Original Article

The effect of niobium addition on the microstructure and properties of cast iron used in cylinder head

Sining Pan\textsuperscript{a,b,*}, Fanzheng Zeng\textsuperscript{a,b}, Nanguang Su\textsuperscript{a}, Zhaokun Xian\textsuperscript{a}

\textsuperscript{a} College of Mechanical and Electrical Engineering, Hezhou University, China
\textsuperscript{b} Guang Xi Key Laboratory of Calcium Carbonate Resources Comprehensive Utilization, Hezhou University, China

\section*{ARTICLE INFO}

Article history:
Received 29 September 2019
Accepted 28 November 2019
Available online xxx

Keywords:
Cast iron
Microstructure
Mechanical properties
Residual stress
Niobium alloyed

\section*{ABSTRACT}

Cylinder head is one of the most important parts of heated components in the engine, while cracking due to low strength and large residual stress at high temperature is the main failure mode of cylinder head. With the growing demand of good performance and high reliability, gray cast iron with trace alloying element and optimized annealing process are probably effective ways in obtaining suitable materials. The effect of niobium addition on the microstructure and properties of cast iron used in cylinder head is studied in this paper. The results show that, the tensile strength, toughness, fatigue properties and thermal fatigue properties of gray cast iron are improved by adding trace niobium elements. The specimen with 0.20% niobium shows better comprehensive mechanical properties than others. The addition of trace niobium elements can not only refine the graphite, eutectic cell, carbide and phosphorus eutectic, but also reduce the pearlite lamellar space, thus strengthening the matrix. The cylinder head is made by cast iron with 0.20% niobium addition, and the annealing process of thermal aging is optimized. The residual stress of cylinder head can be maintained at a low level by adopting annealing process with higher holding temperature, longer holding time, lower cooling rate and lower outlet temperature. The analysis of microstructure, mechanical properties and residual stress for niobium alloyed cast iron is helpful for solving the cracking problem of cylinder head, and providing scientific basis for improving engine reliability.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

\section*{1. Introduction}

Cast iron is widely used in vehicle industrial, because of its low cost, outstanding casting properties, high thermal conductivity, advanced mechanical performance and so on [1–4]. Due to its excellent mechanical properties at high temperature, gray cast iron is typically applied as the cylinder head of diesel engine. The engine usually works under transient operating conditions, including the start-stop cycles and the regular combustion cycles [5–7]. Strict service environment puts forward high requirements for cast iron materials, such as high strength and toughness, good thermal fatigue resistance, working under a large temperature gradient. In recent years, the cracking failure of cylinder head caused by

\* Corresponding author.
E-mail: supereve122@163.com (S. Pan).
https://doi.org/10.1016/j.jmrt.2019.11.076
2238-7854/© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

insufficient high temperature strength and excessive casting residual stress, becomes one of the urgent problems to be solved in the application of cast iron materials [8,9].

The mechanical properties of cast iron can be improved by alloy design and structure control techniques. From the perspective of material science, the effect of material composition on the structure and properties is significant [10,11]. Recently, many researchers have focused on the addition of trace alloying elements to cast iron. It is well known that alloyed elements such as niobium, molybdenum and vanadium are added in very small quantity in order to improve strength and ductility through Nb, Mo, V (C, N) precipitates [12,13]. Among various alloying elements, niobium is widely used for microstructural control in cast iron [14-21]. The research results indicated that [15,19], the main functions of niobium in cast iron were transformation strengthening, fine grain strengthening and second phase strengthening. The niobium element mainly combined with carbon to form NbC hard particles embedded in the matrix of cast iron [17]. The formation of NbC results in the refinement of primary MₖC₆ carbides, so the wear resistance of cast iron was improved significantly [14]. Zhou et al. [18] found that the 1.48 wt% Nb addition to grey cast irons could increase hardness and wear resistance considerably due to the massive presence of large-sized NbC phases. At the same time, the number of eutectic cells increased, and the graphite size and the pearlite interlamellar spacing decreased. Devcic et al. [20] showed that the addition of 0.65 wt% niobium led to the formation of 10 μm chunky niobium and titanium containing phases in grey cast irons, and improved their abrasion resistance and tensile strength. Chen et al. [21] investigated the effects of niobium addition up to 0.11 wt% on the microstructure and tensile properties of as-cast ductile iron, and the optimum niobium addition was found to be around 0.08 wt%. However, the effect of Nb-rich phase, especially the strip-like Nb-rich phase widely existing at the boundary of eutectic cell, on the properties of gray cast iron deserves further discussion.

