Heat Treatment of the SiMo Iron Castings – Case Study in the Automotive Foundry

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Abstract

Silicon – molybdenum cast iron commonly called SiMo due to its unique properties has becoming more and more interesting engineering material. The history and development of this alloy is relatively long but, due to the significant difficulties during the manufacturing process resulting in the lower final quality than expected, it has not been applied to often in practice. The biggest challenge is its brittleness as a result of the carbides precipitations. During last few years, thanks to the many important researches made and the general foundry technology development, the interest in SiMo iron has been rapidly growing, especially for the castings for heavy duty applications like corrosion, high temperature and wear abrasion resistant parts. In the article the heat treatment attempts to improve the microstructure of SiMo castings has been presented. The goal was to destroy or at least to refine and uniformly distribute the carbides precipitations to improve mechanical properties of the exhaust manifold castings for the cars.

The experiments were carried out for the alloy contains approx. 4% Si, 1% Mo and 3.2%C. The range of the research included: hardness measuring, standard mechanical properties and microstructure for as-cast state and after that the subsequent heat treatment process with another properties check. The result of the heat treatment was the elimination of pearlite from the metal matrix. Moreover, the changes of the carbide molybdenum – rich phase morphology were observed. The dispersion of the carbides precipitations in the carbides area was observed. The experiments proved the possibility to control the microstructure and the mechanical properties of the SiMo castings by means of heat treatment but only to some extent.

Keywords: Heat Treatment; Solidification Process; SiMo Cast Iron; Exhaust Manifold; Automotive Parts

1. Introduction

The automotive castings producers face continuously growing clients demands regarding the quality and mechanical properties of their products [1-4]. This requires not only the constant technological competency grow and plant’s know-how but continuous research effort to develop and implement new and improved casting alloys [5-6]. During such explorations it is quite often the alloys available on the market but due to various reasons not yet very popular, are tested again. In most cases the decisive factors are technological problems, causing the quality of the casting is far from desired [7-9]. The article is a case study of such example – casting made of cast iron of particular grade – silicon molybdenum, so-called SiMo. The SiMo iron has been known since tens of years but its increasing use has been observed since the last dozen years [10-12]. It is mostly popular in applications working in heavy duty conditions as: corrosive
environment, elevated temperature and/or abrasive wear. SiMo iron is especially good alloy for exhaust manifolds or turbocompressor housing. One of its best advantages is dimensional stability in the temperature range from well below 0 to over 750°C [13-14]. Typically, this iron contains around 4.6%Si despite the higher content increases high-temperature creep resistance. It is because in the same time, the ductility significantly decreases, particularly elongation and the brittleness problem in the ambient temperature appears [15-16]. The SiMo iron microstructure is typically ferritic, (ferrite has a better toughness) but may contain some pearlite fraction, which is not desired phase, and obviously carbides precipitations. The carbides significantly increase the hardness and abrasive wear resistance but are the main cause of the casting brittleness. The molybdenum carbides in the alloy microstructure increase its creep resistance. Small carbides precipitations, which do not create „the network” have the advantage they almost do not lower the iron ductility. Therefore the intergranular (on the grains borders) carbide network must be avoided.

Hence, the necessity, especially with the higher carbide-supporting elements (mainly molybdenum), of the dedicated heat treatment, leading to microstructure matrix and carbides morphology changes [17].

The attempts to increase the utility properties of the exhaust manifold castings made of SiMo iron thanks to heat treatment, were described in the article.

Inside the temperature range between 600°C and Ac1, pearlite, bainite and martensite will transform into ferrite and graphite. This phase transition causes the strength decrease and some microstructure elements volume increase what finally results in micro cracks. If in as-cast state to much pearlite exists, it must be corrected during heat treatment process. The higher the working temperature, the lower maximum allowed pearlite content. This is because with the temperature increase the pearlite transform faster into ferrite and graphite what is unfavorable.

2. Description of the experiments

To check the heat treatment influence on the mechanical properties improvement due to SiMo cast iron microstructure transition, the exhaust manifold casting produced in automotive foundry has been chosen. The casting is presented in Fig. 1.

