Chill-free Permanent Mold Casting of Spheroidal Graphite Iron

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ABSTRUCT

The chill-free permanent mold casting of spheroidal graphite iron was attempted under as-cast conditions in this study. The base molten iron was treated with a ferrosilicon-magnesium alloy and inoculant. The treated molten iron was then gravity-cast in a preheated permanent mold. The mold cavity was 5.4 mm in thickness and 35 mm in diameter, equivalent in shape to the sample used for daily spectrometer analysis in the foundry. The mold was designed to induce full chilling in samples for good analytical results. The nitrogen contents of the iron were minimized intentionally as a countermeasure against chill during melting, treating, pouring, and solidification. Chill-free samples were obtained with graphite nodule densities exceeding 3,000 count/mm^2, the highest nodule count yet reported. A steering knuckle for automobiles was poured with the same procedure to verify the castability.

Keywords: melting, iron, nitrogen, magnesium treatment, inoculation, permanent mold, coating, chill, nodule count, steering knuckle

INTRODUCTION

The achievement of chill-free permanent mold casting of spheroidal graphite iron would transform iron foundry works in a manner similar to breakthroughs in aluminum casting. Molding sand and related facilities would be unnecessary with this method; therefore, the natural environment can be maintained, improving the work place by removing sand dust. Some foundries have already begun producing permanent mold castings of spheroidal graphite iron in commercial applications. However, most of these castings require heat treatment because of the precipitation of ledeburite structure [1-3]. On the other hand, some researchers have successfully achieved chill-free permanent mold casting of spheroidal graphite iron in the as-cast condition at laboratory scales [4-6]. Many factors could cause the precipitation of ledeburite structure; multiple countermeasures have been implemented against them. However, these are not always effective, because the actual phenomena underlying ledeburite precipitation remain poorly understood. The problem of chill in as-cast castings is among the factors impairing the popularization of permanent mold casting.

In this study, free nitrogen (N_F) was considered as the key point to prevent chill. In iron castings, the chill phase is the ledeburite structure in the iron-carbon equilibrium phase diagram. This ledeburite structure comprises austenite and cementite (Fe_3C). N_F may substitute for carbon in the Fe_3C crystal structure, promoting the formation of chill. This is why the concentration of nitrogen [N] is relevant to metastable solidification when experimentation for drawing the iron-carbon equilibrium phase diagram is performed in atmospheric conditions.

To succeed in the chill-free permanent mold casting of spheroidal graphite iron under as-cast conditions, previous reports and our own experiences were reviewed to consider the promotion of denitrification and the prevention of nitrogen adsorption. The minimization of N_F was tried in the molten iron before solidification began. The procedure for the full experimental process was set as follows [2,4-15]:

1. The sulfur content is not too low to prevent N_F adsorption, but not too high to prevent the degeneration of graphite nodularity[7, 8].
2. The base molten iron contains no additive elements, such as manganese, chromium, molybdenum, or vanadium, which can promote chill formation [4, 5].
3. The oxygen [O] content is minimized by superheating to temperatures exceeding 1500 ℃ [6, 7, 9].
4. After superheating, the temperature of the molten iron is gradually decreased to the critical temperature (T_C) of the CO/SiO_2 reaction for denitrifying [7].
6. Magnesium treatment is conducted at T_C [7, 9].
7. A magnesium alloy that reacts gently with molten iron, without causing waves, is used [6, 7].
8. The content of free magnesium (Mg_F) [10,11] is controlled to remain as low as possible.
9. The inoculant contains elements that offset N_F.
10. After inoculation, the molten iron is poured into the permanent mold as quickly as possible to maintain the strong segregation of silicon and to prevent the adsorption of N_F[7, 10,12].
11. The permanent mold is preheated to permit good liquid flow and to adjust the solidification speed [13, 14].
12. The permanent mold is coated with an insulation-type wash as the foundation to slow the solidification speed [2, 14, 15].

In this study, the chill-free permanent mold casting was attempted at a pilot plant.

EXPERIMENTAL PROCEDURE

The raw materials shown in Table 1 were melted using a 30-kg high-frequency induction furnace. Melting, magnesium treatment, inoculation, and pouring were conducted using the time-temperature schedule shown in Fig.1. After being melted, the base molten iron was super-heated and slowly cooled to T_C[16]. Then, magnesium treatment was conducted at the actual T_C using a plunger in the furnace. The chemical composition of the spheroidizing agent and the amount added are shown in Table 2. T_C was calculated according to the carbon and silicon contents in the base molten iron, according to Eq. (1). The actual T_C was selected as the temperature at which a SiO_2 film formed on the surface of the base molten iron.