In addition, one of the ways to reduce excessive residual stress in casting, is the application of stress relief treatment for the castings. The residual stress of cylinder head is mainly produced during casting. In the cooling process of after solidification, due to the different cooling rate of each region and the obstruction of shrinkage by molding materials, residual stress is induced in the casting. Due to the presence of residual stresses, fatigue cracks may be initiated because of overstrain as the local residual stresses may be larger than the flow stress of matrix [22,23]. The residual stress will reduce the dimensional stability and mechanical properties of the cylinder head, and then affect the reliability and performance of the diesel engine. During actual production, either natural aging, thermal aging or vibration aging can be used to eliminate the residual stress of castings. Among them, the thermal aging is widely used in the production of cylinder head. In order to eliminate the residual stress, the thermal aging consists of heating the castings to a certain temperature in the annealing furnace, relaxing the stress of the castings at the holding temperature, and controlling the cooling process of the castings. Adding alloying elements to cast iron will increase the residual stress of castings, so it is necessary to study that, how to reduce the residual stress of castings through the design of annealing process.

The main objective of this paper is to analyze the microstructure, mechanical properties and residual stress of niobium alloyed cast iron used in cylinder head. In order to solve the cracking failure in cylinder head, the effect of niobium addition on the microstructure and mechanical properties of cast iron is investigated. Cast iron with different niobium addition is designed, and the corresponding microstructures and mechanical properties are tested. Based on the experimental results of microstructure and mechanical properties, the optimum chemical composition of cast iron with trace niobium addition is obtained, and is applied to the actual production of cylinder head. The effect of different annealing processes on the residual stress of cylinder head is studied. The results of this paper provide effective ways to improve high temperature strength and reduce casting residual stress of cast iron.

<table>
<thead>
<tr>
<th>No.</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>3.27</td>
<td>1.79</td>
<td>0.566</td>
<td>0.071</td>
<td>0.034</td>
<td>0</td>
<td>Bal.</td>
</tr>
<tr>
<td>2#</td>
<td>3.28</td>
<td>1.83</td>
<td>0.575</td>
<td>0.069</td>
<td>0.033</td>
<td>0.05</td>
<td>Bal.</td>
</tr>
<tr>
<td>3#</td>
<td>3.34</td>
<td>1.85</td>
<td>0.562</td>
<td>0.068</td>
<td>0.036</td>
<td>0.11</td>
<td>Bal.</td>
</tr>
<tr>
<td>4#</td>
<td>3.23</td>
<td>1.89</td>
<td>0.545</td>
<td>0.069</td>
<td>0.035</td>
<td>0.16</td>
<td>Bal.</td>
</tr>
<tr>
<td>5#</td>
<td>3.22</td>
<td>1.93</td>
<td>0.576</td>
<td>0.071</td>
<td>0.037</td>
<td>0.20</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

### 2. Experimental procedure

#### 2.1. Materials

The investigated material in this study is based on an EN-GJL-250 cast iron. During the composition design, the alloys are added with niobium content of 0, 0.05%, 0.10%, 0.15% and 0.20% respectively. The alloys are melted in the induction furnace of medium frequency, with the pouring temperature of 1650–1700 K. The chemical composition of specimens are listed in Table 1.

#### 2.2. Microstructure observation

The microstructure observation is carried out by OLYMPUS-PMG3 optical microscope (OM) and ZEISS EVO18 Special Edition scanning electron microscope (SEM). Optical microscopy is used to observe the content of graphite, pearlite, carbide and phosphorous eutectic, eutectic cell and niobium-rich phase. Scanning electron microscopy is used to observe pearlite slices.

#### 2.3. Mechanical properties testing

The tensile strength and fatigue properties of cast iron specimens are tested with MTS880 electro-hydraulic and servo-controlled material testing machine, and the specimen size of fatigue test is displayed in Fig. 1. The fatigue loading is applied sinusoidally as follows: \( \sigma_{\text{max}} \) is 180 MPa, \( \sigma_{\text{min}} \) is 18 MPa, and the frequency is 10 Hz. The impact tests are conducted with WOLPERT PW 36/15 impact testing machine. The impact
specimen is with the diameter of 20 mm, and the length of 120 mm. Three samples are tested under each condition, and the results are discussed by taking the average value.

The thermal fatigue test is carried out by heating-cooling cycle. The sample size is $20 \times 20 \times 20$ mm. The sample is heated in a box resistance furnace at 773 K for 8 min, and then is cooled with water quenching for 1 min, which is called a complete heating-cooling cycle. The surface cracks of specimens are observed after every 25 cycles. The thermal fatigue life is defined as the number of cycles when the length of main crack reaches 7 mm.

