CHARACTERIZATION OF CRYOGENICALLY TREATED CARBIDIC AUSTEMPERED DUCTILE IRON (CADI)

S.A.Patil¹, Ajay Likhite², S.U.Pathak³, C.L.Gogte⁴

¹Ph.D. Scholar, VNIT-Nagpur-440010, INDIA
²³Senior Faculty, Department of MME, VNIT Nagpur-440010, INDIA
⁴Senior Faculty, COE-MME laboratory, MIT Aurangabad-431005, INDIA

ABSTRACT
The abrasion wear resistance of ductile iron is improved by the reinforcement of an extra phase in the matrix, typically consisting of carbides. However, the brittleness induced due to carbides in ductile iron is counteracted by the process of austempering. Carbidic austempered ductile iron, thus obtained has superior wear resistance than as-cast carbidic ductile iron. The positive effects of cryogenic treatment on the wear resistance of tool steels have been very well researched so far. However, the response of carbidic austempered ductile iron to cryogenic treatment is not yet known. The objective of the present work is to evaluate the response of austempered pre-inoculated carbidic ductile iron (CADI) to cryogenic treatment. The characterisation of the cryogenically treated CADI was carried out by using optical microscopy, SEM, and hardness measurement. The wear characteristics were obtained by using pin-on-disc machine.

Keywords: CADI, Carbides, Characterization, Cryogenic-Treatment, Wear.

I INTRODUCTION
The research on the austempered ductile iron (ADI) has established that good, consistent and improved wear characteristics can be obtained on selection of proper austempering parameters[1]. By incorporating the carbides in the typical matrix of DI, the Carbidic ductile iron CDI has been developed. Austempering the CDI, lead to a microstructure of carbides distributed in the typical ausferritic matrix, resulting in to CADI. The available literature of CADI focuses on engineering rather than the technology of its production. CADI is a ductile cast iron containing carbides that is subsequently austempered to produce an ausferritic matrix[1-2].

Presently ADI has variety of commercial applications. For example, Buckets of bucket conveyor, drilling bits of bore well drills, Soil aerator used in agriculture purposes, conveyor chutes etc. The applications involved are where the components are subjected to maximum wear. Some automotive applications are also reported by automotive industry in engine cam shaft, valves, gears etc. The development of CADI and its superiority over ADI makes it a next competitive material for the above mentioned applications.

Therefore improvement in the wear characteristics of CADI is an important area to be investigated. Last decade has seen an extensive research on the cryogenic treatment of tool steels and many other ferrous and nonferrous
materials. However the effects of the cryogenic treatment on CADI are not yet investigated. The following two sections give the brief outline of CADI and the cryogenic treatment.

1.1 CADI
The development of CADI was reported by S.Liano et al. by three methods. In the first methodology they followed to obtain a microstructure with as-cast carbides by reducing the quantity of graphitizing elements (in particular Si), in order to promote the precipitation of ledeburitic carbides during solidification due to a closer interval between the stable and metastable diagrams[3]. In the second methodology alloy the melt with carbide stabilizing elements, such as chromium, molybdenum or titanium [4,5], which strongly reduce the interval between stable and metastable eutectic temperatures and promote total or partial solidification according to the metastable diagram[6]. In third methodology under cooling also affects the size and count of the solidification units. The lower the cooling rate, the greater the micro segregation effect, increasing the probability for carbide precipitation in the last to freeze dendrite zones[3], thereby favoring, formation of alloyed carbides. The size and composition of carbides may vary, from typical unalloyed ledeburitic to thin plate shaped high-alloyed carbides, depending on the chemical composition and cooling rate[6-7]. It has been reported that ledeburitic carbides produced either by controlling the cooling rate or the silicon level (nonalloyed carbides) have a high tendency to dissolve during the austenitizing stage and are less stable than alloyed carbides[8]. Alloyed carbides are stable, without any dissolution of carbides during heat treatment[9].

1.2 Cryogenic Treatment
It has been found that cryogenic treatment actually affects the microstructure of the entire object. Because it is not a surface treatment, it affects the entire cross section of material and lasts throughout the life of the object. Even after Continuous use, the material will still maintain its strength. Due to this treatment hardness is not much affected, but the material becomes more resistant to wear[10]. The improvement in wear resistance is mainly attributed to the conversion of retained austenite to martensite[11], and precipitation of fine secondary carbides during the cryogenic treatment[12-13].