$$\log[Si]/[C]^2 = -27{,}486/T_K + 15.47 \qquad (1)^{16}$$

$$T_C\,(℃) = T_K - 273$$

Stream inoculation was performed by adding the inoculant while tapping after the magnesium treatment. The chemical composition of the inoculant and the amount added are also shown in Table 2. The magnesium-treated and inoculated molten iron was poured into the preheated permanent mold using an alumina-silica ceramic spoon within 30 s after inoculation. The target pouring temperature was 1320 ± 20℃. The shape and dimensions of the permanent mold is shown in Fig. 2. This mold was originally manufactured to take chill samples for chemical analysis by spectrometry in general foundry operations. This means that the mold was designed to obtain a full chill-phase structure in the sample for high analytical accuracy (Fig. 3)[17]. This is why the graphite structure was expected in the as-cast sample, assuming that the ideas described above were correct and that the content of N_F could be controlled as planned. The mold was preheated to 350℃ in an electric holding furnace. The as-cast sample was shaken out at a temperature below 550℃ and was cut vertically from the gate to the bottom of the mold. A piece of the cut sample was buried in resin and the vertical-sectional sample microstructure was observed using optical microscopy. Graphite nodules were counted by visual observation in the microstructures of 100 magnified areas after photographing. The microscopic area was 0.77 mm^2; knowing this, the graphite nodule count was converted into an areal density per mm^2. One place of the graphite nodule count was down. Chill samples for chemical analysis were taken by pouring the same molten iron into a second non-preheated and non-coated permanent mold. The chemical composition of the conventional sample was analyzed using spectrometry. The magnesium-treated sample was also analyzed using the infrared absorption method (CS-LS600, Leco Corp.).

A steering knuckle component for automobile use was also poured into a permanent mold; the quality of the component was surveyed by observing the surface, shrinkage, and microstructure. The heat of melting was different, but otherwise, the same procedure as described above was followed during casting. The permanent mold was preheated to 350℃ using electric stick heaters in this case. The riserless casting design is shown in Fig. 4. A gating system is not included; the sprue connects directly with the knuckle.

Table 1 Chemical composition of raw materials for melting and their charging ratios.

Raw material	Chemical composition (mass %)						Ratio
	C	**Si**	**Mn**	**P**	**S**	**Al**	(Wt. %)
Pig iron	3.69	1.02	0.11	0.025	0.006	0.009	97.09
Fe-Si	0.10	75.03	—	0.026	0.004	1.340	2.48
Fe-S	—	—	—	—	48.760	—	(0.002)
Carbon	99.24	—	—	—	0.026	—	0.43

Table 2 Chemical composition of agents and amount of their addition.

Agent	Chemical composition (mass %)						Addition
	Si	**Mg**	**Ca**	**RE**	**Al**	**Bl**	(Wt. %)
Spheroidizer	44.08	3.85	0.66	1.47	0.37	Fe	0.8
Inoculant	75.81	—	1.82	—	2.16	Fe	0.6

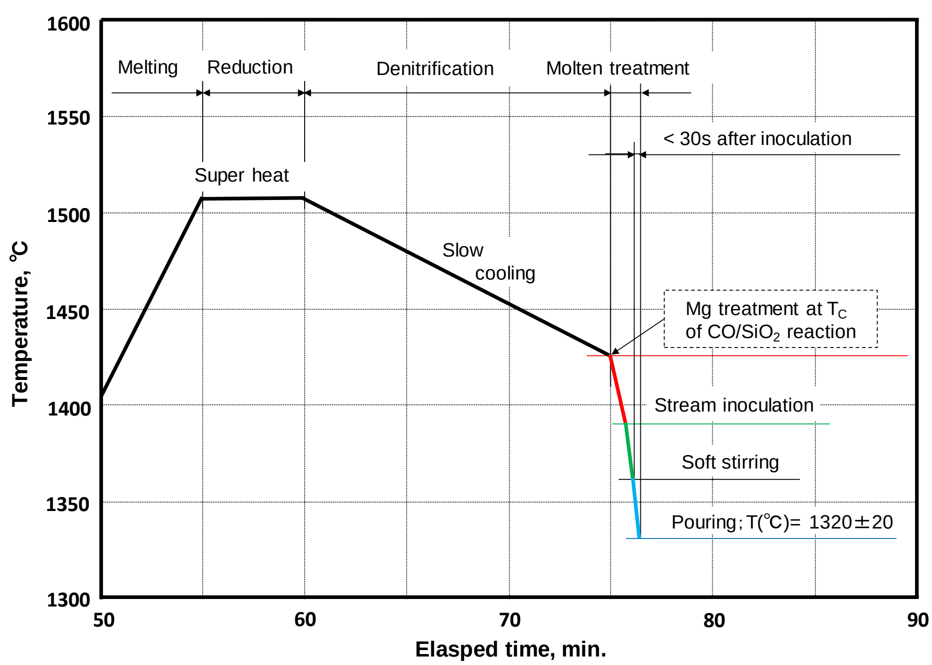


Fig. 1 Time-temperature schedule for melting, treatment, and pouring.

