STEREOLOGICAL PARAMETERS OF CARBIDES
IN MODIFIED WEAR RESISTANT Fe-C-Cr ALLOYS

Andrzej STUDNICKI, Jan JEZIERSKI

Department of Foundry, Faculty of Mechanical Engineering,
Silesian University of Technology, Towarowa 7, 44-100 Gliwice, Poland
Corresponding author. E-mail address: Andrzej.Studnicki@polsl.pl

Abstract:
The results of investigations on stereological parameters of carbides in high wear resistant modified Fe-C-Cr alloys were presented in the article. The inoculants were composed of the following elements: boron, niobium, vanadium, cerium and lanthanum (RE Rare Earth metals) and nitrogen. The influence of applied inoculants on stereological parameters of carbides such as: size, circumference, shape coefficient and volume fraction was shown in form of tables and diagrams. The results of carbide phase investigations were the basis to the analysis of the effectiveness of the particulate inoculants treatment. One can recognize that the use of complex inoculants caused the best effects in the aspect of the structure fragmentation and improvement of shape coefficient. Ferroniobium and ferrovanadium mixture with RE in almost all examined groups of cast iron improves stereological parameters causing the insignificant fall of the volume fraction of the chromium carbides. This is probably connected with high carbide creation effect of the niobium and vanadium which small carbides crystallize from the liquid first and become base-plates for the crystallization of the austenite. The similar situation occurred during inoculation when boron carbide was introduced except of niobium and vanadium. The benefits of the boron carbide added separately was not proved during the experiments probably due to fact of its dissolution in liquid alloy. The boron carbide can be perfect base-plate for the austenite nucleation but it should not dissolve before the crystallization of the austenite begins. The solution of this problem can be for example the boron carbide introduction into liquid cast iron along with so called micro-chills.

Keywords: wear, stereological parameters, Fe-C-Cr alloys, chromium carbide

1. INTRODUCTION
Chromium cast iron is highly valued casting material used in production of castings working in abrasive environment, rarely impact-abrasive [1+4]. The requirement for this alloy is good resistance on initiating and unreeling cracks what may extent the area of use of chromium cast iron, that is cast iron of good ductility. It is known that the mechanical and tribological properties of chromium cast iron depend mainly on metallographic structure formed during the crystallization process. One can describe the structure of chromium cast iron as an in-situ composite in which hard carbides are distributed in the matrix being the bearing element of the casting. In purpose to raise the plastic properties should carbides cast irons aim to crystallization of the structure consisting of the small carbides of rounded shapes distributed in plastic matrix uniformly. The basic elements of chromium cast iron, such as iron, chromium and carbon decide in this alloy of the main phase components which give it specific usable properties that is the high resistance on abrasive wear. Introducing to this configuration of another elements e.g. nickel and molybdenum was mainly on purpose to improve its mechanical properties e.g. due to the changing of the morphology of carbides or making easier the heat treatment of matrix. It is not advisable to produce of chromium cast iron of different character, to introduce a disorder inside the structural configuration the chromium carbides-matrix by e.g. the introduction of considerable quantities of the alloy additions which will create completely new phases. One of the basic usable properties of the cast materials modification method without the change of chemical
composition of the material is the inoculation process. This process is often ambiguously and variously interpreted. Fras [5] explains the term inoculation as „process consisting of the introduction to the metal bath some particular substances, called the inoculants, which significantly enlarge the density of grains in the metal even in minimal quantities, that is their number in the volume unit. The mechanical properties of the metal improvement is the consequence of the larger density of grains as well as decrease of the components segregation degree and the susceptibility of the metal to hot cracks."

The density of grains increase causes higher metal ability for nucleation process what changes the kinetics of crystallization. The inoculants from the point of view of its working mechanism based on the density of the crystallization nucleus increase can be divided as follows [5]:
1. reducing the wetting angle between the nucleus and the base-plate and a surface tension on the liquid-nucleus border,
2. increasing of the density of base-plates for nucleation,
3. decrease the rate of the grains growth.

The listed above mechanisms of the inoculants working may appear together what takes place in many real processes. The inoculants used in the presented work were applied in the form of fine ferroalloys mixtures (FeNb, FeV), the powdered boron carbide (B₃C) and the rare-earth metals (RE). The metal bath after inoculants introducing was in several cases purified with nitrogen activated in electric arc.

