Study on the serialization and applications of low carbon ductile iron

*SHU Xin-fu, SHU Rui, CHANG Dian-cun, ZHANG Xiao-long, ZHU Yan-dong, LI Ling-fang, LI Yu-zhong
(Republican University of Science and Technology, Kunming University of Science and Technology, Kunming 650093, Yunnan, P. R. China)

Abstract: Both the production process and the chemical composition of Sx were studied, and the serialization of low carbon ductile iron was also discussed. It was indicated that Sx modifier was sensitive to the carbon equivalent (CE) of molten iron and to some alloying elements too. When the CE of molten iron and the contents of alloying elements were changed, the content of Sx must be revised with the change correspondingly. Low carbon ductile iron can be stably changed into the one that non-carbon acicular ferrite and retained austenite (about 25%-28%) by quasi-casting bainitic process of using Sx-2 modifier treated Si-Mn-Cr-Cu-alloyed low carbon molten iron. The austenitic low carbon as-cast ductile iron could be obtained by the Ni-Si-Cr 35 5 2 percent alloys molten iron with less than 2% carbon treated by type Sx-3 modifier. The high-toughness ferritic low carbon as-cast ductile iron which contained more than 85 % ferrite in matrix could be got after the molten iron treated by type Sx-4 modifier, and its elongation was more than 10 %.

Key words: low carbon ductile iron; Sx modifier; series; modification treatment; application

CLC number: TG 143.5
Document code: A
Article ID: 1672-6421 (2005)04-0254-06

1 Introduction

Ductile cast iron can be got after the molten iron in either eutectic or hypereutectic compositions modified by RE-Mg alloy or treated by enough inoculation and heat treatment, since the birth of ductile cast iron. During the development of ordinary ductile cast iron, the content of carbon is never lower than 2.0%, the low carbon ductile iron that is not treated by heat treatment and modified by inoculation alloy mainly composed of anti-spherical surface active elements never emerged\cite{4-5}.

The new type low carbon ductile iron, in which matrix the graphite is small and spherical, with excellent mechanical properties can be obtained, after the molten iron with 1.2%-2.0% C, 1.8%-3.0% Si is modified by Sx mainly composed of some chemical elements that is considered as anti-spherical elements in common instead of RE and Mg \cite{6}. The index report by Yunnan Scientific Intelligence Agency in 2005 indicates that there are no reports about manufacturing ferritic low carbon as-cast ductile iron, pearlitic low carbon as-cast ductile iron, austenitic low carbon as-cast ductile iron and quasi-casting bainitic low carbon ductile iron except our achievements in scientific research, invention and issued papers. In our research, the method to produce low carbon ductile iron using the molten iron treated by Sx in which contains anti-spherical chemical elements is innovative and original\cite{10}.

During the earlier stage, low carbon ductile iron has been applied to fork of machining-tools. But with the development of science and technology, the strict requirements to the microstructure and properties are posed in our modern society. As a new engineering material, the low carbon ductile iron is facing new opportunities and challenge to be approved by the same occupations in the home and in the world as the first selective engineering material for designers and for more industrial applications. So, low carbon ductile iron must adopt variable microstructures to meet variable working conditions, and fully play its high potentiality.

In our research, we discuss the composition, microstructure, properties and process according to different cast part, and make experiments under industry conditions. We have successfully manufactured cylinder of diesel engine, crankshaft, products of military industry, the exhaust pipe of Audi A6 car, grinding balls, twist-duct of rolling mill, roller, hammerhead of crusher, hammerhead of roller, parts of motorcar chassis, and made profit for the enterprises. What we have provided are the reliable theory
and practice, as reference, for the large-scale manufacturing of low carbon ductile iron.

2 Experimental condition and method

2.1 Experimental condition of serials of low carbon ductile iron

Carbon steel scrap, pig iron of Kunming Steel Group, ferrosilicon 75, ferromanganese, medium-carbon ferrochromium, electrolytic nickel, electrolytic copper and Sx-1, Sx-2, Sx-3 and Sx-4 are the raw materials to produce low carbon ductile iron.