2.4. Residual stresses evaluation

In this paper, the measurement of residual stress is based on the cylinder head made of niobium alloyed cast iron, and the blind-hole method is applied. Three-dimensional strain gauges are attached to the measured points after surface cleaning. The half-bridge strain gauge connection is used for measurement, while other strain gauges are served as public compensators. After adjusting and balancing the strain gauge, small hole with the diameter of 1 mm and the depth of 2 mm is drilled at the center of the strain gauge, and then the diameter is broadened to 1.5 mm gradually. The stable value of strain gauge is read by the strain equipment. Finally, the strain value of the measured point is calculated by formula (1).

$$
\begin{align*}
\sigma_{1,2} &= \frac{E}{4A} (\varepsilon_1 + \varepsilon_3) \pm \frac{E}{4B} \sqrt{(\varepsilon_1 - \varepsilon_3)^2 + (2\varepsilon_2 - \varepsilon_1 - \varepsilon_3)^2} \\
tl_2 &= \frac{2\varepsilon_2 - \varepsilon_1 - \varepsilon_3}{\varepsilon_3 - \varepsilon_1} \\
\sigma &= \sqrt{\sigma_1^2 + \sigma_2^2 - \sigma_1 \sigma_2}
\end{align*}
$$

(1)

where $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the release strain in three directions in formula (1), E is elastic modulus of material, $\theta$ is the angle between $\sigma_1$ and the reference axis of strain gauge No. 1. A and B are the release coefficient of material, which are measured by experiments as the value of 0.586 and 1.112, respectively.

Residual stresses are measured at 12 points for each cylinder head, which the distribution is shown in Fig. 2. Since the residual stress on the surface is in the state of plane stress, it is appropriate to calculate the comprehensive stress by the fourth strength theory, as shown in formula (2).

3. Results and discussion

3.1. Microstructure

Fig. 3 shows the optical micrograph of graphite structure with different niobium content. It can be seen that, the graphite morphology of each sample is similar, and the addition of niobium shows no obvious effect on the distribution of graphite. However, due to the addition of niobium, the graphite phases are refined. With the increase of niobium content, the length of graphite (the average length of the three longest graphite in the optical micrograph) gradually decreases from 180 µm to 160 µm. Since niobium is with strong tendency for carbide formation, it will combine with carbon to form fine NbC particles in molten iron before solidification. These particles will become the core of nucleation and incubation for the graphite, resulting in the refinement of graphite.

The effect of niobium content on eutectic cell structure is demonstrated as in Fig. 4. The boundaries of eutectic cells are depicted with red outlines. As similar with the effect on graphite structure, the addition of niobium can also refine the eutectic cell, with the distribution density increasing from 250/cm² to 515/cm². The eutectic cell is formed by the eutectic precipitation of graphite and austenite. During the solidification process of gray iron, graphite is the leading phase. After graphite nucleation, it grows divergently around. The austenite nucleates and grows adhering to the graphite, and finally forms a eutectic cell. Therefore, the number of eutectic cells is equal to the number of graphite cores. The formation of NbC particles increases the number of graphite cores and eutectic cells, which can be used to explain the similar refining trend of graphite and eutectic cell in Figs. 3 and 4.

Fig. 5 shows the effect of niobium content on matrix structure. The addition of niobium has little effect on the content of pearlite, carbide and phosphorus eutectic. The content of pearlite in every sample is 98%, while the content of carbide and phosphorus eutectic is 1~2%. However, with the increase of niobium content, the bulk carbide and phosphorus eutectic are refined continuously. In Fig. 5(e), the boundary of eutectic cells is represented by yellow lines, while the Nb-rich phases are depicted with red circles. The Nb-rich phase precipitates along the boundary of eutectic cells, which indicates that the Nb-rich phase formed in the late stage of eutectic transformation. The Nb-rich phase is strip-like (including Y-shaped and V-shaped), and the length is about 2~30 µm.