The objective of present work is to Cryo-treat the produced CADI alloying with Chromium content and study their microstructural characteristics and evaluate the abrasion resistance. These Cryogenically-treated CADI alloys are compared with austempered pre-inoculated Carbide ductile iron (CADI).

II EXPERIMENTAL PROCEDURE

2.1. Material and Sample Preparation
The compositions in cast iron heat C1 was melted in a 100 kg capacity core-less, high frequency induction furnace. Silicon steel scrap and foundry returns were used as charge materials along with make up additions for Si, Ni, Cu, C etc. The heat was alloyed with Cr to favor the precipitation of alloyed cementite (Fe Cr)3 C. All the heat was pre-inoculated ladle inoculation nodulized by sandwich method with Fe–Si–Mg (9 wt% Mg) alloy, at the temperature of 1500°C, the small additions of copper and nickel were made so as to provide enough hardenability,
austemperability[9]. The standard test bars sectioning 15x15x200mm (long) are cast. TABLE 1 shows the chemical composition of As-cast CDI. The CDI bars are austempered and the CADI samples produced. The same is used as reference material. Sample identification, depending on the composition and heat treatment, is given in TABLE 2.

Table No. 1 shows Chemical Composition CADI

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>C%</th>
<th>Si%</th>
<th>Mn%</th>
<th>S%</th>
<th>P%</th>
<th>Cr%</th>
<th>Cu%</th>
<th>Ni%</th>
<th>Ti%</th>
<th>Mg%</th>
<th>CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>percent</td>
<td>3.6</td>
<td>1.90</td>
<td>0.64</td>
<td>0.0122</td>
<td>0.0294</td>
<td>4.30</td>
<td>0.610</td>
<td>0.431</td>
<td>0.016</td>
<td>0.044</td>
<td>4.23</td>
</tr>
</tbody>
</table>

Table-2 Identification of Sample according to process parameter

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Process parameter</th>
<th>ID for 24 hrs Cryo</th>
<th>ID for 36 hrs Cryo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Composition C1, Austempered at 250°C for 1 Hr (C1-250-1hr) and CRYO -185°C</td>
<td>E1-24</td>
<td>E1-36</td>
</tr>
<tr>
<td>2</td>
<td>Composition C1, Austempered at 250°C for 2 Hr (C1-250-2hr) and CRYO -185°C</td>
<td>E2-24</td>
<td>E2-36</td>
</tr>
<tr>
<td>3</td>
<td>Composition C1, Austempered at 250°C for 3 Hr (C1-250-3hr) and CRYO -185°C</td>
<td>E3-24</td>
<td>E3-36</td>
</tr>
<tr>
<td>4</td>
<td>Composition C1, Austempered at 325°C for 1 Hr (C1-325-1hr) and CRYO -185°C</td>
<td>E4-24</td>
<td>E4-36</td>
</tr>
<tr>
<td>5</td>
<td>Composition C1, Austempered at 325°C for 1 Hr (C1-325-2hr) and CRYO -185°C</td>
<td>E5-24</td>
<td>E5-36</td>
</tr>
<tr>
<td>6</td>
<td>Composition C1, Austempered at 325°C for 3 Hr (C1-325-3hr) and CRYO -185°C</td>
<td>E6-24</td>
<td>E6-36</td>
</tr>
<tr>
<td>7</td>
<td>Composition C1, Austempered at 400°C for 1 Hr (C1-400-1hr) and CRYO -185°C</td>
<td>E7-24</td>
<td>E7-36</td>
</tr>
<tr>
<td>8</td>
<td>Composition C1, Austempered at 400°C for 2 Hr (C1-400-2hr) and CRYO -185°C</td>
<td>E8-24</td>
<td>E8-36</td>
</tr>
<tr>
<td>9</td>
<td>Composition C1, Austempered at 400°C for 3 Hr (C1-400-3hr) and CRYO -185°C</td>
<td>E9-24</td>
<td>E9-36</td>
</tr>
</tbody>
</table>

2.2 Austempering and Cryo-treatment cycle

The cast sample after initial fettling and surface cleaning are subjected to heat treatment, a heat treatment which involves an austenitizing in the temperature range of 900-920°C in a muffle furnace for 1h, followed by an austempering in a salt bath at three different temperatures and three different time intervals 250°C, 325°C, 400°C and 1h, 2h, 3h, these process parameters selected are slightly different than the previously quoted literature. Less work is available on CADI to provide the heat treatment parameters. The samples for metallographic investigations, wear and hardness testing were cut from the heat treated bars of CADI, as-cast for CDI samples. The prepared samples are Cryo-treated at -185°C for 24 hrs and 36 hrs. The heat treatment cycle is as shown in Fig 1.
2.3. Microstructural Investigation