The introduction into liquid chromium cast iron of the high-melting elements which can additionally create high-melting compounds (carbides, nitrides) should cause mostly the increase of the nucleus of crystallization density due to its base-plate-creative effect.

2. MATERIAL AND RESEARCH METHODOLOGY

Chromium cast iron of 2-3.5 % C and 12-25 % Cr in which the carbide of the type M⁷C₃ is a main carbide phase was chosen for investigations of inoculation process. In figure 1 the melts labels were shown and the interesting for authors area on the projection of liquidus surface of threefold Fe-Cr-C system were marked. This area extends from hypoeutectic to hypereutectic cast irons. The basic „paths“ of primary crystallization in this area are:

1. hypo-eutectic cast iron: liquid → primary austenite γ → eutectic (γ+Cr₇C₃)
2. eutectic cast iron: liquid → eutectic (γ+Cr₇C₃)
3. hypereutectic cast iron: liquid → primary carbide (Cr₇C₃) → eutectic (γ+Cr₇C₃)

The following assumptions were made during the experiments when the chromium cast iron grade and the inoculants were being selected:

- the carbon and chromium weight concentration range: 2 ≤%C ≤3.5; 12≤%Cr≤25;
- Cr/C=6 ratio;
- hypo-eutectic, near-eutectic and hypereutectic chromium cast iron;
- inoculant components in the form of powders B₃C, FeNb, FeV, except of RE;
- total weight inoculant addition ≤0.6%;
- grain size of the fine inoculant ≤0.25 mm;
- refining with nitrogen activated in electric arc.

Melts were conducted in the crucible inductive electric furnace with neutral lining and capacity of 20 kg. Charging materials and additions which were used were: raw chromium cast iron: 2.82%C; 17.69%Cr; 0.56%Mn; 0.64%Si; 0.49%Ni; 0.030%S; 0.050%P melted in industrial conditions in the electric arc furnace; steel scrap; ferroalloys: FeCr015, FeCr800; graphite; deoxidizers: Al; FeTi; inoculants (mixture of B₃C, FeNb, FeV and RE); nitrogen. After the proper temperature of liquid cast iron in the furnace was reached (for cast iron of 2 %C -1540°C, 2.8%C i 3.5%C – 1520°C) deoxidizing with Al and FeTi was carried out inside the furnace. The inoculation was conducted in well heated ladle by adding the proper inoculant on its bottom. The compounds and their mixtures were used as inoculants. The weight chemical composition of the particular components of inoculants regarding to the mass of the liquid metal was presented in figure 1. In the case when nitrogen was used, the bath was being stirred with gas activated in the electric arc approx. 5 min. After
the tapping of the metal and waiting approx. 20 s the DTA testers (Derivative Thermal Analysis) were poured in. The samples from castings solidified in testers DTA-C and DTA-IS were cut to prepare the microsections used for the stereological parameters of carbides in studied chromium cast iron analysis. The castings solidifying in these two testers differ from each other in terms of cooling rate (the time of primary crystallization of the casting in the DTA-IS tester is about twice longer than primary crystallization in the DTA-C tester). DTA research stand and the way of the samples preparation for the microsections were presented in figure 2. Samples for quantitative examinations were prepared according to standard methods - grinding and polishing. The deep matrix etching process was conducted after microsections polishing. Aqua regia was applied as the etchant.

<table>
<thead>
<tr>
<th>Cr</th>
<th>C</th>
<th>nW0</th>
<th>sW0</th>
<th>WW0</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 %C</td>
<td>2 %C</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>18 %C</td>
<td>2.8 %C</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>12 %C</td>
<td>3.5 %C</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.25 %B</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.30 %FeNb</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>0.25 %FeNb+0.15%FeV+0.20 %MZR</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>0.05 %B 0.25 %FeNb+0.15 %FeV+0.15 %RE</td>
<td>10</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>4a</td>
<td>0.05 %B +0.25 %FeNb+0.15 %FeV+0.15 %RE +nitrogen</td>
<td>13</td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

The mass concentration of inoculants and their marks
0 – without inoculant,
1 – 0.25 %B,C,
2 – 0.30 %FeNb,
3 – 0.25 %FeNb+0.15%FeV+0.20 %MZR,
4 – 0.05 %B 0.25 %FeNb+0.15 %FeV+0.15 %RE,
4a – 0.05 %B +0.25 %FeNb+0.15 %FeV+0.15 %RE +nitrogen

