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Research Paper

A high-performance and low cost nitrogen-containing gray cast iron

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ABSTRACT

To meet the demand for high-strength gray iron castings while lowering casting production costs, nitrogen micro alloyed gray cast iron with manganese nitride inoculant was developed, and the effects of manganese nitride addition on its microstructure, mechanical properties, and casting cost were investigated. The test results show that with different manganese nitride additions, the graphite flakes have round and blunt ends and short, thick, and slightly curved shapes; as the nitrogen content in the iron increases, the graphite forms become shorter and curved, and the pearlite content increases, which is conducive to improving the strength and hardness of gray cast iron. Excess nitrogen content in castings causes nitrogen porosity defects, which significantly degrades the material properties. The addition of alloying elements such as Cu and Sn can be reduced by adding an appropriate amount of manganese nitride to the process, and the casting cost can be reduced by 180 RMB/ton to realize low-cost production of high-performance gray cast iron.

1 Introduction

Gray cast iron is widely used in diesel engine blocks, cylinder heads, and other thin-walled complex machine parts for its superior casting formability, good wear resistance, and heat transfer property [1]. In recent years, with the formation and requirements of the "carbon peaking and carbon neutrality goals", the lower mechanical properties of ordinary gray cast iron can no longer meet the demand for high-power, low-emission, and lightweight iterations of related products, and the demand for high-performance gray cast iron in the market segment is gradually increasing. Currently, Vanadium is often added to the cast iron by alloying, in order to improve to the strength of the material. [2-5]. However, multiply high-alloyed gray cast iron has poor iron fluidity, high scrap rate, and low casting and machining properties. At the same time, the rising global prices of alloy metals such as copper and tin and the scarcity of high-quality ore resources have also led to the increasingly

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demanding requirements of high-alloyed gray cast iron materials in terms of raw materials as well as costs, which seriously limits their promotion and application [6]. Therefore, preparing high-performance gray cast iron with less precious alloy content and lower production cost has become a research hotspot and exploration direction for domestic and foreign foundry workers.

Yongshou Zhou [7] showed that the addition of the appropriate amount of N could change the microstructure morphology of gray cast iron and effectively improve the mechanical properties of gray cast iron. Svensson, I.L. et al. [8] prepared a nitrogen-containing gray cast iron using an N-containing inoculant, and its tensile strength and elongation reached 393 MPa and 1.6%, respectively, with significant performance enhancement. Wang, Q.-G. et al. [9] also pointed out that the tensile strength of gray cast iron could reach 395 MPa with 0.012% N content of the molten iron. Alexis, V. et al. [10] investigated the effect of free N content on the enhanced aging of gray cast iron, and the results showed that controlling the free N content in the molten iron is an effective way to improve the enhanced aging effect. Jin, C. et al. [11] pointed out that N needs to be in the proper range to play its role, and too high N content will form nitrogen porosity defects, which generally requires controlling the N content at 50-100 ppm.

Based on the above analysis and purpose, this experiment adds nitrogen into the grey iron casting process to optimise the existing production process. We strive to achieve good results in controlling the metal alloy content in iron, improving mechanical properties and reducing production costs. This paper focuses on the effect of different nitrogen content on the microstructure and mechanical properties of grey cast iron, and compares the performance and production cost of grey cast iron castings prepared by the existing casting process, to provide reference for the low-cost production of high-performance nitrogen-containing grey cast iron.