The EDS result of Nb-rich phase in cast iron with 0.20% niobium addition is illustrated in Fig. 6. The added niobium elements precipitate almost in the form of Nb-rich phase. The Nb-rich phase is the carbide of Nb, Mo and Ti, which is mainly of Nb carbide. From the point of free energy for chemical reaction and electronegativity of elements, niobium is a strong carbide-forming element. The affinity of niobium to carbon is much higher than that of iron and carbon. When a small amount of niobium is added to cast iron, during solidification, most niobium elements will combine with carbon in molten iron to form Nb-rich phase particles, which are located at the boundary of eutectic cells. Nb-rich phase is the main existence form of niobium, while a small amount of niobium is soluble in pearlite lamella.
The pearlite lamellar structures in cast iron are shown in Fig. 7. In order to analyze the effect of niobium quantitatively, the lamellar spacing of pearlite is calculated with the following equation: 

\[ S = \frac{\pi D}{N M} \]  

where \( D \) is the diameter of the red circle shown in Fig. 7, \( M \) is the magnification of pictures, and \( N \) is the number of intersection point for the red circumference and cementite sheet. Three pictures are measured for each sample, and different positions are selected for multiple measurements. The average values of measured results are shown in Fig. 8. The addition of niobium shortens the distance between pearlite lamellar, therefore refining them. These phenomena are closely related to changes in mechanical properties and will be discussed below.

### 3.2. Mechanical properties

The effect of different niobium content on the tensile strength and toughness is shown in Fig. 9. It can be seen that, when
the niobium content increases from 0% to 0.20%, the tensile strength increases from 246 MPa to 300 MPa, and the maximum appears when the niobium content is 0.20%. The impact energy of specimens with niobium addition is similar with that of tensile strength. The maximal impact energy appears when niobium content is 0.20%, which is 10% higher than that without niobium. Fig. 10 shows the effect of niobium content on mechanical fatigue and thermal fatigue properties. It is clear that, the addition of niobium can improve both mechanical fatigue and thermal fatigue properties. The maximal values of both mechanical fatigue and thermal fatigue occur when niobium content is 0.16%.

The change of mechanical properties of cast iron is closely related to the change of its chemical composition and microstructures. Firstly, the finer the graphite is, the smaller the splitting effect on the matrix. Therefore, the addition of niobium can improve the tensile strength, toughness, mechanical fatigue and thermal fatigue properties of gray iron. The refinement of graphite is one of the main reasons for the improvement of mechanical properties. It can be found that, the refinement of eutectic cell is accompanied by the refinement of graphite. The hard phases such as carbide and phosphorus eutectic are formed at the boundary of eutectic cells.

**Fig. 4 – The effect of niobium content on eutectic cell structure (red outlines: the boundaries of eutectic cells).** (a) 0%, (b) 0.05%, (c) 0.11%, (d) 0.16%, (e) 0.20%.
Fig. 5 – The effect of niobium content on matrix structure (yellow lines: the boundary of eutectic cells, red circles: the Nb-rich phases).
(a) 0%, (b) 0.05%, (c) 0.11%, (d) 0.16%, (e) 0.20%.

Fig. 6 – The EDS result of Nb-rich phase in cast iron with 0.20% niobium addition.
Fig. 7 – The effect of niobium content on pearlite lamellar structure. (a) 0%, (b) 0.05%, (c) 0.11%, (d) 0.16%, (e) 0.20%.

Fig. 8 – The effect of niobium content on pearlite spacing.

Fig. 9 – The effect of niobium content on tensile strength and toughness.
tic cell, which is significantly different from austenite grain boundary in steel.

Secondly, the spacing of pearlite lamellar is mainly determined by eutectoid supercooling. The addition of niobium can reduce the transformation temperature of pearlite and increase the eutectoid supercooling. Moreover, the dragging effect of niobium in solid solution prevents the diffusion of carbon atoms, therefore, only fine pearlite lamellar can be formed. The decrease of pearlite spacing further strengthens the pearlite structure, increases the deformation resistance and tensile strength. Fine pearlite lamellar prevents fatigue and thermal fatigue cracks from propagating in pearlite, resulting in the improved fatigue properties.

Generally, the carbides located at the grain boundary are with large bulk form. However, the Nb-rich phase is fine in strip shape. It is evident that the fine Nb-rich phase will not have a greater splitting effect on the matrix. The precipitation of Nb-rich phase along the boundary of eutectic cell indicates that, the combination of niobium and carbon happens in the late solidification stage, which consuming the carbon in the final solidification zone and preventing the formation of large carbides and phosphorus eutectics. Therefore, the large carbides and phosphorus eutectics become smaller as shown in Fig. 5. Such effect results in stronger bonding force at the boundary of eutectic cells, and prevents cracks from propagating along the boundary, which helps to improve the strength, toughness and fatigue properties of gray iron. The solid solution of niobium in the pearlite can reduce the transformation temperature of pearlite, and increase the eutectoid supercooling. Therefore, the spacing of pearlite lamellar in Fig. 7 decreases, and the pearlite lamellar is refined. Moreover, the solid solution of niobium can also strengthen the pearlite matrix, prevent cracks from propagating along the matrix, and improve the strength and fatigue life.

