fewer cracks were found on the corroded layer suggesting precipitation of corrosion products when subjected to longer time period. The porous products were also found to have Fe and O in major quantity.

Fig. 6.1: Surface morphology of corroded surfaces and the porous product after 1st week of immersion.

3.3.2 X-Ray Diffraction Study of Corrosion Product

To understand the role of alloying elements in the process of corrosion, specimens after 1st week of exposure and 12th week of exposure, were subjected to XRD investigation. Two different corrosion products were analysed. One was the precipitated layer over the specimen surface and another was the porous settled product in the reactor that was taken carefully and dried. The XRD patterns were shown in Fig. 7. It was observed from the XRD analysis that Chromium, Iron and Oxygen have played a major role. Besides these elements Copper and Nickel also had significant role in the process. The major compounds found from the specimen surface are FeOOH, Cr2O3and Fe-Cr-Ni. The result was quite obvious and convincing as it was well known that when iron comes in contact with water it forms iron hydroxide. The results are also in agreement with that obtained from the EDAX analysis. It was observed that after the end of 1st week oxides of Chromium, Magnesium, Chlorine, and Iron were found. The as-cast specimen was observed to have FeOOH, and Cr3O were found after 1st week of immersion, which was absent after 12th week. At the end of 12th week FeOOH compound was found in as-cast and heat treated specimens, justifying the observation of EDAX analysis. Copper and Molybdenum was found to have significant role in case of normalized and quench & tempered specimen after 12th week of exposure, whereas in case of austempered and DMS specimens, MgO was found to be replaced by FeOOH.

Fig. 6.2: Surface morphology of corroded surfaces and the porous product after 12th week of immersion.
Fig. 7: XRD pattern for corroded surfaces after 1st and 12th week of exposure.

IV. Conclusion

SGCI cast blocks with %CE of 4.14 and 4.30 were fabricated by conventional sand casting technique, from which tensile and Izod impact specimens were machined. The specimens were then subjected to annealing, normalizing, quench & tempering, austempering and intercritically austenitizing followed by quenching, heat treatment processes. The mechanical properties and corrosion studies were carried out on the as-cast and heat treated specimens and the results were correlated to the morphological characteristics as well as effect of alloying was studied. The concluding remarks of the whole research work is stated as follows.

1. Alloy SG – 2 possesses ferritic matrix and alloys – 9 had pearlitic matrix with graphite spheroids embedded within in as-received state. The graphite spheroids belong to Type I (fully spherical) nodule with nodularity value more than 90% and the nodule count ranges from 28 - 40 nodules per unit area.

2. Ferrite volume fraction was observed to increase with increased Si content whereas the nodularity and nodule count was attributed to the increased amount of Mg as well as presence Ce, Cu and Si.

3. Normalizing, quench & tempering, austempering treatment resulted in pearlitic/ferritic, tempered martensitic and coarse upper bainitic matrix respectively with graphite nodule lodged into the respective matrix. On the other hand, the intercritically austenitized followed by quenching in mineral oil led to transformation of as-cast ferritic matrix into ferritic + martensitic matrix.

4. The soft ferritic matrix of as-cast and annealed specimens resulted in microvoid coalescence leading to formation of dimples around the graphite globules and on the matrix suggesting ductile nature failure. Whereas the normalized, quench & tempered and austempered specimens showed the brittle nature of material characterized by the presence of low energy stress paths (river markings) and cleavage facets. The DMS treated specimens have illustrated both dimples around the nodules as well as river marking on the matrix elucidating mixed mode of fracture. There was no significant difference observed in the fracture phenomena of tensile and impact fracture.

5. The corrosion behaviour of as-cast and heat treated specimens of respective alloys didn’t show any significant pattern over the time. This unusual corrosion behaviour in as-cast and heat treated condition can only be attributed to two reasons. The first one is that after every regular time interval the specimens had been subjected to fresh sea water, resulting variation in the reactivity level of sea water with the exposed surfaces of specimens. And secondly, the area of specimen exposed to the corrosion environment.

6. The austempered specimens observed to corrode more rapidly than the other heat treated and as-cast specimens, whereas the DMS treated specimen had the least rate of corrosion. The rate of corrosion was also decreased with increased amount of Nickel.

7. The mechanical properties obtained for respective alloys in as-cast and heat treated condition are well above the desired properties of SGCI nuclear fuel cask specification.

V. Acknowledgement

The authors deeply acknowledge the financial support provided by Board of Research in Nuclear Science (Project Grant No. 2011/36/18-BRNS), India in order to carry out this investigation. The authors also express their gratitude towards the help of L&T Kansbahal, India for providing test blocks for this investigation & M/S Steelage Engineering works,