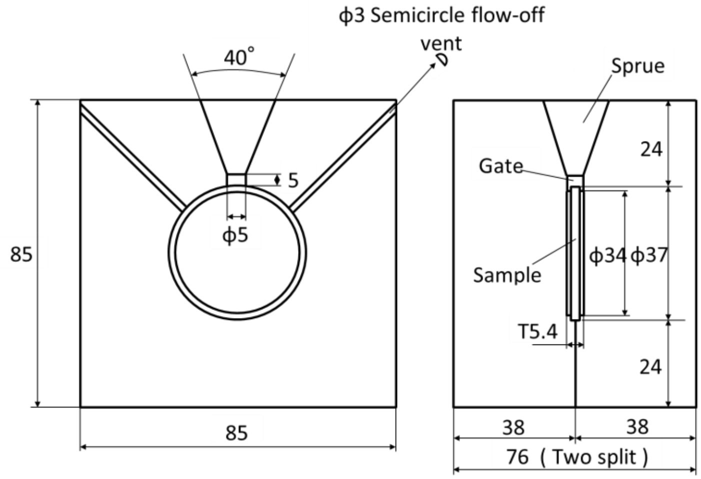


Fig. 2 Shape and dimensions of the medium-carbon steel permanent mold (unit: mm).

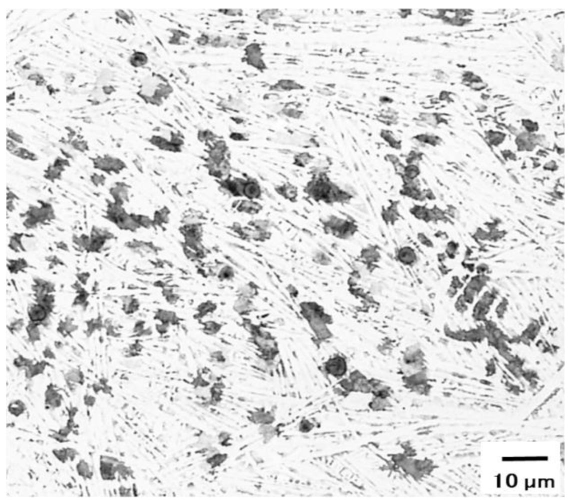
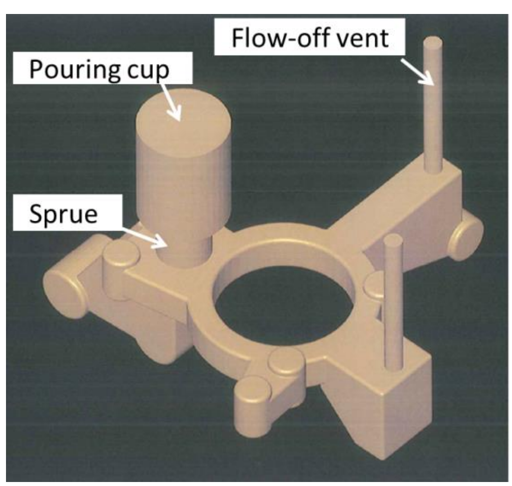


Fig. 3 Microstructure of the permanent mold sample for spectrometric analysis in general foundry operation[17].



Pouring weight : 5.3kg
Casting weight : 4.6kg
Yield : 86.8%

Fig. 4 Cast design of steering knuckle for automobile.

RESULTS

The chemical compositions of the molten irons are shown in Table 3. The T_C of the base molten iron was calculated by Eqn. (1) as 1425℃. After the base molten iron was super-heated to 1540℃, it was cooled slowly to 1425℃. Magnesium treatment was conducted at 1429℃ using the spheroidizing agent in the furnace. Soon after the magnesium reaction finished, the stream inoculation was conducted while tapping. The treated molten iron was poured into the preheated permanent mold at 1340℃ using the same spoon as above. The time elapsed from inoculation to pouring was 23 s. The sample was shaken out from the mold at 350℃. The sample is shown in Fig. 5. A depression is observed on the side of the sample. The sprue, gate, and vents were knocked off using a hand hammer. Because the fractured surface appeared darker in color (see Fig. 6), the dominant precipitate phase of graphite was expected. The general sample was white in color.

