The influence of free magnesium on some properties in spheroidal graphite irons

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A new concept, in which free magnesium might be a key indicator of the state of graphite spheroidization in spheroidal graphite irons, is proposed and verified in this study. Chilled samples containing different amounts of total magnesium were prepared. The total, inclusive and free state magnesium contents were analysed by a special procedure. Free magnesium increased in steps as total magnesium increased. On the other hand, inclusive magnesium was nearly equal among the chilled samples. The nodularity and the tensile properties in 50 mm Y-blocks showed good correlation to the value of the free magnesium, but no relation to that of the inclusive magnesium. The quality of spheroidal graphite cast iron should be controlled by the content of free magnesium in practice. The experimental results well supported the site theory.

Keywords: spheroidal graphite iron, spectrochemical analysis, state analysis, graphite nodularity, spheroidization theory

Introduction

Magnesium is generally used for the production of spheroidal graphite cast iron, as it is considered to be the best spheroidizing element. From a metallurgical point of view, however, magnesium is also a strong deoxidizer and desulfurizer element in liquid iron. If magnesium is added in excess of the stoichiometric amount, against oxygen and sulfur content, two states of magnesium will exist in liquid iron. One would be the metallic state and the other would be inclusion such as oxide, sulfide, etc. In this study, the former is defined as free magnesium and the later is defined as inclusive magnesium. So far, no one has shown clear evidence about which state is more effective for the graphite spheroidization.

According to the site theory[1,2] proposed by the author, it has been considered that free magnesium would be the indispensable state and contribute in the form of gas bubbles for the graphite spheroidization. This theory is rather reasonable since magnesium has a low boiling point and is less soluble in both liquid and solid iron. The magnesium halo, which would be located around the spheroidal graphite, and would be evidence of gas bubble, has been already found using the Computer-Aided Micro Analyser (CMA).[1,2] On the other hand, many researchers have asserted that the magnesium-containing inclusions contribute as nuclei for the graphite spheroidization. Actually, these inclusions have been found in some graphite nodules. No one has, however, found evidence for how these inclusions cause spheroidal graphite to grow to the final typical form. It is very important to know the contribution of magnesium towards the graphite

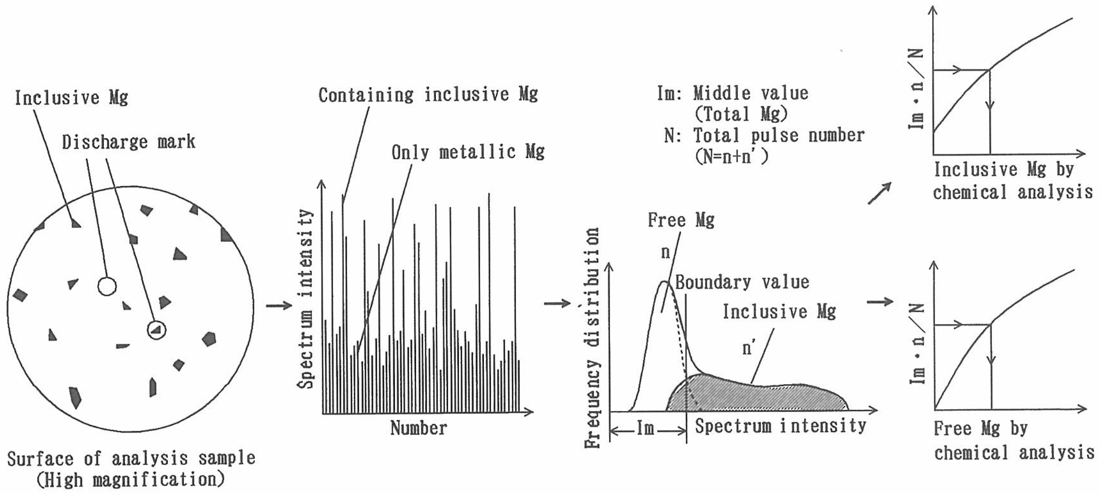

Fig. 1 Principle of state analysis for magnesium in chilled sample of spheroidal graphite iron. The original[3,4] was arranged for magnesium