2 Experimental materials and methods

2.1 Specimen preparation

The company adopted a medium-frequency induction furnace for melting in casting production. The main ingredients were gray iron returns (50%), high manganese scrap (50%), silicon-barium-calcium inoculant (0.55%). Since manganese nitride as an additive medium can greatly increase the content of manganese in a local range, it is beneficial to the rapid dissolution of nitrogen in gray cast iron solution [12]. In this paper, different contents of ferromanganese nitride (0.1%, 0.15%, 0.2%, 0.25%, 0.35%) were added to control the nitrogen content in the molten iron. The main chemical composition of the furnace (mass fraction) was controlled before inoculation as follows: 3.3-3.4%C、1.75-1.85%Si、0.7-0.8%Mn、0.08-0.12%S、≤0.03%P、0.4-0.6% Cu、0.04-0.06%Sn、0.2-0.3%Cr、≤0.0045%N; the main chemical composition after breeding was shown in Table 1. The control group used high-alloy gray cast iron (without manganese nitride) from the company's existing process. The main ingredients were selected from gray iron returns (50%), high manganese scrap (50%), silicon-barium-calcium inoculant (0.55%), and ferrosilicon inoculant (0.1%), with the same specific chemical composition control before inoculation, and the following specific chemical composition after inoculation: 3.32C%、2.05%Si、0.75%Mn、0.02%P、0.09%S、0.51%Cu、0.05%Sn、0.22%Cr、0.0036%N.

Table 1 - Main chemical composition of gray cast iron with different additions of ferromanganese nitride (wt%)

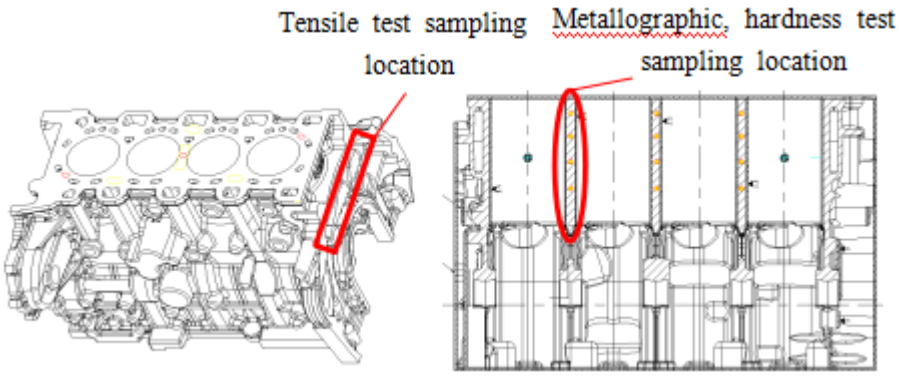
ferromanganese nitrid	C	Si	Mn	P	S	Cu	Sn	Cr	N
0.1%	3.32	2.05	0.77	0.02	0.09	0.50	0.05	0.23	0.0066
0.15%	3.31	2.06	0.81	0.02	0.09	0.52	0.05	0.24	0.0079
0.2%	3.29	2.04	0.85	0.02	0.09	0.51	0.05	0.23	0.0093
0.25%	3.29	2.06	0.88	0.02	0.09	0.51	0.05	0.25	0.0105
0.35%	3.27	2.05	0.95	0.02	0.09	0.52	0.05	0.22	0.0122

The specimen casting steps were as follow: firstly, scrap steel and furnace iron were put into the electric furnace to melt into iron fluid, and recarburizer is added to adjust the composition, then the temperature is increased to 1510℃, and after the iron is completely melted, the composition is analyzed by Optical Emission Spectrometer and oxygen analyzer to control the

chemical composition Secondly, 0.55%silicon-barium-calcium and ferromanganese nitride (0.1%, 0.15%, 0.2%, 0.25%, 0.35%) were used as inoculants for inoculation with molten iron, and N-type gray cast iron specimens with different N contents were prepared to obtain the optimal manganese nitride addition process. Finally, 0.1% ferrosilicon inoculant was selected for pouring, and the method was stream inoculation with a pouring temperature of 1450°C.