3.3. Residual stresses

According to the previous results, the original material with 0.20% niobium addition can improve the mechanical properties significantly. During the casting process of cylinder head, cast iron with the addition of 0.20% niobium can make the cost and performance of the product matching better. Therefore, the range of 0.17–0.22% is adopted to control the content of niobium element. For the comparison of different annealing processes, nine cylinder heads are cast with the molten iron of the same composition. In order to eliminate the casting residual stress of cylinder head, three annealing processes are designed, and the schematic diagram is shown in Fig. 11.

It can be seen from Fig. 11 that, the heating rate of process A and B is faster than that of process C, and the holding temperature of process B and C is higher than that of process A. The holding time of process A and C is equal and shorter than that of process B, and the cooling rate of process A and C is faster than that of process B. Specific parameters of each process are listed in Table 2.

In order to compare the effect of three annealing processes on the elimination of casting stress, three cylinder heads for each process are selected for the measurement of residual stress. These three cylinder heads for each process are with the same annealing process, however, they are not annealed at the same time. Twelve points of each cylinder head are selected for the measurement of residual stress, according to the positions shown in Fig. 2. The residual stress of each cylinder head is defined as the average of the twelve points, which are shown in Fig. 12. The A-1# or A-2# means the 1# or 2#
cylinder head annealed by process A, respectively, while B-1# denotes 1# cylinder head annealed by process B, and so on.

As can be seen from Fig. 12, compared with process B and C, the residual stresses of three cylinder heads annealed by process A are larger, and the data are relatively dispersed. The stress levels of six cylinder heads annealed by process B and C are lower, and the data are less dispersive. Higher holding temperature than process A is designed for process C, for releasing casting stress to a greater extent. Based on that, further improvement is made in process B, such as prolonging holding time to make the temperature field of cylinder head more uniform, reducing the cooling rate, and maintaining lower outlet temperature to make stress release completely.

Reducing the cooling rate shows obvious effect on eliminating the residual stress. According to the principle that most of the residual stress is caused by uneven cooling in the elastic-plastic zone of cast iron (350–450 °C), the cooling rate of annealing process must be slow enough. If the cooling rate is too fast above 350 °C, secondary residual stress is tended to induce. Higher holding temperature, longer holding time and lower cooling rate are designed in process B, in order to keep the residual stress at a lower level after annealing. Therefore, process B is recommended as the annealing process of niobium alloyed cast iron used in cylinder head.

4. Conclusion

In this paper, in order to solve the cracking failure in cylinder head, the effect of niobium addition on the microstructure and properties of cast iron is investigated. The effect of different annealing processes on the residual stress of cylinder head made by cast iron is also studied. The main conclusions are listed as following:

(1) There are three forms for the existence of niobium in cast iron. The first one is that, niobium combines with carbon to form fine NbC particles in molten iron before solidification. These NbC particles become the core of nucleation and incubation for the graphite, leading to the refinement of graphite and eutectic cell. The second one is that, niobium is solid dissolved in matrix, leading to solid solution strengthening. The third one is that, the stripped Nb-rich phase is formed by embedding on the boundary of eutectic cell, which is the main existing form of niobium in cast iron.

(2) The addition of niobium can reduce the transition temperature of pearlite, and increase the eutectoid supercooling. Moreover, the dragging effect of solid-dissolved niobium prevents the diffusion of carbon atoms, resulting in the decrease of pearlite lamellar spacing. The precipitation of stripped Nb-rich phase located along the boundary of eutectic cell, consumes part of carbon element in molten iron during the late solidification stage, and prevents the formation of carbides and phosphorus eutectics with large block, which leading to the refinement of carbides and phosphorus eutectics.

(3) When the niobium content is 0.20%, the tensile strength and toughness of gray iron material shows maximal value, and the mechanical fatigue and thermal-fatigue property are obviously improved. The comprehensive mechanical properties of cast iron are better compared with that without niobium addition. The addition of niobium can refine graphite, eutectic cell, carbide and phosphorus eutectic, reduce pearlite lamellar spacing and strengthen matrix. This is the main reason for the remarkable improvement of mechanical properties for the niobium alloyed cast iron.

(4) The residual stress of cylinder head treated by three different annealing processes is tested and compared. The results show that the residual stress can be maintained at a lower level by adopting higher holding temperature, longer holding time, lower cooling rate and lower outlet temperature in process B.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by the doctor’s scientific research foundation of Hezhou University (No. HZUBS201806), and the Hezhou Foundation for Research and Development of Science and Technology (No. 201908007 & No. 201808011).

References