According to different matrix, we adopt different content of molten iron and different modification process, adding Si-Fe, Mn-Fe and Cr-Fe, electrolytic Ni, electrolytic Cu into furnace to adjust the composition of molten and alloying treatment. Slab reheating temperature (SRT) controlled between 1500 °C and 1550 °C, and the molten iron treated by different Sx according to different kinds of low carbon ductile iron, the ideal effects of spherical graphite will be obtainable.

The sample of microstructure analysis and mechanical properties are taken from the worksite. The instruments we used are JSM-5600LV SEM and D/MAX-30 X-ray diffraction apparatus and Cambridge S250 MK2 SEM and ZSX100e X-ray fluorescence spectrocomparator.

2.2 As cast structures and properties of low carbon ductile iron before and after modification by Sx

The matrix is netted wustite cementite (Fig. 1) before the molten iron with 1.2% -2.0% carbon treated by Sx, its hardness is high, and toughness and machinability are worse, so this material is usually not to be used in industry. After the molten iron treated by Sx, the matrix is small, spherical well-distributed graphite as-cast without netted cementite. The microstructure is composed of pearlite and ferrite (Fig. 2), the hardness decreases from HRC 42-45 to HRC 26-30, α decreases from 3-5 J / cm² to 10.4-14.3 J/cm², and the machining properties is improved greatly.

3 The results and analysis

3.1 Study on the serials of Sx

The serial study of Sx is carried out in the Ductile Iron Research Institute of Kunming University of Science and Technology (KUST). During our research, we use over ten chemical elements including Pb, Al, Ti, Sb, Zr, B, Sn, Bi, Zn, Te, As, Se, Cu, and etc. to make the Sx. Many of the chemical elements belong to surface active elements, and most of them are considered as anti-spherical elements in producing nodular cast iron in common. We must pay attention to the points during producing Sx: firstly, Sx is sensitive to the quantity of the elements added in it, so we adjust only the content of the elements added in it, so we adjust only the content of the elements at low level; secondly, Sx is also sensitive to the CE of molten iron and to some alloying elements, and when the CE of molten iron or alloy are changed, the content of Sx must be adjusted.

We finally select eight elements after we study all the elements according to different kinds of low carbon ductile iron. After we know the mutual function between Sx and low carbon ductile iron, we develop four kinds of Sx inoculants, i.e. Sx-1, Sx-2, Sx-3 and Sx-4 according to different matrix of low carbon ductile iron including pearlitic, quasi-casting bainitic, austenitic and ferritic microstructure. The distribution of eight elements in four serials of Sx inoculants is shown in Fig. 3 by ZSX100e X-ray diffraction fluorescence spectrum.

At present, pearlitic low carbon ductile iron can easily be got after treated by Sx-1, and the volume of pearlite can reach more than 90%; austenitic-bainitic low carbon ductile iron can be got after treated by Sx-2, and the volume of austenite can be about 26% -28% . Heat-resisting and corrosion-resisting austenitic low
carbon ductile iron can be got after treated by Sx-3, and the volume of austenite reaches more than 90%. High-toughness ferritic low carbon ductile iron can be got after treated by Sx-4, and the volume of ferrite reaches more than 85%. The quantity of Sx is only 1/3-1/2 of RE-Mg inoculant, and Sx is added into ladle only once.

3.2 Study on the serials of low carbon ductile iron

The objects of serial experiments of low carbon ductile iron are high-intensity pearlitic low carbon ductile iron, quasi-casting bainitic wear-resisting low carbon ductile iron, heat-resisting and corrosion-resisting austenitic low carbon ductile iron, and high-toughness ferritic low carbon ductile iron. The main components of these 4 kinds of low carbon ductile iron are summarized in Table 1. According to different requests to matrix and property of low carbon ductile iron, proper Sx inoculant can be chosen. Weighting the Sx as much as you need and inoculating with corresponding liquid iron, then low carbon ductile iron with proper structure and properties can be obtained.

The pilot production of low carbon ductile iron was performed at the Ductile Iron Institute of KUST, Yunnan Huayun Iron Corporation and 991 State Run Company. Melting facility was a 500 kg of medium frequency furnace. Molding methods were resin bonded sand shell mold casting and vacuum investment casting.