The chemical composition of the magnesium-treated molten iron is shown in Table 3. A morphological analysis was conducted on the magnesium. Mg_F is metallic in nature and contributes to graphite spheroidization[10, 15]. Mg_T, or total magnesium, is conventionally known as residual magnesium in foundry operations. The microstructure of the sample is shown in Fig. 7. Spectrometric analysis shows poor accuracy for the values of carbon and sulfur, because the analyzed sample is both magnesium-treated and inoculated, with significant graphite precipitation despite the general permanent mold. Therefore, carbon and sulfur are also analyzed by the infrared absorption method (CS-LS600, Leco Corp.).

No chill phase was visually observed on the fractured cross-sectional surface. Instead, a superior spheroidal graphite structure was observed. The microstructure representative of that with the fastest cooling rate, that is, the structure at the bottom of the sample, is shown in Fig. 8. Most spheroidal graphite is fine, with particle diameters of 4–7 μm. Some larger spheroidal graphite exists, but remains at approximately 20 μm in size. These are assumed to be hypereutectic graphite that formed during pouring. The number density of spheroidal graphite nodules (SG_N) is over 3200 count/mm^2.

Table 3 Chemical composition of molten irons.

Sample		Chemical composition (mass %)							
		C	Si	Mn	P	S	MgF	MgT	CE
t5.4 x φ34 mm Casting	Base	3.66	2.58	0.09	0.022	0.006	—	—	4.52
	After treatment	3.61	3.11	0.10	0.024	0.008	0.013	0.018	4.65
Steering Knuckle	Base	3.46	2.59	0.07	0.020	0.013	—	—	3.32
	After treatment	3.40	3.26	0.07	0.020	0.009	0.016	0.020	4.49

CE = C + 1/3Si

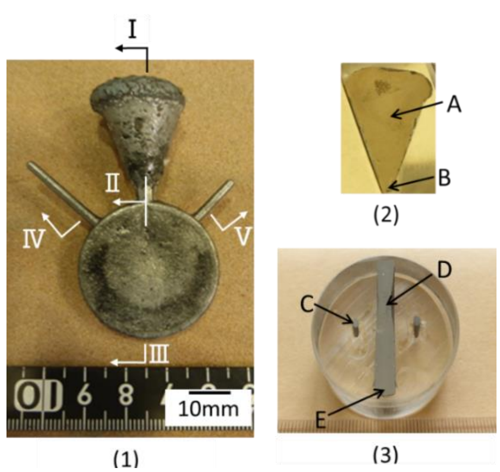


Fig. 5 As-cast sample: (1) appearance, (2) section Ⅰ-Ⅱ, and (3) section Ⅱ - Ⅲ, Ⅳ and Ⅴ.

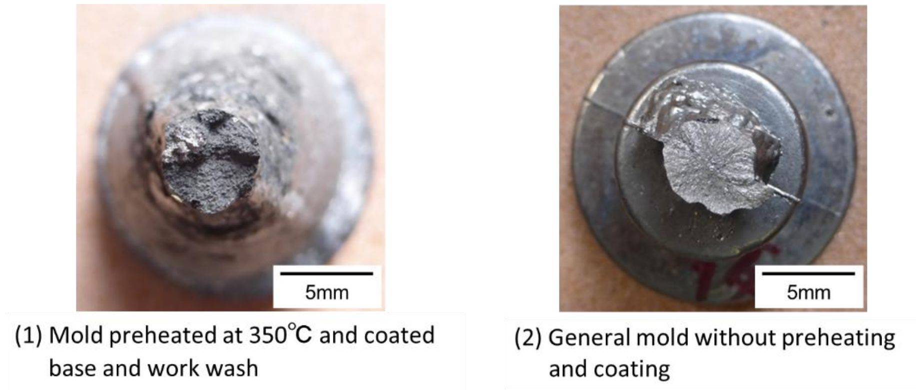


Fig. 6 Fracture surfaces of as-cast samples.

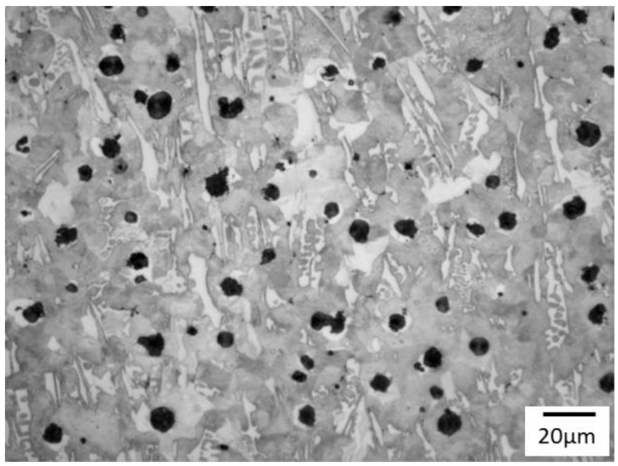


Fig.7 Microstructure of analyzed sample, which has both chill and graphite phases (etched with 3 vol.% nital).