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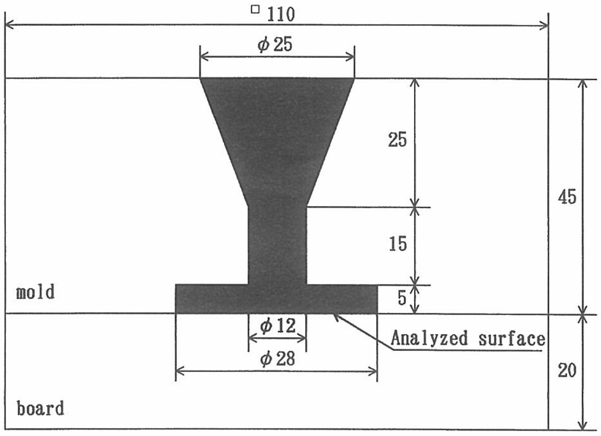


Fig. 2 Steel mould and board for sampling. Dimensions in mm

spheroidization in order to further the improvement of the quality of spheroidal graphite iron casting.

If an element has a strong affinity with oxygen, nitrogen, sulfur, etc. and forms stable precipitates, such an element would be easy to detect the metallic state and the precipitates using an emission spectrometer in conjunction with a Pulse-height Distribution Analysis (PDA) system.[3,4] This is the reason why there is a large difference in the spectrum intensity between the metallic state and the precipitates in such an element. The spectrum intensity detected at an analysis spot, which contains inclusions, is much higher than that spot containing only the metallic state. In this system, each spectrum intensity detected during discharging is converted into pulse height and is arranged into a distribution. The pulse-height distribution for magnesium would appear as two peaks. One is for the area with inclusive magnesium and shows an indistinct peak. The other is for the area with only metallic magnesium and shows a distinct peak. The principle for the state analysis on magnesium using emission spectrometer in conjunction with the PDA system is schematically illustrated as shown by Fig. 1. State analysis by emission spectrometer has been previously conducted on aluminium, boron, calcium, niobium, titanium, etc. in steel making practice.

In this paper, the analysis of free magnesium in spheroidal graphite iron would be attempted by chemical