2.2 Test Methods

Referring to GB/T228.1-2010 standard system, three tensile specimens were cut in the cylinder bore wall as shown in Figure 1a, and the specimens were tested by a WDW3100 microcomputer-controlled electronic universal testing machine for tensile test, and the results were taken as the average. According to GB/T 231.1-2009 standard, in the cylinder bore wall as shown in Figure 1b intercept hardness and metallographic specimens, using HBS-3000 type digital display Brinell hardness tester for the hardness test. Five positions of the sample, namely, (middle, upper, lower, left and right) were taken as hardness test points, and the results were averaged. Carl Zeiss Axio Scope.A1 optical microscope was used to observe the graphite morphology of the specimen, and the type and length of graphite were classified and rated consulting GB/T7216-2009 method and standard metallographic atlas.



(a) Tensile specimen sampling location: main oil channel

(b) Metallographic and hardness specimen sampling location: cylinder bore clamp wall

Fig. 1 - Sampling position of test test

3 Results and analysis

3.1 Microstructure analysis

Graphite in gray cast iron is in the form of thin flakes, which can have a cutting effect on the metal matrix, and its sharp ends, which tend to cause stress concentration phenomena at the sharp corners, resulting in end stress well above the average stress [13]. The morphology, size, quantity, and distribution of flake graphite significantly influence the material properties of gray cast iron. Figure 2 shows the graphite morphology of specimens with different amounts of manganese nitride addition. As shown in the figure, the specimens are all A-type graphite, uniformly distributed in the metal matrix, and the distribution shows no directionality or irregularity. Among them, Fig.2a shows that the graphite flakes of high-alloyed gray cast iron specimens are coarse and flat with long lengths, and the graphite length rating reaches grade 4.

Compared to the high-alloyed grey cast iron specimens (Fig.2a), the nitrogen-containing grey cast iron has a shorter flake graphite, a slight increase in curvature, and the graphite ends begin to passivate. Moreover, with the increase of nitrogen content in the tissue, the graphite length gradually changes from grade 4 to grade 5, and when the nitrogen content increases to 122 ppm, a small amount of shorter grade 6 graphite starts to appear in the tissue. At the same time, the width and bending degree of graphite flakes slightly increased, and the graphite ends were further rounded and blunted. It can be seen that the addition of certain ferromanganese nitride improves the graphite morphology and reduces the stress concentration phenomenon caused by flake graphite ends. The main reason is that the addition of ferromanganese nitride has increased the content of nitrogen atoms in the organization. In the eutectic transformation process, the iron fluid nitrogen atoms are continuously adsorbed in the graphite growth front and solidly solved in the graphite [14]. Several layers of nitrogen atoms

formed on the graphite surface prevent the diffusion of carbon atoms in the metal liquid into the graphite, which limits the growth of flake graphite and forms short graphite. At the same time, the presence of a large number of nitrogen atoms on the fronts increases the difficulty of forwarding growth of graphite ends, and some of the nitrogen atoms solidly dissolved in graphite distort the graphite crystal punctures, which together promotes the lateral growth of graphite and produce more short, thick and curved graphite phases with rounded and blunt ends [15].