3.2.1 Study on quasi-casting bainitic low carbon ductile iron

To apply low carbon ductile iron in the area of liner and grinding ball used in metallurgical industry and mine, cement, electric power and the shaft, gear used in car making, the best way is to use the quasi-casting bainitic low carbon ductile iron which is composed of bainite and austenite treated by the process of quasi-casting. The process can enlarge the austenitic region, moving the C curve forward right, inhibiting the decomposition of austenite; by adding some alloy, to affect the curve of kinetics of low carbon ductile iron, and change the curve into S curve which contain 2 "tip of the nose", so we can obtain the matrix of bainite and retained austenite (≥20%). The matrix can improve the strength, toughness and the comprehensive mechanical properties. To produce quasi-casting bainite low carbon ductile iron, we use the cheaper alloy, Si-Mn-Cr-Cu (Cr+Cu ≤1%), instead of the expensive one, Ni-Mo-Cu (Ni+Mo+Cu ≥2.5%) [7], and open the mold in high temperature, quench by the retained heat, and keep the temperature of bainitic transformation, then the matrix will change into austenite-bainite phase, the wear resistance has been improved greatly [8].

The functions of each element in the Si-Mn-Cr-Cu alloy are described below, respectively. Si can reduce the activity of carbon in the molten iron, and make the carbon emerged by means of graphite, but when the level of Mn is high, improving the content of Si and enhancing inoculation can reduce the formation of (Fe,Mn)3C, and reduce the disadvantages of Mn. But, when the level of Si is more than 3%, with the promoted ferrite, it can improve the hardness and brittleness of low carbon ductile, and reduce the toughness. Therefore, the content of Si is better to be controlled between 1.8% and 3.0%. Mn can enlarge the region of austenite in the phase diagram of cast iron, strongly stabilize austenite, hinder the first transformation phase of bainite, change the shape and position of the same temperature transformation.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pearlite</td>
<td>1.2-1.6</td>
<td>1.8-2.2</td>
<td>0.4-0.8</td>
<td>≤0.07</td>
<td>≤0.05</td>
<td>Si-Mn-Cr-Cr</td>
</tr>
<tr>
<td>Bainite</td>
<td>1.4-1.8</td>
<td>2.2-3.0</td>
<td>1.2-2.0</td>
<td>≤0.07</td>
<td>≤0.05</td>
<td>3SN15Si2Cr</td>
</tr>
<tr>
<td>Austenite</td>
<td>1.6-2.0</td>
<td>4.0-5.0</td>
<td>1.0-1.5</td>
<td>≤0.07</td>
<td>≤0.05</td>
<td></td>
</tr>
<tr>
<td>Ferrite</td>
<td>1.6-2.0</td>
<td>2.4-3.0</td>
<td>0.2-0.4</td>
<td>≤0.07</td>
<td>≤0.05</td>
<td></td>
</tr>
</tbody>
</table>