**Fig. 1** The labels of melts, the inoculants and the interesting for authors area on the projection of liquidus surface of Fe-Cr-C system [6]

**Fig. 2** Research DTA stand and method of samples from casting preparation for quantitative examinations [7]

The X-ray diffraction analysis (fig.3 – cast iron sS3) allowed to identify in the examined chromium cast irons the basic phases. It was confirmed that examined chromium cast irons consisted of the matrix with changing
part of phase $\alpha$ and $\gamma$ and carbide phase with the dominant part of the carbides of $M_7C_3$ type. The occurrence of the carbide of the $M_3C_6$ type in hypereutectic cast irons of the group wW was also confirmed. Quantitative examinations were carried out at magnification from x200 to x600 on ten fields (photos) for each microsections. The quantitative analysis of the structure was conducted based on the photos taken in half of microsection radius using NIS ELEMENTS BR 3.10 software. The software package contains two applications: the first NIS ELEMETS F for image form the camera capturing and the second NIS ELEMETS BR 3.10 for making the stereological parameters calculations (precipitates counting, shape coefficient, length, surface, volume and so on). The typical image postprocessing consisted of gathering data from the image hidden in the color.

3. STEREOLOGICAL PARAMETERS OF CARBIDES

The average values of stereological parameters of carbides in examined chromium cast irons were used to estimate of the influence degree of the inoculants on carbides in chromium cast irons. The set of average values of analyzed parameters was shown in table 1 only for hypoeutectic chromium cast iron of the group sS as an example. The distribution histograms of selected stereological parameters of carbides were prepared, too. The example of the quantity of carbides histogram as a function of their size class for hypoeutectic chromium cast iron inoculated with the FeNb+FeV+RE mixture was shown in figure 4.

Table 1 The set of the average values of stereological parameters of carbide phase of examined chromium cast irons (samples taken from DTA-C and DTA-IS castings with the index ‘i’)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>sS0</td>
<td>11.03</td>
<td>11.51</td>
<td>4.87</td>
<td>0.96</td>
<td>0.197</td>
<td>22.06</td>
</tr>
<tr>
<td>sS0i</td>
<td>14.43</td>
<td>14.78</td>
<td>6.31</td>
<td>1.16</td>
<td>0.189</td>
<td>25.55</td>
</tr>
<tr>
<td>sS1</td>
<td>13.86</td>
<td>14.83</td>
<td>6.56</td>
<td>0.94</td>
<td>0.143</td>
<td>28.28</td>
</tr>
<tr>
<td>sS1i</td>
<td>17.38</td>
<td>14.83</td>
<td>6.49</td>
<td>1.03</td>
<td>0.159</td>
<td>30.07</td>
</tr>
<tr>
<td>sS2</td>
<td>10.88</td>
<td>13.55</td>
<td>6.02</td>
<td>0.85</td>
<td>0.141</td>
<td>27.99</td>
</tr>
<tr>
<td>sS2i</td>
<td>15.34</td>
<td>14.50</td>
<td>6.49</td>
<td>0.84</td>
<td>0.129</td>
<td>23.79</td>
</tr>
<tr>
<td>sS3</td>
<td>4.14</td>
<td>6.96</td>
<td>2.74</td>
<td>0.83</td>
<td>0.303</td>
<td>13.56</td>
</tr>
<tr>
<td>sS3i</td>
<td>8.75</td>
<td>9.95</td>
<td>3.90</td>
<td>1.16</td>
<td>0.297</td>
<td>16.92</td>
</tr>
<tr>
<td>sS4</td>
<td>13.59</td>
<td>14.44</td>
<td>5.76</td>
<td>1.52</td>
<td>0.264</td>
<td>25.12</td>
</tr>
<tr>
<td>sS4i</td>
<td>19.15</td>
<td>16.11</td>
<td>6.31</td>
<td>1.81</td>
<td>0.287</td>
<td>24.17</td>
</tr>
<tr>
<td>sS4a</td>
<td>6.96</td>
<td>9.44</td>
<td>3.75</td>
<td>1.04</td>
<td>0.277</td>
<td>24.76</td>
</tr>
<tr>
<td>sS4ai</td>
<td>131.63</td>
<td>59.92</td>
<td>27.87</td>
<td>2.23</td>
<td>0.080</td>
<td>24.76</td>
</tr>
</tbody>
</table>