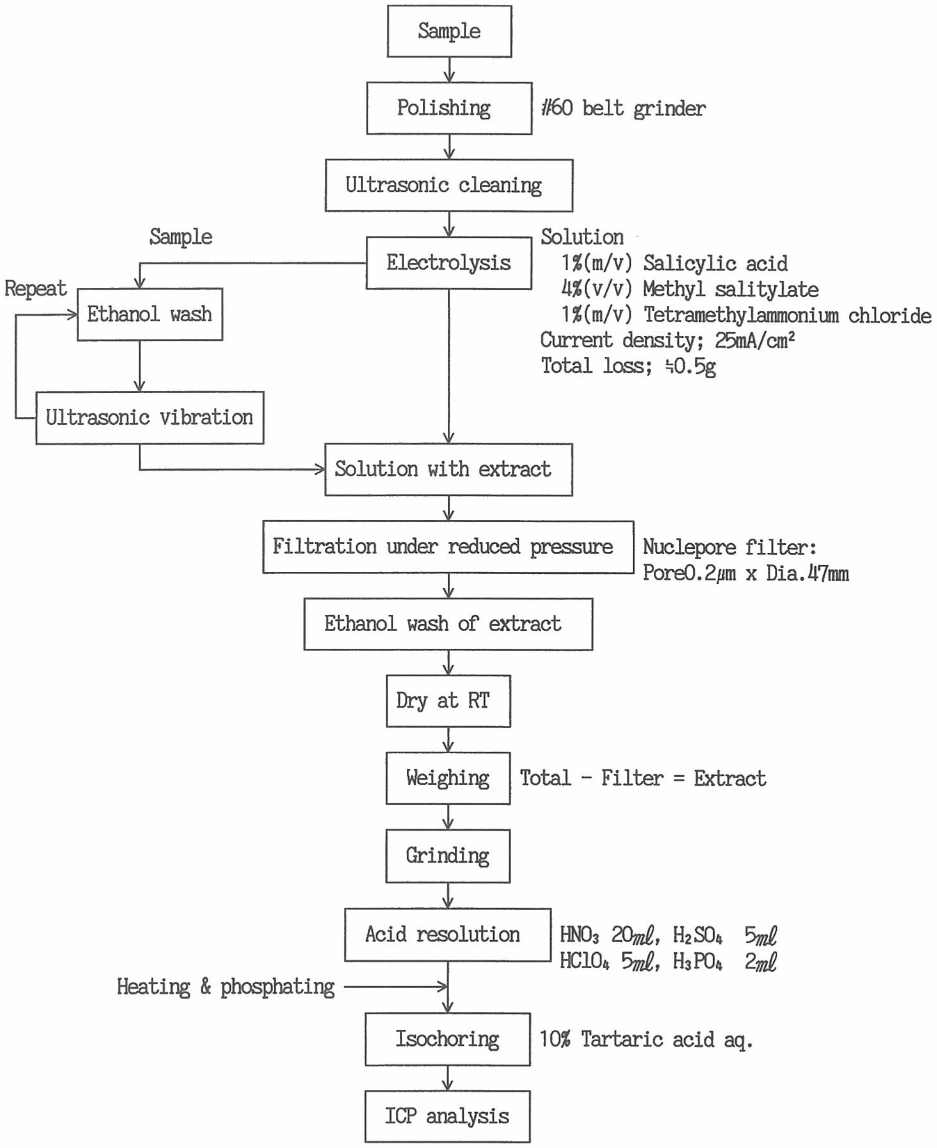


Fig. 3 Flow chart of electrolytic extraction and quantitative analysis for extractive magnesium

Table 1 Results of conventional emission spectrum analysis and free oxygen measurement in magnesium treated liquid irons

	Chemical composition (Mass%)						*O* measurement		
Sample No.	C	Si	Mn	P	S	Mg	*O* (Mass PPM)	EMF (mV)	Temp. (°C)
1	3.43	2.26	0.11	0.034	0.015	0.011	0.29	−199	1413
2	3.54	2.31	0.20	0.039	0.012	0.022	0.10	−219	1339
3	3.45	2.56	0.21	0.037	0.014	0.031	0.08	−226	1326
4	3.42	2.66	0.21	0.038	0.013	0.040	0.10	−218	1335
5′ (base)	3.52	1.43	0.14	0.031	0.019	–	0.93	−137	1434
5	3.49	2.41	0.16	0.031	0.014	0.048	0.09	−239	1363
6	3.52	2.93	0.12	0.039	0.012	0.056	0.07	−259	1370

and spectrochemical means. The existence of free magnesium would be confirmed, and its influence on some properties in spheroidal graphite irons would be surveyed.

Experimental procedure

Base iron was smelted in low frequency induction furnace. After the chemical composition was adjusted, the liquid iron was superheated to above 1500 °C for about five minutes. Since tap weights varied among different heats, tap temperature was controlled to within the range of 1405 °C to 1480 °C. Nodulization and inoculation were conducted in the ladle by the ‘‘sandwich’’ method during tapping. Fe-Si-5.5Mg and Fe-75Si alloys were used for each agent, respectively. Chilled samples for analysis were taken from magnesium-treated liquid irons with standard methods. The metal mould used for sampling is shown in Fig. 2. The residual magnesium content was adjusted in a stepwise fashion among six heats by adding different amounts of Fe-Si-5.5%Mg alloy. Residual magnesium will be described as total magnesium later in this paper. The aimed-for content was temporarily checked with the same emission spectrometer as used for this study but by the conventional analytical procedure. To survey the deoxidation degree in liquid irons with different magnesium levels, free oxygen was also measured in each heat using an Electro Motive Force (EMF) probe. 50 mm Y-blocks were cast in furan-bonded sand moulds for each heat. It took about three minutes for the whole operation, from the magnesium treatment to the end of pouring.