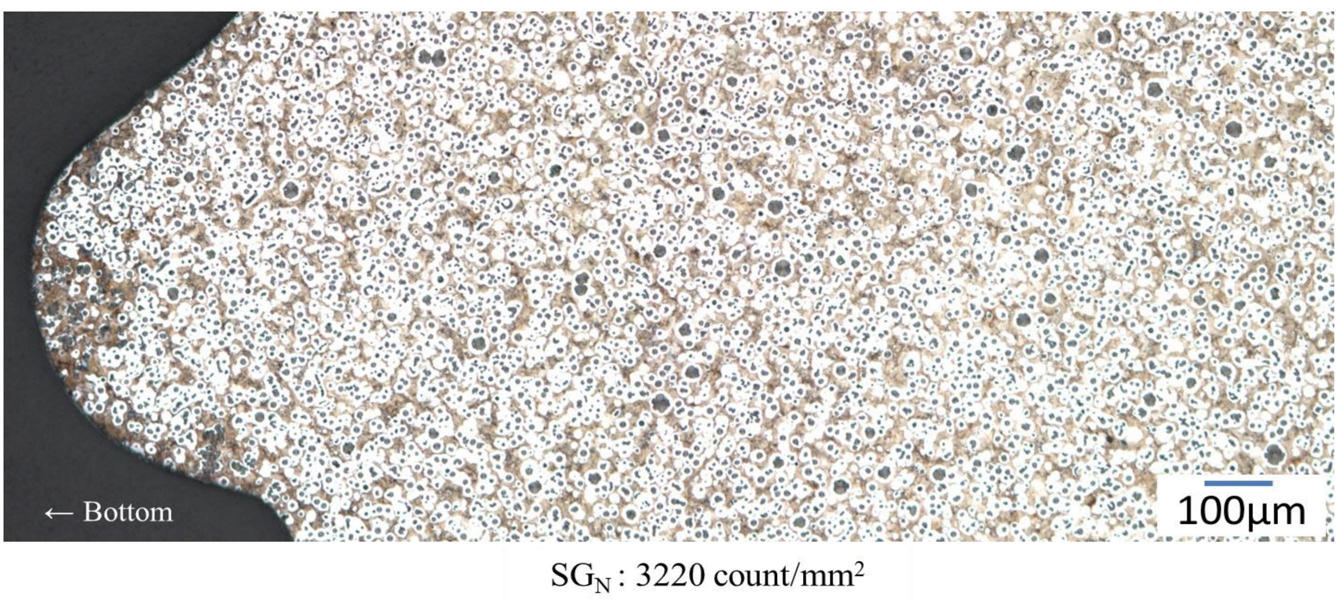
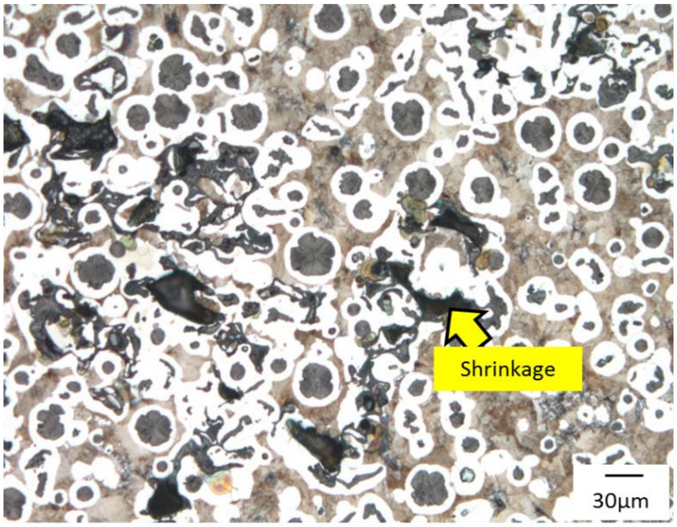


Fig. 8 Microstructure at bottom of sample casting in as-cast condition; position E shown in Fig. 5(3) (etched with 3 vol.% nital).

Fine shrinkage occured beneath the depression on the side surface of the sample casting. This might be caused by the narrowness of the gate. The microstructure of this region is shown in Fig. 9. In addition to the shrinkage, there was a good spheroidal graphite structure, although the size of the spheroidal graphite particles was increased and SG_N was smaller than that of the sound area (Fig. 8).