![Fig. 1. Exhaust manifold made of SiMo iron; X – location of the sample for microstructure examination](image)

The test castings were made of medium – silicon ductile iron and the alloy chemical analysis according to customer specification is given in Tab. 1. The melt was carried out based on the following charging materials: SiMo castings returns = 50%, special foundry pig iron = 35%, steel scrap = 15%, carburizers and ferroalloys – to the content given in the specification. It can be seen that maximum carbon content 3.6% is much higher than typical for similar SiMo iron grades (2.6-3.4%) and the common rule is to not exceed maximum level of 3.0%.

<table>
<thead>
<tr>
<th>Chemical composition – customer specification</th>
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</thead>
<tbody>
<tr>
<td>Indicative percentage</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>3.6</td>
</tr>
</tbody>
</table>

The higher carbon content in combination with silicon and for example cerium, causes “chunky” graphite creation, graphite flotation and gas porosity.

The required mechanical properties in the room temperature (RT) measured for the separately cast samples were given in Tab. 2. Each result is an average of three measurements.

<table>
<thead>
<tr>
<th>Mechanical properties at RT – customer specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>condition</td>
</tr>
<tr>
<td>Annealed</td>
</tr>
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</table>

The charge was melted down in the medium frequency induction furnace of 12 tons capacity. After the melting stage and reaching the temperature of 1450°C the slag was removed, the sample for carbon content analysis (ATAS system) was taken and the chemical analysis sample, too. Then, the chemical composition was adjusted and the liquid alloy was superheated up to 1550°C. After 3 minutes holding the alloy was cooled down to the spheroidizing and inoculation temperature. The secondary metallurgy was conducted in 1 ton Sandwich ladle and then after de-slagging, the alloy was transported into the cold pouring unit working on the automatic flask molding line. The pouring temperature was 1450°C and time between pouring the mold and its knock-out was around 56 minutes. The molds were prepared in green sand technology with bentonite with the cold box and hot-box cores.

For further experiments 6 test castings were selected labelled P1 – P6, and the chemical composition for all of them is given in Tab. 3. The carbon content was measured on the Leco analyzer and the residual magnesium was analyzed on Avanta device (AAS method). P0 casting is as-cast piece while P1 – P6 castings were subject to the heat treatment process according to different procedures.

<table>
<thead>
<tr>
<th>Chemical composition of Si-Mo cast iron</th>
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<tbody>
<tr>
<td>Chemical content [%] wt.</td>
</tr>
<tr>
<td>casting</td>
</tr>
<tr>
<td>P0</td>
</tr>
<tr>
<td>P1</td>
</tr>
<tr>
<td>P2</td>
</tr>
<tr>
<td>P3</td>
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<tr>
<td>P4</td>
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<tr>
<td>P5</td>
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<tr>
<td>P6</td>
</tr>
</tbody>
</table>
To evaluate the heat treatment results, the mechanical properties of the castings were tested again (standardized samples of 5mm diameter) and the microstructure, too. Then the values were compared with as-cast condition. The mechanical properties for all castings after HT were given in Tab. 4.

Table 4. Mechanical properties of examined castings

<table>
<thead>
<tr>
<th>casting</th>
<th>Mechanical properties of castings after HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>UTS [MPa] 541</td>
</tr>
<tr>
<td>P1</td>
<td>661 545</td>
</tr>
<tr>
<td>P2</td>
<td>642 528</td>
</tr>
<tr>
<td>P3</td>
<td>637 535</td>
</tr>
<tr>
<td>P4</td>
<td>645 536</td>
</tr>
<tr>
<td>P5</td>
<td>645 538</td>
</tr>
<tr>
<td>P6</td>
<td>590 506</td>
</tr>
</tbody>
</table>

For SiMo castings the most popular is stress annealing which is recognized as a standard process, ferritizing annealing to pearlite elimination from the alloy microstructure, or carbide free annealing, for carbides elimination from the microstructure. The last one is used rarely and only for thin-walled castings. In the described experiments the castings were heat treated in 6 different procedures, with the annealing temperature changing in the range of 800-1100°C. For the P5 casting the annealing time was extended to try to dissolve the carbides completely. In turn, for the P6 casting the annealing temperature was intentionally set too high to observe the microstructure behavior in such extremal conditions. The heat treatment characteristics were presented in Fig. 2.