State analysis on magnesium was attempted by two different procedures. In the first, total and inclusive magnesium in each chilled sample was chemically analysed, and free magnesium was calculated according to Formula (1);

$$\text{Free Mg} = \text{Total Mg} - \text{Inclusive Mg} \qquad (1)$$

Subsequently, the other samples taken from the same heats were analysed by spectrochemical methods for total and free magnesium. The details are described below.

Total magnesium was analysed using the Inductively-Coupled Vacuum Plasma Spectrometer (ICP). Inclusive magnesium was analysed using ICP after electrolytic separation. The flow chart of the electrolytic extraction

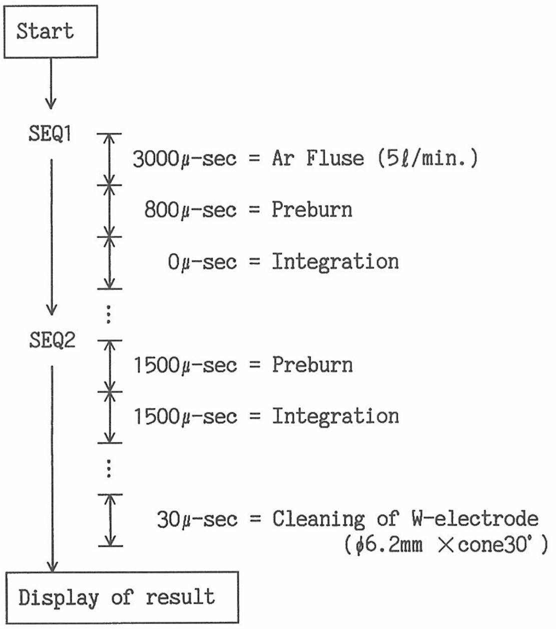


Fig. 4 Sequence programmed into emission spectrometer software for magnesium state analysis

Table 2 Results of chemical analysis on magnesium states

	Mg (Mass%)		
Sample No.	Total	Inclusion	Free
1	0.0114	0.0076	0.0038
2	0.0185	0.0065	0.0120
3	0.0316	0.0075	0.0241
4	0.0368	0.0059	0.0309
5′ (base)	–	–	–
5	0.0500	0.0075	0.0425
6	0.0549	0.0082	0.0467