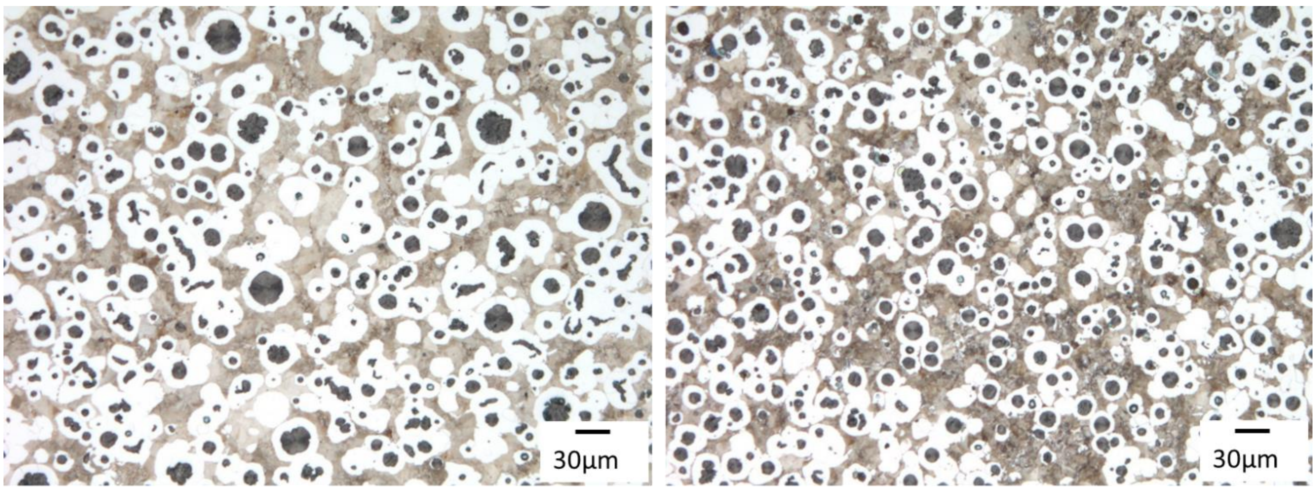
As expected from the fracture surface shown in Fig.6(1), no ledeburite structure forms in the sprue cup, but only fully spheroidal graphite (Fig. 10). The SG_N is lower than that of the sample casting.

The microstructure of the flow-off vent is shown in Fig.11. This is observed with special interest because the fracture surfaces appear to be darker, implying the precipitation of graphite despite the thinness of the vent. SG_N is 3640 count/mm^2, the highest from the sample. However, about 20 area% of ledeburite is present among old eutectic cells.



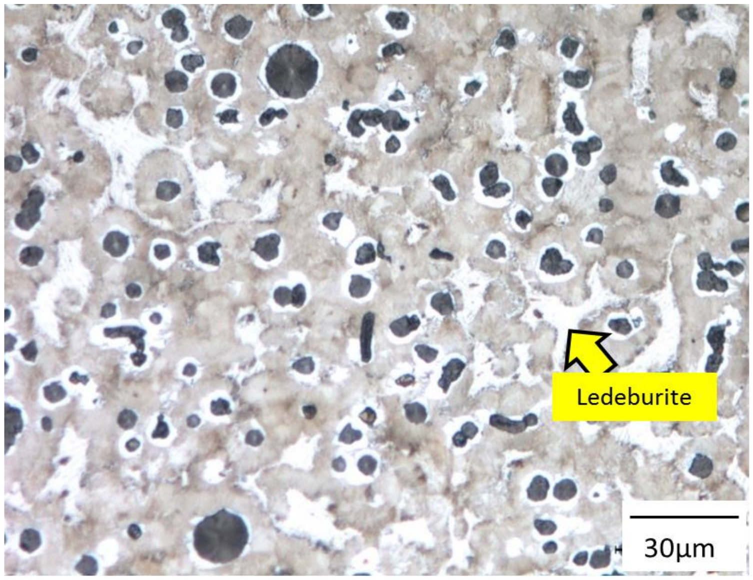
SG_N : 1090 count/mm^2

Fig. 9 Microstructure at the subsurface of the depression in the sample casting; position D shown in Fig. 5 (3) (etched with 3 vol.% nital).



A. Sprue (SG_N :1600 count/mm^2) B. Gate (SG_N :1840 count/mm^2)

Fig. 10 Microstructures at gate and sprue of sample casting; positions A and B shown in Fig. 5 (2) (etched with 3 vol.% nital).



SG_N : 3640count/mm^2

Fig. 11 Microstructure of flow-off vent (left) for sample casting: position C shown in Fig. 5 (3) (etched with 3 vol.% nital).

The steering knuckle was poured into the permanent mold at 1322℃. The time elapsed between inoculation and pouring was 27 s. The filling time was 6 s. The knuckle was removed from the mold at a temperature below 500℃. The as-cast appearance of the steering knuckle is shown in Fig. 12. The surface appears good without any visible magnesium dross, flow marks, cold shot, or other defects. The sprue remains, but all flow-off vents dropped out during the shake-out from the mold. The knuckle was cut at the points A, B, and C in Fig. 12 (1) and the vertical-sectional surfaces were visually observed. The results are also shown in Fig. 12. No shrinkage is observed in any section. The nodule density reaches over 1900 count/mm^2. As an example, the microstructure of section B in the steering knuckle is shown in Fig. 13. This count is over 10 times greater than that found in similarly sized sand-cast steering knuckles[18]. Neither is any chill observed.