The photo-micrographs were taken after standard polishing and etching with 2% nital on SEM of JEOL JSM-6380A Analytical Scanning Electron Microscope. Volume fraction of carbides was measured by optical image analyzer. Carbides were revealed by etching with 10% ammonium persulfate in aqueous solution. The X50 magnification was used to obtain data from a sufficiently large area. Each reported value is the average of four observations over the cross-section.

2.4. Hardness Tests

Rockwell hardness was measured at 150 kg load (HRc) on C-scale. A hardness profile was obtained for each alloy. In order to determine the hardness of the carbides and the matrix separately, micro indentation tests were carried out by using a Vickers indenter at a 200g load (HV200).

2.5 Wear test

The abrasion wear resistance was evaluated by performing the “Pin on disc Abrasion Test”. The disc is of diamond coated ring having hardness of around 3000HV and width of 10mm (Fig. 2) according to the ASTM G-99 standard, and using the procedure A (test load 20N, distance traveled for 14450 meter, at 400rpm and track radius 58mm pin diameter is 8mm and length 25mm). The relative wear resistance index (E) was obtained as the ratio between the weight loss experienced by the Carbidic Ductile Iron (CDI) samples, used as reference material (WLR), and the Cryo-treated CADI samples (WLS), according to (1). The weight loss values were measured by means of a 0.1 mg precision scale.
Figure.2 Pin and Disc of Diamond coated ring for wear test

\[ E = \frac{WLR}{WLS} = \frac{\text{Weight Loss Reference (CDI) sample}}{\text{Weight Loss Test (Cryo-CADI) sample}} \] -- (1)

2.5 XRD

The XRD of C1 as-cast and austempered sample is done at copper k-α radiation, which revealed the peaks of present composition. The XRD graph of as-cast is shown in the results.

III RESULTS AND DISCUSSION

3.1. Microstructural Characterization

TABLE 1 lists the chemical compositions of Carbidic Ductile Irons C1. The C1 is nearly eutectic (CE=4.23%) and alloyed with 4.30% Cr. The heat was alloyed with chromium in order to promote partial solidification according to the Fe–C metastable diagram[3]. Fig 5, 6 and 7 show the microstructures images of as-cast condition for C1 at magnification 200x and SEM micrograph at 5000x magnification, of austempered and Cryo-treated CADI at three temperatures (250°C, 325°C, 400°C), three time durations (1h, 2h, 3h) and (-185°C for 24hrs, 36hrs)of samples E1 to E9. Carbides were precipitated in plate needle form at random and pearlite is present in as-cast sample while in Austempered (CADI) the carbides are at random in thick net plate needle form. The matrix is completely ausferritic and in Cryo-treated CADI samples the carbides and ausferrite is reinforced perfectly in the matrix. In all heat treated samples the Ausferrite size is larger for two hrs austempering , which is clearly seen in the SEM micrograph images. The volume fraction of carbide in microstructure is shown in TABLE 3.

Table 3 shows volume fraction carbide in CDI Microstructure in as-cast

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Volume % carbide</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>54.9</td>
</tr>
</tbody>
</table>

3.1.1 As-cast samples

The as-cast sample microstructure is shown in Fig. 4 which indicates the microstructure of C1 consists of thick net and needles of carbide plates and ferrite is present in between the carbides which are revealed by XRD. The carbide is precipitated as a function of the Cr%, CE and Silicon.
3.1.2 XRD

The XRD of C1 as-cast and austempered sample is done at copper k-α radiation, which revealed the peaks of Ferrite, Iron carbide and Chromium iron carbide in as-cast sample and Austenite, Ferrite, Iron carbide and Chromium iron carbide in austempered samples of C1. The same peaks are observed in all austempered E1 to E9; only the variation is the little shift of peaks and the counts (AU) of various elements as observed in XRD, as shown in Fig. 3.