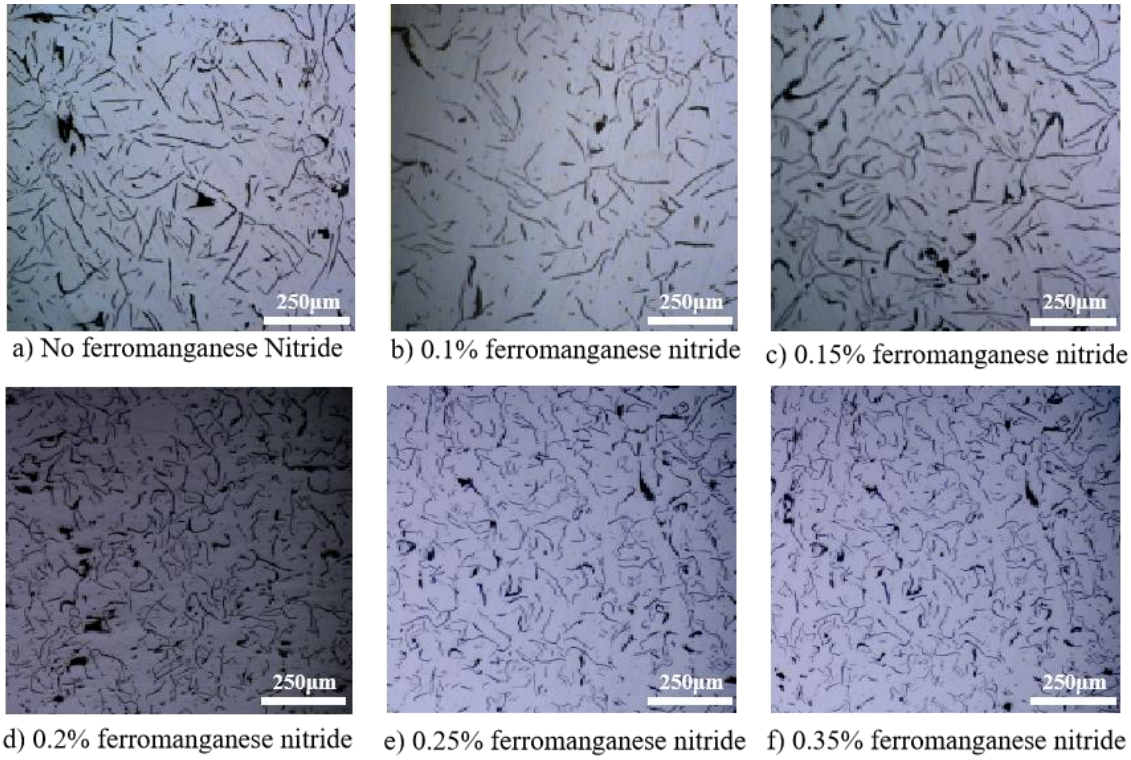


Fig. 2 - Graphite morphology of gray cast iron (100×)

In addition to improving graphite morphology, nitrogen can also promote the generation and refinement of pearlite because the eutectic transition temperature of gray cast iron has a significant linear relationship with the amount of nitrogen content. With the increase of nitrogen content in the tissue, the eutectic transition temperature and end temperature of gray cast iron decrease, but the end temperature of eutectic transition decreases more, resulting in the increase of the eutectic transition temperature interval and the increase of the eutectic transition subcooling, thus generating more and finer pearlite [16]. The finer pearlite and the passivated graphite strengthen the matrix, which makes the matrix obtain higher properties. Although the nitrogen content in cast iron increase is beneficial to improve the graphite morphology, stabilize and refine the pearlite organization, the excessive nitrogen will precipitate as nitrogen during the solidification of cast iron and cause porosity defects in the casting. Therefore, the nitrogen content should be strictly controlled in improving the microstructure of gray cast iron to avoid the adverse effects of nitrogen porosity.

3.2 Mechanical performance test

Graphite largely determines the tensile strength of gray cast iron because the graphite phase cuts the continuity of the matrix organization, and its strength is reduced, while the effect of the matrix organization is relatively weak [17]. As shown in the mechanical property test results in Fig. 3, compared with gray cast iron without manganese nitride addition, the strength and hardness of the material continued to increase with the addition of ferromanganese nitride. The tensile strength of gray cast iron increased by 20.74% (326 MPa), and the hardness increased by 18.23% (HB) when the addition amount reached 0.25%, and the iron nitrogen amount was 105 ppm, and the strength and hardness of the material increased significantly. However, we found in our tests that when the addition of ferromanganese nitride was further increased to 0.35% and the nitrogen content reached 122 PPM, trace amounts of nitrogen pores appeared in the performance test specimens(Fig. 4), and the tensile strength was significantly reduced by 24.43% (262 MPa), which harmed the material properties. Therefore, the

nitrogen content should be strictly controlled during the nitrogen-type gray iron casting process to avoid the adverse effects of nitrogen porosity, generally controlled within 100 PPM.

