Influence on the morphology of spheroidic graphite nodules of nodular cast iron obtained by CO$_2$ process

Influência sobre a morfologia dos nódulos da grafita esferoidal do ferro fundido nodular obtido pelo processo CO$_2$

Antônio Carlos de Araújo Santos 1
Mauro Carlos Lopes Souza 2
Wilma Clemente de Lima Pinto 2
Mila Rosendal Avelino 3

Abstract
The mechanical properties of cast metallic materials are strongly influenced by processing parameters, such as percentage of silicate, sand granulometry, and metallurgical processing. The ductile iron cast produced by the CO$_2$ process depends on variables that determine the behavior of the material in service, such as the cooling rate and chemical composition. This study evaluated the influence of the cooling rate on the spheroidic graphite. In order to determine this effect, a simulation was performed in specimens with 20, 25, and 30 mm in thickness, through the characterization of type, measurement of nodule size, and distribution of nodules. Chemical analysis and mechanical resistance tests were performed. The 25 mm thick specimen showed the best behavior among the three thicknesses evaluated, presenting the formation of many small nodules and a small amount of larger nodules in the center. The comparison of the nodule size, as well as the counting of these, associated to the used cooling rate is according to standard test method for structure evaluation of graphite in iron cast.

Keywords:
Solidification
Casting
Ductile iron cast
Morphology

Resumo
As propriedades mecânicas dos materiais metálicos fundidos são fortemente influenciadas por parâmetros de processamento, tais como a percentagem de silicato, granulometria da areia, e o processamento metalúrgico. O ferro fundido dúctil produzido pelo processo de CO$_2$ depende de variáveis que determinam o comportamento do material em serviço, tal como a velocidade de resfriamento e a composição química. Este estudo avaliou a influência da taxa de resfriamento sobre a grafita esferoidal. Com o objetivo de se determinar este efeito, uma simulação foi realizada em amostras de 20, 25, e 30 mm de espessura, através da caracterização de medição do tipo, do tamanho do nódulo e distribuição dos nódulos. A análise química e ensaios de resistência mecânica foram realizados. O corpo de prova de 25 mm de espessura mostrou o melhor comportamento entre as três espessuras avaliadas, apresentando a formação de muitos pequenos nódulos e uma pequena quantidade de nódulos maiores no centro. A comparação do tamanho dos nódulos, bem como, a contagem destes, associados à taxa de resfriamento utilizada, está de acordo com a norma dos métodos de testes para avaliação da microestrutura dos nódulos de grafita dos ferros fundidos nodulares.

Palavras-chave
Solidificação
Fundição
Ferro fundido ductil
Morfologia

1 Master of Science Student in Mechanical Engineering at the Rio de Janeiro State University, UERJ.
2 Doctor in Metallurgy and Materials, Department of Metallurgy at the West Zone State University, UEZO.
3 Doctor in Mechanical Engineering of Department of Mechanical Engineering at the Rio de Janeiro State University, UERJ.
1. Introduction

The nodular cast iron produced by the CO2 process is among the most studied metal material today. However, to study their solidification, it is necessary to control some variables such as the cooling rate, chemical composition, process control, as well as the interaction of these variables in order to understand the mechanical behavior of these materials during the process. The ductile iron cast has been increasingly used in the modern industry. It is known that the most important feature of these materials is related to its mechanical strength when compared to other types of iron cast (gray and malleable) and even to some carbon steels. This is a consequence of the spheroidic graphite in the microstructure, which does not interrupt the continuity of the matrix as graphite in the veins of grey iron do (Campos Filho, et al. 1978).

In the ductile iron cast, in general, the morphology of the graphite formed from metal plating during the solidification can be altered in several ways. Graphite crystallizes anisotropically (the mechanical properties vary with the crystallographic directions), and its growth is largely influenced by small amounts of chemical elements present in the metal plating and by thermal variables which intervene in the solidification process (Sadosha, et al. 1975);

The nodular graphite in the ductile iron cast is constituted by a second phase born from the liquid metal during solidification. Its appearance is subjected to the theory of phase nucleation, to which the most accepted model is the one from Dos Santos, et al., (1977).