Fig.3 Main components of 4 kinds of Sx inoculants
curve, increase the phase decomposition of austenite, and obviously separate the high temperature phase transformation from the low one and move the C curve forward right, postpone and restrain the austenite decomposition, so it can transform austenite into bainite easily. On the other hand, Mn can give more chance to cause segregation. Mn forms normal segregation in the molten iron un-solidified, and builds up along the borders of eutectic colony, and forms \((\text{Fe},\text{Mn})_3\text{C}\) which is disadvantage in the toughness and ductility of ductile iron in the quais-casting bainitic low carbon ductile iron. Because of non-existence of Ni and Mo alloy, we use Mn instead of Ni to improve the microstructure and properties. In the study, the content of Mn is controlled between 1.2% and 2.0%. On the other hand, Mn/Si has direct influence on microstructure, the content of Mn/Si is usually controlled between 0.40% and 0.65% in quasi-casting bainitic low carbon ductile iron. In general, little amount of Cr can improve the hardenability, move the isotherm curve forward to the right, enlarge inoculation time, move the pearlitic transformation part of C curve forward to higher region and the bainite transformation part to lower region, so two "tip of nose" are formed. But when the content of Cr exceeds 0.4% , cementite will appear, and hardness increases, toughness and ductile decrease. Mo can be replaced by Cr, and has economic advantages. The content of Cr is usually controlled between 0.2% and 0.3% in quasi-casting bainitic low carbon ductile iron. Cu can expend the austenitic region and improve hardenability of cast iron, and dissolve in austenite, not forming cementite. To some extent, the characteristics of Cu can repeat with that of Mn. Cu can replace Ni, and makes the matrix of low carbon ductile iron transform into austenitic-bainite microstructure by the quasi-casting bainitic process. Considering the cost issue, the content of Cu in low carbon ductile iron is controlled between 0.30% and 0.50% . The process of quasi-casting bainitic overcome not only the disadvantages of energy consuming during isothermal harden, time consuming and complexity of process but also the scattered standard of austenitic-bainite ductile iron, lower level as a whole, high cost because of more Ni, Mo and Cu alloy added \(^7\). In our research, after adopting the quasi-casting bainitic process, we obtain more advantages. For example, we save the cost of Ni and Mo adding, we cast aside the process of high-temperature heat treatment and nitrate isothermal quenching treatment, we also cut down the energy consumption, protect the environment, reduce the labor intensity. And the environment in enterprise and it is surrounding have been ameliorated greatly, the contradiction between the enterprise and his neighborhood has been alleviated greatly too.

The grinding ball which diameter is 70 mm treated by quasi-casting bainitic process in Furnace Charge Sub-Company of Yunnan Huayun Company is shown in Fig.4. The impact results between the low chromium alloy grinding ball and grinding ball treated by quasi-casting bainitic process which are applied in Xilin Cement Factory of Yunnan Huayun Company is shown in Fig.5 and Fig.6 respectively. The former is broken within 30 s impacted, but, the quasi-casting low carbon ductile iron ball has not been broken until 3 minutes 20 s impacted, (because of the pneumatic hammer is broken), so the impact properties of latter is as 6 times as the former.
3.2.2 Heat-resisting and corrosion-resisting austenitic low carbon ductile iron

The output of cast iron in our country is the first in the world, and our country is known as the large country of producing castings. But contrast with developed country, the foundry technology is backward as a whole. For example, Audi A6 car has been produced for many years since the first car made in our country, but some main parts (including exhaust pipe, as shown in Fig. 7) must be imported from Germany. The technical requirement of exhaust pipe in Germany is DIN1694GGG-NiSiCr 35 5 2, and the cementite in matrix is less than 3%, spherical rate is less than 2-3 grade, the diameter of graphite is 6-8 μm, the properties are: Rm ≥ 370 MPa, Aς ≥ 10% and the instantaneous temperature is more than 920°C, and has corrosion-resisting property. We can know that the material is the typical austenitic low carbon ductile iron, but, according to the chemical composition, we use the inoculate processing in common, both the spherical graphite and mechanical properties can not be got. As a matter of fact, no matter the content changing of austenitic low carbon ductile iron in which the carbon level is lower than 2.0%, we can get the required properties treated by Sx.

It is indicated that the molten iron can maintain better fluidity, and the spherical rate reaches 2-3 grade, the diameter of graphite reaches 7-8 μm, the volume of austenite in the matrix reaches 95%. At the same time, the mechanical properties are: Aς ≥ 13%, Rm ≥ 390 MPa, the instantaneous temperature is more than 900 °C, and has an excellent corrosion-resistance to the solution of sulphuric acid and hydroxide. From the data, we can know that the properties have reached the standard of Germany DIN1694GGG-NiSiCr 35 5 2. Now the material has been used to the Audi A6 car’s exhaust pipe.

Fig. 7 Exhaust pipe rough casting of Audi car made with heat-resisting and acid-proof austenitic low carbon ductile iron

3.2.3 Study on high-toughness ferritic low carbon ductile iron

Because ferritic ductile iron has high-toughness it can be used under the conditions of heavy loading, vibration and lash, for example, the basic part of cars and the parts of agricultural machinery, the gear shell, the different diameter water pipe and gas pipe etc. In many cases, ferritic carbon ductile iron can be applied in safety parts instead of malleable iron. When it is used to produce pipe, the cost is far lower than steel pipe’s. It can endure the deformation caused by the sinking and shaking of the ground and also has excellent anti-corrosion property. People are fond of this kind of material because of it’s high reliability and economic performance. But the high pure pig iron is required when producing the ferritic carbon ductile iron, and it usually can be used after treated by high temperature annealing.