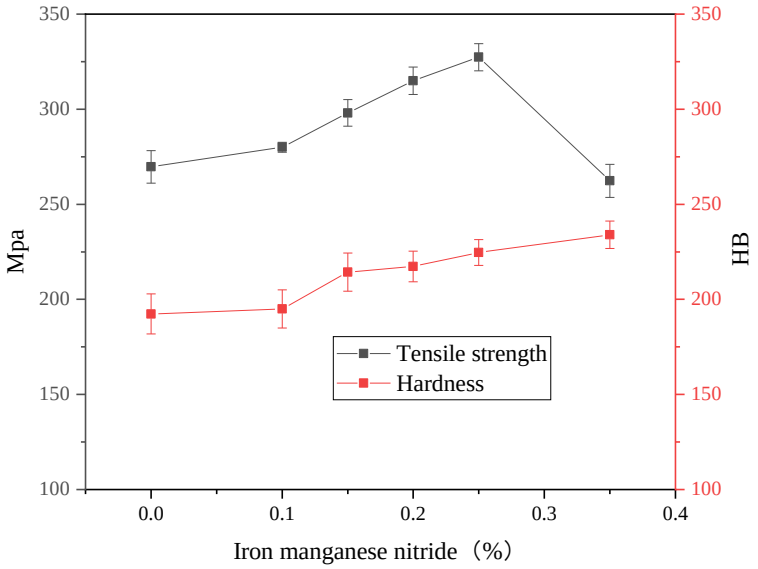


Fig. 3 - Mechanical properties of gray cast iron

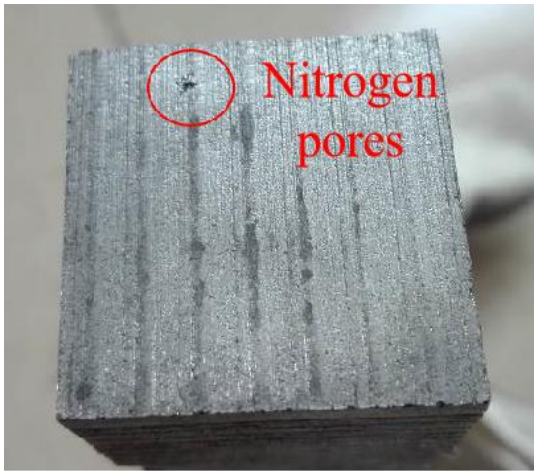


Fig. 4 - Nitrogen holes in casting(0.35% manganese nitride)

The formation of nitrogen porosity is explained by the decreasing solubility of nitrogen in molten iron during solidification. As the melt temperature decreases, dissolved nitrogen precipitates in molecular form. When the nitrogen content exceeds its solubility limit, excessive nitrogen bubbles form and are unable to escape from the casting, eventually becoming entrapped as porosity defects.

In summary, the mechanical properties of gray cast iron can be significantly improved by adding ferromanganese nitride to have a certain nitrogen content in the tissue. This is because, after the micro-alloying effect of nitrogen element, the graphite in gray cast iron has a short, thick, curved, and rounded end morphology, which reduces the cutting effect of graphite and effectively improves the stress concentration at the end. In addition, the effect of nitrogen leads to high pearlite content and pearlite refinement, which can effectively improve the strength and toughness of gray cast iron and facilitate the local resistance of the material to the indentation of complex objects, which further enhances the strength and hardness of the material [18]. Compared with GB/T9439-2010 gray iron castings, it is known that when manganese nitride is added to 0.15%, the tensile strength and hardness of gray cast iron reach the requirements of grade HT300.With the increasing addition of ferromanganese nitride, the strength and hardness of the material exhibit a continuous upward trend. However, when the

addition reaches 0.35%, a sudden decrease in mechanical performance occurs. This deterioration is attributed to the formation of nitrogen porosity, indicating that the nitrogen content has exceeded its critical solubility during solidification.