Fig. 2. Heat treatment characteristics for particular castings
In each HT process the heating up to the annealing temperature was conducted for 40 minutes and then the holding (annealing) time was 3hrs20mins. The cooling rate was very low – in furnace cooling down to 400°C. For the P5 casting the annealing time was intentionally extended to 8hrs. The samples were cut from the castings after HT for the mechanical properties and metallographic examinations. The microstructure was analyzed on the scanning microscope Phenom Pro-X equipped with EDS). The polished samples were etched in 5% Nital solution. Below the microstructure and the chemical elements distribution (EDS examination results) was presented for each sample casting (Fig. 3 – Fig. 9).

Fig. 3. P0 sample (as cast); a) graphite precipitations, b) carbides, c, d, e) Fe, Si and Mo content respectively

Fig. 4. P1 sample (as cast); a) graphite precipitations, b) carbides, c, d, e) Fe, Si and Mo content respectively

Fig. 5. P2 sample (as cast); a) graphite precipitations, b) carbides, c, d, e) Fe, Si and Mo content respectively

Fig. 6. P3 sample (as cast); a) graphite precipitations, b) carbides, c, d, e) Fe, Si and Mo content respectively
3. Discussion

The mechanical properties analysis after the heat treatment process in general did not show the UTS and YS increase. Only for the casting annealed at 800°C the slight increase of these values was visible. For the samples cut from the castings P2, P3 and P4 after HT the small properties drop was recorded but for P4 a small elongation increase was observed. For the sample P5 after much longer annealing period of 8hrs significant elongation improvement was measured: from E = 7.8% to E = 10.2% (ca. 31% more). It must be emphasized that the mechanical properties of the casting in as-cast state are significantly higher than these given in the customer specification. This proves the high skills and competences of the foundry in the SiMo production process.

The results of the P6 casting examination, after the annealing at 1100°C are definitely worse in the matter of mechanical properties. The UTS dropped to 590MPa (647MPa before the heat treatment). The YS lowered to 480MPa while for as-cast state it was equal 541MPa. The elongation decreased from 7.8% in as-cast condition to down 3.15% after HT process. Finally, the mechanical properties after the P6 heat treatment variant are far lower than the customer demands (see Tab. 2).

The metallographic examination and microanalysis of the chemical composition in the selected areas shown, that for both as-cast and after HT cases, the graphite precipitations are partly compacted (vermicular) type instead of spheroidal (nodular) one, and this is visible on majority of the samples. The significant variety of the graphite precipitations size is visible too, especially for the samples P2 and P3, annealed at 850°C and 900°C respectively.

Looking for the reasons of such graphite feature degradation, no relationship between Mg content (all samples has Mg higher
than 0.03%) and spheroidizing rate was found. The analyzed castings have no thick walls in which apart from Mg content on the graphite form the cooling time influences significantly. In the analyzed cases the small graphite degeneration can be caused by improper C and Si ratio in the relation to the wall thickness what is suggested by the small primary graphite precipitations visible in the microstructure. Thus, the proper CE value selection for the casting is so important and should be correlated with its wall thickness and cooling rate. The aim is to obtain in the microstructure if possible, the uniform precipitations with no primary graphite what is particularly important for so-called "safety castings".

It is worth to mention that on the right amount of the graphite precipitations the cast iron melting process has a big influence, too. This is a liquid iron metallurgical quality which has a big impact on graphite nucleation potential. The right superheating level above the inversion temperature is another important issue and must not be omitted.

A high carbon content in the ductile iron is generally beneficial, because it decreases the shrinkage tendency but, when the CE value is too high, the iron loses its castability, and the cold shut defects may occur. The direct cause of such defects is not a low pouring temperature or to long pouring time but too high carbon and silicon content which are prone to oxidation in the melting temperature. It is crucial to fill the mold as fast as possible but with the limited turbulence. The pouring temperature should be around 40°C higher than this typically used for castings of similar wall cross section surface. High carbon content in combination with increased silicon and cerium amount may supports the "chunky" type graphite creation and/or its flotation.