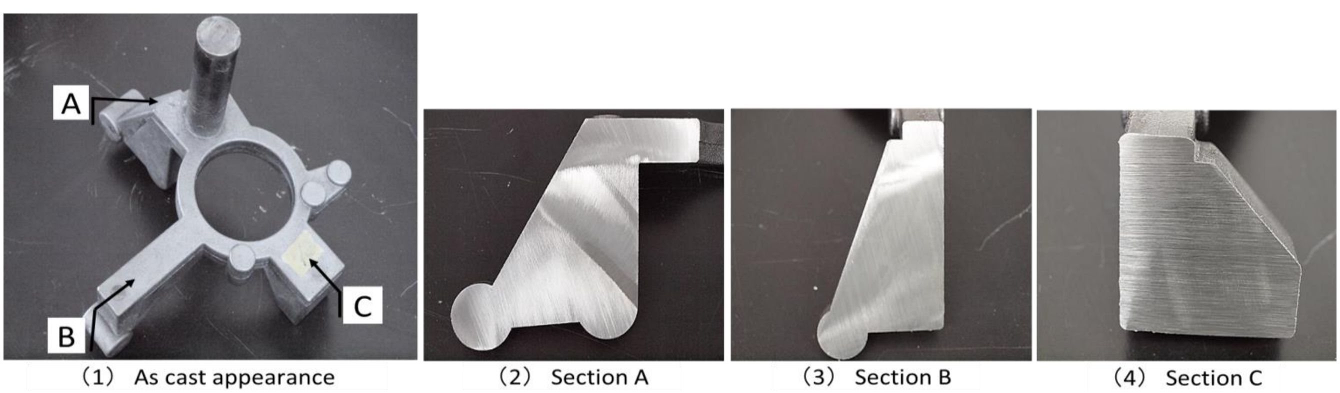
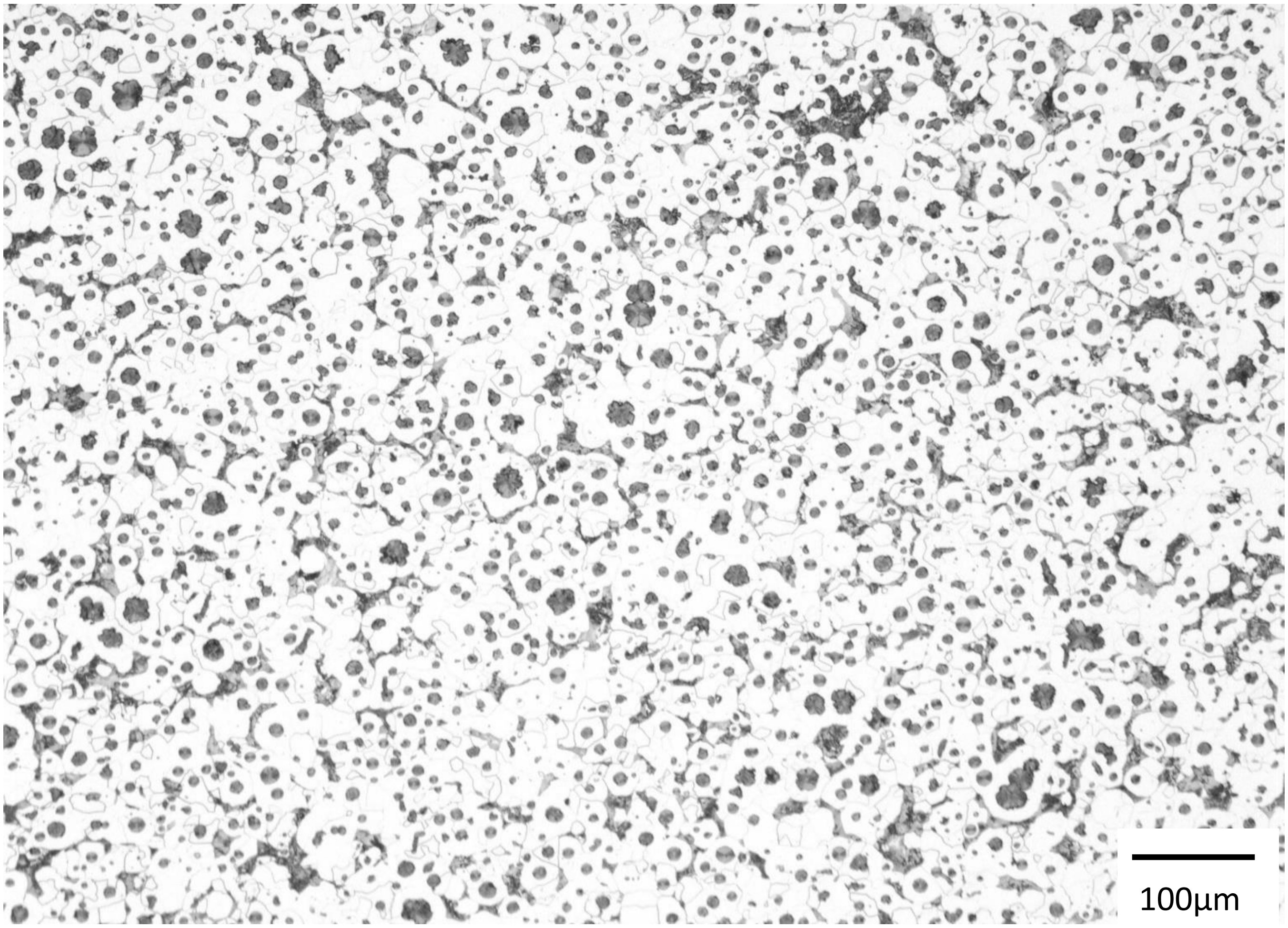