In addition, it was observed that when the ferromanganese nitride addition reached 0.35%, the graphite flakes became shorter and more curved. Although this morphology change typically benefits mechanical properties, the simultaneous formation of nitrogen pores offsets these advantages, making this nitrogen level unsuitable for industrial production.

4 New process solution and improvement

4.1 Ingredient control

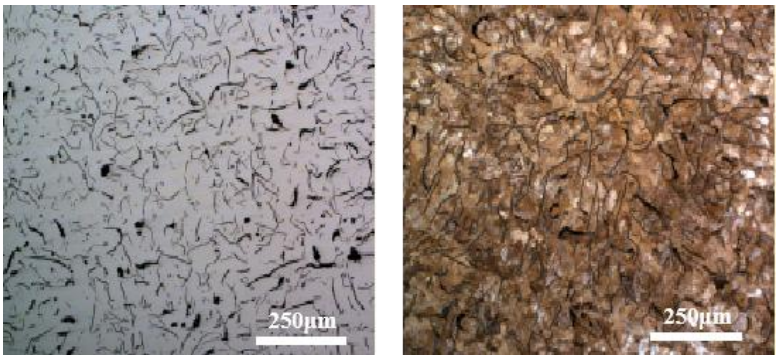
According to the microstructure and mechanical test results described above, adding a moderate amount of manganese nitride can improve the graphite morphology, stabilize and refine the pearlite. After reducing Cu and Sn, and increasing the addition of N based on the existing process, the refining and strengthening effect of Cu and Sn on pearlite decreases. In contrast, with the high nitrogen content in the tissue, the apparent microstructure optimization ensures the product's performance and brings a certain degree of improvement. The addition of ferromanganese nitride can weaken the influence of other strengthening alloys to reduce the amount of alloy added to ensure the performance of gray cast iron to achieve low-cost production of high-grade gray cast iron. It is worth noting that the casting process should strictly control the nitrogen content to avoid the adverse effects of nitrogen porosity. According to the previous test results, the amount of manganese nitride added should be 0.15%-0.25%, so the nitrogen content is controlled within 100 PPM. Therefore, the target values of each element in the new process are shown in Table 2.For industrial application, the gating and venting system must be designed to ensure adequate gas escape during solidification. When using nitrogen-enhanced processes, special attention should be paid to melt handling procedures and solidification behavior to prevent nitrogen entrapment.

Table 2 -Target values of chemical composition of nitrogen type gray cast iron parts (wt%)

Element	C	Si	Mn	P	S	Cu	Sn	Cr	N
Content	3.25-3.35	2.05-2.15	0.75-0.9	≤0.03	0.08-0.12	0.2-0.25	0.015-0.025	0.2-0.3	0.008-0.01

4.2 Experimental validation

According to the improved process, several engine block casting tests were conducted with the addition of 0.15% ferromanganese nitride as an example to verify the stability of the process. After the test, the corresponding specimens were intercepted according to the position shown in Figure 1, and all the specimens were observed to have no nitrogen porosity defects on the surface and cross-section. The corresponding metallographic and mechanical test results are shown in Figure 5 and Table 3, respectively. It can be seen that the graphite is short and thick, curved, with rounded and blunt ends, the graphite length is grade 5, and the pearlite content in the matrix organization is more than 95%. The average tensile strength of the specimen is 285 MPa, and the average hardness is 201 HB, which is 5% and 4.7% higher than the original process scheme, respectively, and the performance is significantly improved and close to the index of HT300 grade.