Figure 3 show the XRD of As-cast C1 which reveals the presence of ferrite, iron carbide and chromium iron carbide

3.1.3 Effect of Austempering temperature

After austempering CDI samples, the matrix was ausferritic exhibiting the typical morphology i.e. reinforcement of carbide and ausferritic matrix[14] is found in the SEM microstructure and complete ausferritic matrix in C1 samples (E1 to E9) there was no change in the morphology and volume percent of carbide. The average chromium content is same. This result clearly demonstrates the effect of the eutectic composition of C1, i.e. the lower silicon level[15]. Then, the graphitizing potential seems to be a dominant parameter controlling carbide formation. It can be further observed that the carbide content in all samples E1-E9 remain same after the heat treatment cycle. No dissolution of alloy carbides was observed at the austenitizing temperature[14].

Above Figure 4 C1 As-cast-200X carbide in thick net plate form
Above Figure. 5 shows the SEM micro-photographs of E1, E2 and E3 CADI and cryogenically treated CADI

Below Figure 6 shows the SEM micro-photographs of E4, E5 and E6 CADI and cryogenically treated CADI
Above Figure 7 shows the SEM micro-photographs of E4, E5 and E6 CADI and cryogenically treated CADI
3.2. Wear resistance and Hardness

The Pin on disc wear test is conducted in accordance with ASTM G-99 standard,[16] Fig. 9 shows the weight loss values of the E0 As-cast and of CADI samples (E1 to E9) measured on pin of 8mm diameter 25mm long and Diamond ring Disc as shown in Fig 2. The overall wear resistance is the combined effect of austempering and Cryo-treatment, the least wear resistance is obtained in as-cast and all austempered samples, but after Cryo-treatment to austempered samples the wear resistance is enhanced in all samples, however this enhancement is directly proportional to austempering time and Cryo-treatment 36hrs duration for selected temperatures except E8 shows more wear resistance compared to all samples. Thus the graph shows weight loss values obtained for ten variants of CADI samples (E0 to E9) at the three austempering temperatures 250°C, 325°C, 400°C, three quenching times 1h, 2h, 3h and Cryo-treatment at -185°C for 24, 36hrs. The reported values are the average of four determinations, in each case, the Cryo-CADI samples were compared against the CADI and CDI samples and wear resistance index E
(Wear resistance index=E, is the Ratio of wt. loss by reference material to Cryo-treated CADI sample) is determined. Weight loss is the functions of the chromium content, carbon equivalent, austempering heat treatment parameters and microstructure matrix. In case of E1-E9 the Cr% is 4.3% it has shown more wear resistant for E8 (C2-400°C-2h). Austempering at 400°Cfor 2hrs and Cryo-treatment at -185°C for 24 hrs the reinforcement effect of carbide and ausferrite is shown in hardness and wear resistance values which are higher, reported in the graph of Fig.8, 9 and 10.

![Comparative graph of bulk hardness CADI-CRYO-185°C for 36Hrs](image1)

![Comparative graph of bulk hardness CADI-CRYO-185°C for 24Hrs](image2)

**Figure. 8** show the comparative graph of bulk hardness in bar form of 24 and 36hrs CRYO at -185°C.
Figure. 9 show the comparative graph of wear in bar form of Austempered (A), Austempered and Cryotreated (AC)

IV CONCLUSIONS

1. It is possible to obtain the wear resistance enhancement of Carbidic ADI (CADI) with precipitation of secondary carbide and reinforcement of carbide in ausferritic matrix after Cryo-treatment at -185°C for soaking time 24hrs and 36hrs.
2. After 36hrs of Cryo-treatment there is change in the morphology i.e. variation in carbide shape which is clearly shown in micro structure.
3. In 36hrs Cryo-treatment the maximum wear resistance is obtained in E6 (C4-325°C-3hrs with -185°C-36hrs Cryo-treated) a sample that is 300% (E=3) more wear resistant than As-cast sample.
4. After 24hrs of Cryo-treatment there is very slight change in the morphology i.e. no variation in carbide shape which is clearly shown in micro structure.

5. In 24hrs Cryo-treatment the maximum wear resistance is obtained in E8-cryo (C4-400°C-2hrs with -185°C-24hrs Cryo-treated) sample that is 400% (E=4) more wear resistant than As-cast sample.

6. Thus enhancement in wear resistance in CADI is a combined effect of austempering and cryogenic treatment parameters and precipitation of secondary carbide in the matrix due to cryotreatment.

V AKNOWLEDGEMENTS

Dept of metallurgy and material engg, COE PUNE, INDIA, who has provided the facility for cryogenic treatment

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