Because of the content of carbon in low carbon ductile iron is less than that in normal ductile iron, we can use 70% scrap steel instead of high grade pig iron. The quality of molten iron can be guaranteed, but Sx is mainly consisted of anti-spherical chemical elements. The molten iron treated by Sx has more white iron tendency, so it is difficult to obtain as-cast ferritic low carbon ductile iron. After having studied for a long time, we finally produce the Sx-4 to get the as-cast high-toughness ferritic low carbon ductile iron. High-toughness ferritic low carbon ductile, as-cast, with more than 85% ferrite in matrix, could be obtainable after the molten iron treated by type Sx-4, and it’s value of percent elongation was about 10%-15%. Now the kind of material has been successfully applied to the parts of cars under the condition of high-toughness. The main properties of different matrix in low carbon ductile iron are shown in Table 2.

The microstructures of pearlitic, quasi-casting bainitic and ferritic low carbon ductile iron are shown in Fig. 8 by JSM-56000LV SEM. We can know that the diameter of graphite is 2-10 μm, spherical rate reaches 1-2 grade, and the graphite is well-distributed. The matrix is typical pearlite (Fig. 8 (a)), quasi-casting bainite which is composed of bainite and retained austenite (Fig.8(b)) and ferrite and little pearlite Fig.8(c), respectively.

The X-ray diffraction patterns of quasi as-cast bainite low carbon ductile iron and austenitic low carbon ductile iron are shown in Fig. 9 (a) and Fig. 9 (b) respectively by the D/max-3B X-ray diffraction apparatus. The condition of quantitative analysis to austenite was target Cu, 40 kV, 30 mA, DS=SS=1° , RS= 0.3 mm, the graphite monochrome. Velocity of scanning was 0.25°/min, and time of taking a sample was 0.01°/Step. After calculating the integral intense, we conclude that the volume proportion of γ-Fe is 28% in Fig. 9(a), 94% in Fig. 9(b).
Table 2 Main properties of low carbon ductile iron with different matrix

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sx weight</th>
<th>$R_m$ MPa</th>
<th>$A$ %</th>
<th>$K_v$ J·cm$^{-2}$</th>
<th>HB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pearlite</td>
<td>Sx-1: 0.4-0.6</td>
<td>680-750</td>
<td>1.7-1.9</td>
<td>10.4-14.3</td>
<td>220-260</td>
</tr>
<tr>
<td>Bainite</td>
<td>Sx-2: 0.4-0.6</td>
<td>816-894</td>
<td>3.2-7.0</td>
<td>12.5-18.8</td>
<td>250-280</td>
</tr>
<tr>
<td>Austenite</td>
<td>Sx-3: 0.6-1.0</td>
<td>392-432</td>
<td>13.4-17.8</td>
<td>32.9-38.4</td>
<td>180-220</td>
</tr>
<tr>
<td>Ferrite</td>
<td>Sx-4: 0.6-1.0</td>
<td>396-451</td>
<td>10.3-15.5</td>
<td>27.6-36.2</td>
<td>170-195</td>
</tr>
</tbody>
</table>

(3) The austenitic low carbon as-cast ductile iron could be obtained after Ni-Si-Cr 35 5 2 percent alloy molten iron with less than 2 % carbon treated by type Sx-3, and the kind of low carbon ductile iron can work under the condition of instantaneous temperature more than 900 °C, and has an excellent corrosion resistance to the solution of sulphuric acid and hydroxide.

(4) High-toughness ferritic low carbon as-cast ductile iron which contained more than 85% ferrite in matrix could be got after the molten iron treated by type Sx-4.

Reference:


(The paper is support by Foundation Key Project of Yunnan: Study on inoculated theory and reliability of low carbon ductile iron, NO. 1999E0004Z)