Fig. 3 X-ray diffraction pattern and photo of hypoeutectic chromium cast iron microstructure - melt sS3
Massive decrease of the average size of the surface as well as the length of carbide precipitations is a result of the inoculation of the cast iron with mixtures containing ferro niobium, ferrovanadium and mischmetal (inoculant No. 3). Slightly smaller influence was observed in case of the inoculants mixture in which except of mentioned earlier, boron carbide (inoculant of No. 4) was introduced. The effect of the inoculant No. 2 (ferro niobium alone) was confirmed as minor. On the basis of investigations conducted it is impossible unambiguously confirm the positive influence of the boron carbide alone on chromium carbide phase fragmentation. The reason can be a significant increase of the volume fraction of carbide phase in alloys inoculated with bigger amount of boron carbide itself (inoculant No. 1). It seems that the technology of the inoculation with the boron carbide is more complex, it is necessary to not allow to its total dissolution in the liquid alloy, because the boron carbide does not become the heterogeneous nucleus for crystallization but it is used only in creating additional carbide phase precipitations. The inoculation with the mixtures of high-melting elements (Nb and V with mischmetal), decreases of the volume fraction of carbides, particularly in low carbon chromium cast iron.

Moreover, the essential influence of these inoculants on the shape of carbides was confirmed, what is visible in decrease of their length with increase of their width in the same time. This caused about two times increase of the shape coefficient (K=B/L), what can suggest the decrease of carbides slenderness, and probably their coagulation. One can believes that it is caused by the surface tension of inoculated carbides increase together with the presence of the rare-earth elements. This change of the shape of carbides most likely can affect the usable properties of castings (their resistance for mechanical shock working conditions).

4. THE STEREOLOGICAL PARAMETERS OF CARBIDES AS A FUNCTION OF INOCULANTS USED

The graphs below presents the influence of particular inoculants on the casting cooling rate on the main carbides stereological parameters. The selected graphs for examined hypoeutectic, eutectic and hypereutectic chromium cast iron are presented in figures 5 to 7.

**Fig. 4** The distribution histograms of the quantity of Na carbides as a function of their size class $P$ - hypoeutectic cast iron inoculated with the FeNb+FeV+RE mixture – sS3

![Distribution histograms of Na carbides](image)
Fig. 6 The influence of inoculant grade and cooling rate of the casting on the stereological parameters of carbides in chromium cast iron - **cast irons nW series**: C=2% and Cr=24%; **sS**: C=2.8% and Cr=18%

Fig. 7 The influence of inoculant grade and cooling rate of the casting on the stereological parameters of carbides in chromium cast iron - **cast irons sW series**: C=2.8% and Cr=24%; **ns**: C=3.5% and Cr=24%

During the graphs analysis the profitable effect of inoculants being the mixtures of high-melting and carbide-creative elements (Nb and V) and the rare-earth metals (RE) were observed. It was observed in every series of the examined cast iron. On the base of the experiments it is impossible to unambiguously confirm the profitable influence of simple inoculants i.e.: boron carbide and ferro niobium on the stereological parameters. The working effect of the boron carbide seems to be particularly interesting because it is the high-melting compound and should become the base-plate for the austenite. Unfortunately its wrong addition method into liquid cast iron during inoculation process can cause its excessive dissolution. In this case the boron carbide supplies only elements for the hard carbide phases formation and does not create the base-plates for the austenite crystallization. So, it should be introduced just before the molds are being poured.

4. SUMMARY

The results of the investigations on carbide phase stereology were the basis for the estimation of the particular inoculants efficiency. It can be stated that the use of complex inoculants gave the best results in the aspect of refinement of structure and improvement of carbides shape coefficient. The mixture of ferro niobium, ferro vanadium and mischmetal in almost every group of tested chromium cast irons improve the stereological parameters causing the small decrease of the volume fraction of chromium carbides. This is probably connected with strong carbide-creative working of the niobium and vanadium whose fine carbides crystallize first from the liquid and become base-plates for the crystallization of the austenite. The similar situation is for the inoculant No. 4, when the boron carbide is additionally introduced. The positive effect of the boron carbide was not confirmed for sure by the experiments what can be result of its dissolving in the alloy because the volume fraction of carbides increase was recorded. The boron carbide can be perfect base-plate to the austenite nucleation but it should not dissolve before the crystallization of the austenite begins. The solution of this problem can be probably its introduction into liquid cast iron together with micro-chills e.g. in the form of ground steel scrap [8].
LITERATURE