(a)Graphite form ***(b)Matrix tissue***

Fig. 5 - Microstructure of cast iron after improved process (100×)

Table 3 - Mechanical properties of improved nitrogen-containing gray cast iron

Test Number	C	Si	Mn	P	S	Cu	Sn	Cr	N	Tensile strength (*MPa*)	Hardness (*HB*)
1	3.32	2.05	0.82	0.02	0.09	0.22	0.018	0.22	0.0080	280	198
2	3.32	2.05	0.79	0.02	0.09	0.21	0.020	0.23	0.0085	288	202
3	3.31	2.06	0.81	0.02	0.09	0.23	0.021	0.25	0.0083	284	205
4	3.29	2.04	0.81	0.02	0.09	0.22	0.017	0.26	0.0079	291	199
5	3.29	2.06	0.78	0.02	0.09	0.23	0.021	0.22	0.0086	281	201
6	3.27	2.05	0.82	0.02	0.09	0.21	0.018	0.25	0.0082	286	202

4.3 Cost Accounting

In this paper, the cost of the casting test was calculated on a furnace basis by recording the metal dosing of the furnace charge input and the variety and quantity of castings poured, using equation (1) to calculate the cost per unit mass of metal liquid [19].

$$C_m = \sum(W_i C_i)/Q_m \tag{1}$$

In the formula, Cm for a furnace melting metal unit mass material cost; Wi for the mass of input material in the furnace charge; Ci for the unit price of a single batch of material in the furnace charge; Qm for a furnace melting to obtain the mass of metal liquid available for pouring.

Accounting for the cost of the two process options by formula (1), the casting costs of the existing and improved options are RMB 8,530/ton and RMB 8,350/ton, respectively, and the casting cost of the improved option is reduced by RMB 180/ton. According to the stable production data of the formula existing process products (20,000 pieces/month, 1,000 tons of iron), the monthly cost saved by using the improved nitrogen-containing gray cast iron is 180,000 yuan, and the annual cost saved is 2.16 million yuan. Compared with the existing process scheme, it can be seen that by adding the right amount of manganese nitride and optimizing the microstructure of cast iron, the amount of alloy added can be effectively reduced to achieve production cost reduction with the premise of ensuring performance. If the strategy of increasing the nitrogen content is to be applied in actual casting production to improve material properties, the design of the casting process must fully account for the exhaust system and the solidification behavior of the molten iron.

5 Conclusion

1) The graphite ends of nitrogen-type gray cast iron with different content of manganese nitride are rounded and blunt, the graphite flakes are short, thick, refined, and slightly curved, and the graphite length grade gradually increases with the increase of manganese nitride content, which effectively reduces the cutting effect of graphite on the matrix organization. The increase of nitrogen content in the tissue is beneficial to improve the graphite phase morphology, stabilize and refine the pearlite.In addition, increasing ferromanganese nitride addition refines the graphite morphology, producing shorter and more curved flakes; however, when the nitrogen content exceeds the critical level of approximately 110–120 ppm, nitrogen porosity forms during solidification, causing the tensile strength to decrease from about 326 MPa to 262 MPa and the Brinell hardness to drop by approximately 20–30 HB, thereby significantly deteriorating the mechanical performance. Therefore, strict control of nitrogen content is essential for industrial applications.

2) When the nitrogen content of iron melt is 80ppm to 110ppm, it can increase the strength of gray iron casting by 20-50Mpa and hardness by 20-40HB to reach the standard of high-grade cast iron. In the nitrogen-type gray iron casting process, the nitrogen content of the iron should be strictly controlled. Excessive nitrogen content is likely to cause nitrogen porosity defects and deteriorate the performance of the casting; At the same time, if the nitrogen content is too low, the morphology and quantity of microstructure will be insignificant, both in strength and hardness as well.

3) By adding ferromanganese nitride, the addition of alloy can be effectively reduced, the casting cost drops by 180 RMB/ton, the annual production cost saved is 2.16 million RMB, and the low-cost production of high-performance gray cast iron can be achieved.

4) This study focuses on nitrogen content optimization but does not discuss the influence of mold design, cooling rate, or section thickness on nitrogen porosity formation. Variations in these parameters may introduce deviations in results, and future work should further quantify their effects.

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