The nucleation during solidification of the ductile iron cast is heterogeneous, and the graphite is considered as the eutectic phase that is most difficult to go into nucleation (Muzundar et al. 1973). There are many particles that act as effective centers for nucleation during this phase; there are evidences that the graphite itself, oxides, sulfides, carbides (ionic or CSI), silicates, gas bubbles, and nitrides increase the nucleation power of the liquid metal. However, the relative importance of each of these factors are due to particular conditions of the operation used (Weizer et al. 1973; Chaves Filho, et al., 1975; Santos, et al., 1977).

It should also be mentioned that the degree of nucleation of the ductile iron cast has an effect on the distribution of the elements that segregate into the liquid and on the morphology of the graphite; it is possible to obtain particles of graphite in a better form through more effective inoculations (Resman, et al., 1967; Santos et al., 1976; Dawson, 1979).

The nodular ductile iron cast cooling rate controls the microstructure and the resulting mechanical properties. Thus, the study of the cooling rate is related to the number of nodules and the metal matrix. More generally, the time for the diffusion of carbon in the eutectoid stable region is determined by the speed of the slow cooling inside the oven, which is referred to as ferritization. The free ferrite can often be observed in slowly cooled ductile iron cast or under isothermal treatments from the pearlite decomposition initially formed (Askeland, et al.,1975).

This study specifically evaluated the influence of the cooling rate on the morphology of the graphite in the ductile iron cast obtained by the CO2 process and cast in specimens 20, 25, and 30 mm in thicknesses. The graphite was classified in terms of type, size, and distribution according to the ASTM A 247 67, standard (1998). The metallographic analyses were used to study the morphology of the graphite through the distribution and size of the nodules obtained using different cooling rates simulated in specimens 20, 25, and 30 mm in thickness, respectively. The results were compared to results produced according to the ASTM A 247-67 standard (1998), approved and reviewed in 1998.

2. Experimental

The CO2/sodium silicate process is an industrial process for the preparation of siliceous sand molds without clay for casting metal parts. The process involves a mixture of sand with sodium silicate (up to 4.5% sodium silicate based on the sand weight). The mixture was prepared in a blender used in molds and males plugs, which were subsequently hardened by the high hygroscopicity from the carbon dioxide through silicate water (silicate hydrate).
The binding process, i.e., the hardening of the sand, involves the formation of sodium carbonate (Na₂CO₃) and silica gel in a combination of three processes:

Precipitation of the silica gel:

\[ \text{Na}_2\text{SiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2 \]

Hardening due to the change in the ratio N₂O/SiO₂ from the silicate,

Drying of the silicate.

The specimens Y-block type ASTM A536, were molded closely following the CO₂/sodium silicate process for the tensile testing. Approximately 20 Kg of the mixture from a batch mixer with 150 Kg mixing capacity was used. The metal was prepared in an electric induction furnace at medium frequency (1200 Hz) in an inductotherm crucible (oven provider) with a capacity of 1,500 Kg and subsequently taken into the foundry step.

The inoculation was directly in the leaking pot itself using 0.6% Si, in the form of Fe-Si (75%) with about 2% Ba, after the nodularisation with Fe-Si-Mg (8% Mg).

The samples for the metallographic examinations were taken from the Y-block from the specimens with 20, 25, and 30 mm in thickness. The samples were prepared following procedures:

- Mechanical grinding using rotary sander brand Ecomet 4000, following the sequence of sandpaper 120, 220, 400, 500, 600 and 1500, all 3M, Norton,
- Then, polishing with diamond past on cloth (suede), brand Struers.

The metallographic examinations to determine the qualitative morphology of the graphite present in the microstructure were executed in specimens not etched. Three fields per specimens (end, middle, and center) were examined using a JEOL-JSM-6490LV scanning electron microscope (SEM), of Microscopy Laboratory of PEMM/COPPE/UFRJ.