Fig. 12 As-cast appearance of steering knuckle and the quality of vertical-sections.



SG_N: 1950 count/mm^2

Fig. 13 Microstructure at section B in steering knuckle, as shown in Fig. 12 (1); vertical-section surface layer (etched with 3 vol.% nital)

CONSIDERATIONS

Generally, SG_N can be increased at increased cooling rates for castings using metal chillers, post-inoculation, and other methods. However, the formation of the chill phase or the ledeburite structure begins when the cooling rate is too high. According to Horie, the critical count of SG_N without any ledeburite structure is approximately 900 count/mm^2. The relationship between SG_N and cooling rate is given by Eq. (2)[19]:

$$SG_N = 0.58R^2 + 19.07R + 1.01 \qquad (2)$$

where

R = Cooling rate (℃/s)

According to Eq. (2), R is about 26.2℃/s when SG_N is 900 count/mm^2. In this study, the critical SG_N is between 3200 and 3400 count/mm^2. Therefore, the cooling rate might be 60–62℃/s. This is a substantial difference from conventional studies. Such a difference may arise from multiple factors. H. Horie had reported from a laboratory study that sulfides, functioning as graphite nucleation sites, were important to increase SG_N. From this perspective, inoculation as a countermeasure against chill formation was not sufficiently considered. On the other hand, N_F control is the important factor in this study. N_F can be reduced by slowly cooling from the superheating temperature, and can be further offset by the addition of inoculant including elements such as silicon, aluminum, calcium and zirconium. The good relationship between N_F and chill depth in wedge-shaped sand mold sample castings was previously proved by the authors and successfully applied in foundry practices[7]. The imaginative control of N_F was conducted and it has effectively prevented chill. As the next step, the relationship between N_F and chilling tendency of permanent mold casting of spheroidal graphite cast irons will be proved.

Alloying elements such as manganese and chromium are known to promote chill formation tendencies [20]. These elements are also known to increase nitrogen resolution in molten iron [21]. This suggests that they may promote chill by increasing N_F levels in molten iron. Such elements may promote chill as the atoms substituting for iron atoms in Fe_3C because they are very similar in atomic size. Furthermore, the electronegativity of such substitution elements with carbon is greater than that between iron and carbon [5]. The same is true for nitrogen and oxygen atoms regarding substitution. N_F and chill are related by the substitutional ability of nitrogen atoms for carbon atoms in Fe_3C, which could promote chill. However, free oxygen (O_F) has less possibility to promote chill according to the results of the previous study [7].

Most graphite nodules shown in Fig.10 have sizes within the range of 4–7μm. This is close to the size of magnesium gas bubbles in molten iron when the magnesium alloy is treated at 1400–1450℃ [17]. Good inoculation and less fading may maintain the strong segregation of silicon, causing the excellent results in this study.

CONCLUSIONS

Permanent mold casting of spheroidal graphite iron was attempted minimizing and offsetting N_F. The followings were concluded as the results:

1. For both the sample and steering knuckle castings, chill-free and full-graphite structures could be obtained without heat treatment.
2. In the test sample casting with 5.4 mm thickness, most graphite nodules were within the range of 4 -7 μm in size; SG_N was over 3200 count/mm^2.
3. SG_N in the steering knuckle casting, was over 10 times than that found in conventional sand castings. Good mechanical properties such as tensile strength, fatigue strength, and fatigue toughness are expected.

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