Sometimes the high carbon cast iron is vulnerable for the gas defects. So, taking all these problems into account, the carbon content must be calculated very carefully because many defects found in the SiMo castings are carbon content related [18].

According to [19] the superheating and holding time in elevated temperature impact on the graphitization process retracts mostly on carbon and silicon oxidation: 

\[ \text{SiO}_2 + 2[\text{CO}] \rightarrow [\text{Si}] + 2[\text{CO}] \]

(\(\text{(}\) – reagents in the slag, [\(\text{}\)] – in liquid alloy and \([\text{}\})\) in gas.

For the cast iron of given chemical composition the specific temperature exists at which the silicon is in balance with dissolved oxygen. Above this point the excessive oxygen is evacuated from the liquid in CO (carbon oxidation, sparking events) while below it the excessive oxygen creates SiO\(_2\) which moves into the slag. This equilibrium temperature is sometimes called the inversion temperature and is growing with the silicon content increase while dropping with the carbon content in the liquid alloy. For the clearly visible inversion phenomenon, the liquid metal bath temperature should exceed the inversion point of approximately 50°C. The liquid alloy superheating and its holding time in the temperature influence is explained by destruction of SiO\(_2\) particles which serve as graphite nucleation pads [19].

With the C and Si content increase in the liquid iron the inversion temperature increases, too. It is very important when the technology of SiMo castings production is designed. The SiMo melting process requires higher superheating and holding time in the temperature inside the furnace. What is more, it is important to ensure the appropriate nucleation potential of the liquid alloy to

be sure that during the whole melting process most thermal parameters (measured during DTA analysis) are high and stable.

After the analysis of the microstructure of the castings in this experimental trial it must be underlined the P0 sample (as-cast) shows slight pearlite amount which is then transformed during the HT process. Such structure is good because there is no bad carbides phases intergranular distribution network. But, a large molybdenum carbide precipitations are surrounded by the cloud-like group of small this phase precipitations. The best results were recorded for the P4 and P6 HT variants. Taking under consideration the carbides phase morphology after P6 treatment its significant refinement and quite uniform distribution inside the metal matrix was achieved and this is beneficial situation. When we look on the grains borders (P6 variant) a small molybdenum carbide amount can be observed which is uniformily distributed on these borders. This is disadvantageous because of the alloy mechanical properties drop what was proved during the tensile tests. Summing up, the microstructure of the alloy being analyzed (P0 - P5 variants) fulfills the metallographic requirements both from the graphite precipitations point of view and the metal matrix even without the expensive and time-consuming heat treatment of the castings. Additionally, it is worth to remember that during the HT process the natural corrosion occurs, the passive layer appears (just under the thin, loose iron oxide skin) thanks to silicon and oxygen reaction. Another phenomenon supporting this is the silicon atomic diffusion process to the casting surface and oxygen atoms to the middle of the passive layer. In most cases this layer is removed unnecessarily during the casting finishing process.

The literature review suggests the carbides in such cast iron are stable up to about 1050°C, what was partly proven in the research. For so high temperature the protective atmosphere in the furnace should be applied due to extensive castings surface oxidation.

### 4. Conclusions

The first conclusion after the described research is that despite of the pearlitic structure traces the P0 casting (as-cast) possesses right metallographic features: metal matrix and graphite precipitations. There are some imperfections of the graphite shape and size (compacted graphite) but their number is relatively low and do not affect the alloy quality parameters.

The heat treatment caused the complete pearlite from the metallic matrix removal. The pearlite ratio in as-cast state (P0 sample) even during the short, cyclic temperature changes should not result in castings micro cracks occurrence causing its quality drop.

The heat treatment especially for P4 case resulted in carbides phase refinement, visible as dissipated cloud of tiny molybdenum carbide precipitations around the primary, large molybdenum carbide inclusion. The next step should be a thorough stereological analysis of these precipitations with the statistical analysis of the results.

For the last HT variant – P6 at 1100°C a significant dissipation of the carbide phase inside the whole microstructure was observed. From the stereology point of view this is the best result. However, small molybdenum carbides were located on the
grains borders, too lowering significantly both strength and toughness of the alloy.

In all other cases P0 – P5 no harmful network of carbides precipitations on the grains borders were found.

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