The results of the final chemical basic composition and the mechanical tests for the determination of the limit of tensile resistance, yield strength, and the elongation percentage were performed and certified by the company that provided the specimens.

3. Results and Discussion

The final chemical composition (wt%) was close to the eutectic as shown in Table 1. Chemical analyses are carried out in laboratories of Fundição Técnica Sul-Americana (Itaguaí RJ).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>3.68</td>
<td>2.25</td>
<td>0.84</td>
<td>0.077</td>
<td>0.006</td>
<td>0.01</td>
<td>0.001</td>
<td>0.01</td>
<td>0.007</td>
<td>0.58</td>
</tr>
</tbody>
</table>

The calculated amount of equivalent carbon (EC) was approximately 4.45. This value was obtained from equation, \(\text{C}_{\text{eq}} = \text{C} + \frac{1}{2} (\%\text{Si} + \%\text{P})\).

The mechanical properties measured by tensile tests were:

- Tensile strength (σr): 819.0 MPa (83.52 kg/mm²)
- Yield strength (σe): 523.35 MPa (53.37 kg/mm²)
- Elongation percentage (ε): 4.0 %

For each different specimen the metallographic analysis were performed in the core of the samples (center), using the SEM.

The larger nodules in the field were analyzed for the assessment of the sizes of the graphite nodules according to figures 1 (CP20), and 2 (CP30).
It was observed that the carbon and silicon contents are in the optimal range for these two elements, according to Hasse (1999).

The process of inoculation practiced by the refiner is not the most recommended by the literature, however, taking into account that the measurements obtained in the MEV for the sizes of the nodules were the largest visualized nodules and according to the ASTM, classified as the smallest (type 5, 6 and 7). Thus, it was concluded that the process was successful because the graphitizing power of the Fe-Si (75%) used was effective in the formation of the number of eutectic cells per unit area. This was observed primarily in CP25, in which thickness, the rupture of the specimen occurred during the tensile test.

Tables 2 and 3 refer to types and the values found for the sizes (mm) of the nodules.

### Table 2. Size of the nodules in mm and their types (ASTM)

<table>
<thead>
<tr>
<th>CP</th>
<th>End</th>
<th>Type</th>
<th>Half radius</th>
<th>Type</th>
<th>Center</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.057</td>
<td>6</td>
<td>0.057</td>
<td>6</td>
<td>0.037</td>
<td>6</td>
</tr>
<tr>
<td>25</td>
<td>0.027</td>
<td>7</td>
<td>0.042</td>
<td>6</td>
<td>0.060</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>0.061</td>
<td>5</td>
<td>0.026</td>
<td>7</td>
<td>0.055</td>
<td>6</td>
</tr>
</tbody>
</table>

### Table 3. Count of the number of nodules (ASTM)

<table>
<thead>
<tr>
<th>CP</th>
<th>End</th>
<th>Half radius</th>
<th>Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>133</td>
<td>84</td>
<td>82</td>
</tr>
<tr>
<td>25</td>
<td>465</td>
<td>387</td>
<td>224</td>
</tr>
<tr>
<td>30</td>
<td>139</td>
<td>355</td>
<td>180</td>
</tr>
</tbody>
</table>
4. Conclusions

According to the ASTM A536-84 norm (2009), the nodular ductile iron cast provided by the company was certified as of high-resistance, 100-70-03 class (equivalent to the DIN GGG 70).

According to its composition and resistance, the material provided can be classified as a hypereutectic ductile iron cast because the C.E. = 4.45.

The ASTM IV type (vermicular graphite), type V (crab graphite), and type VI (exploded graphite) were not found, which proved the excellent spheroidicity of the nodules without degeneration of the spheroidic graphite.

The distribution and size of nodules in CP30 were closest to optimal values reported in the literature, showing a decrease in the number of nodes from the end towards the center and a consequent increase in their size.

5. References


WEIZER, P. F., BATES, C. E., WALLACE, J. F., Cleveland, Malleable Founder’s Soc., p.81 1967

Endereço para Correspondência:

Mauro Carlos Lopes Souza
mauroclsouza@hotmail.com