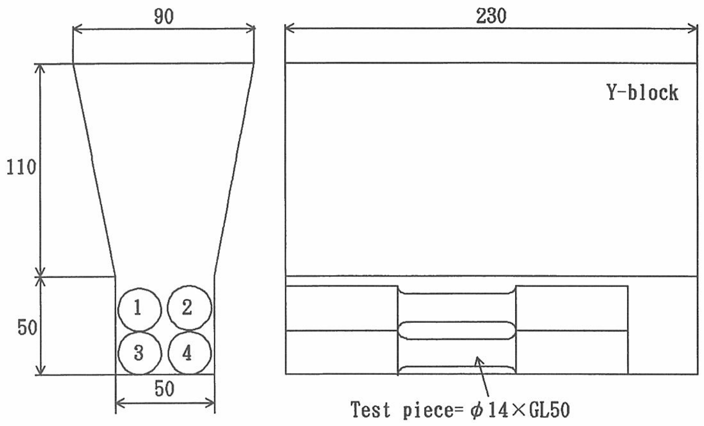
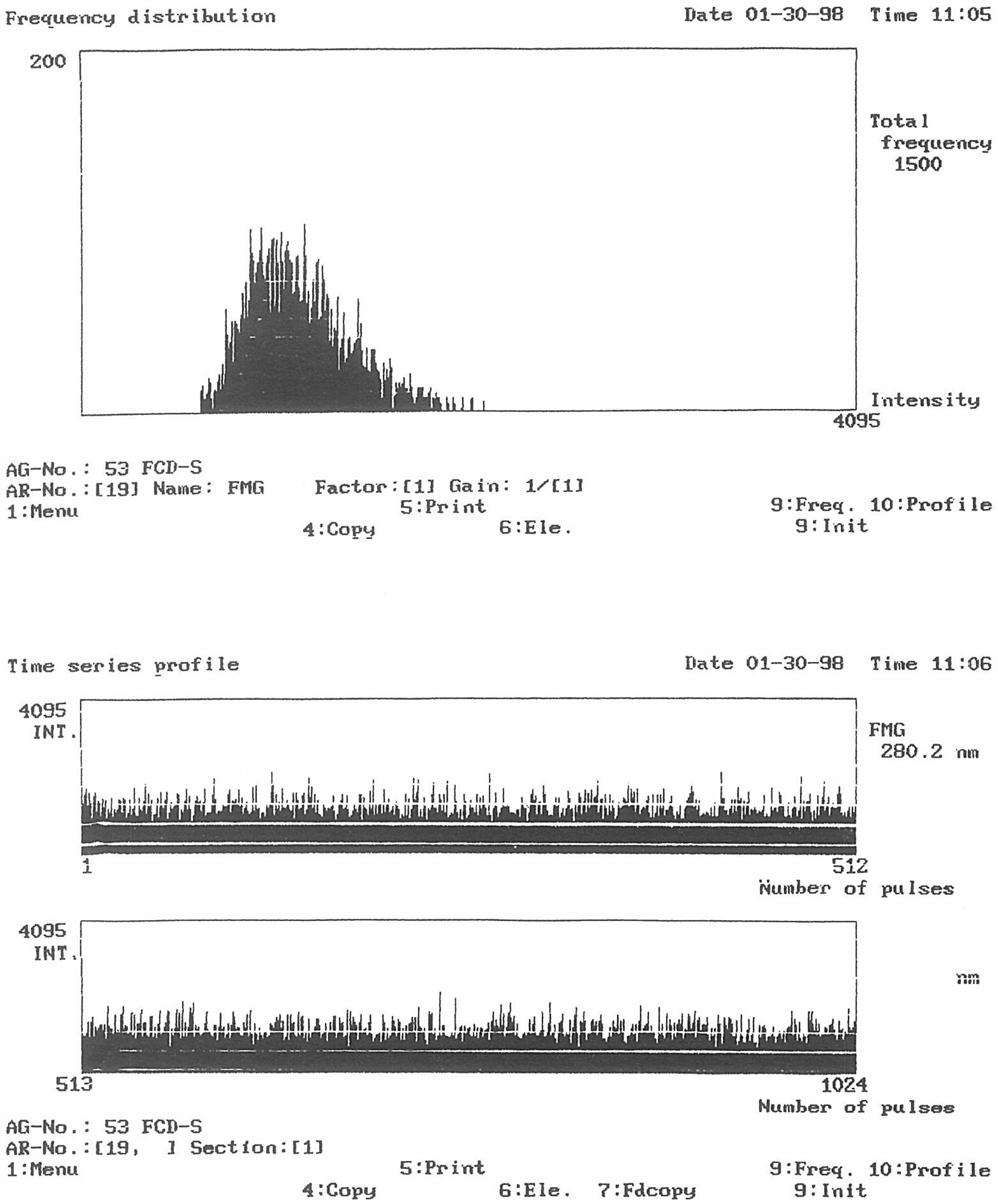


Fig. 5 Schematic illustration of Y-block and tensile test pieces. Dimensions in mm



AG-No.: 53 FCD-S
AR-No.:[19] Name: FMG
Factor:[1] Gain: 1/[1]

AG-No.: 53 FCD-S
AR-No.:[19,] Section:[1]

Fig. 6 Example of pulse profile detected by emission spectrometer in conjunction with a PDA system (Sample No. 6) and the quantitative analysis is shown in Fig. 3. A solution that could dissolve oxide, sulfide, nitride, phosphide and carbide was selected. The electrolytic extraction continued until each sample lost a weight of about 0.5 g. The size of inclusions in the chilled samples was observed at the analysed surface shown in Fig. 2, using optical and scanning electron microscopy. Accordingly, a nuclepore filter with the pore size of 0.2 μm was selected to collect inclusions. Such collected inclusions were ground, dissolved in acid and then analysed using ICP.

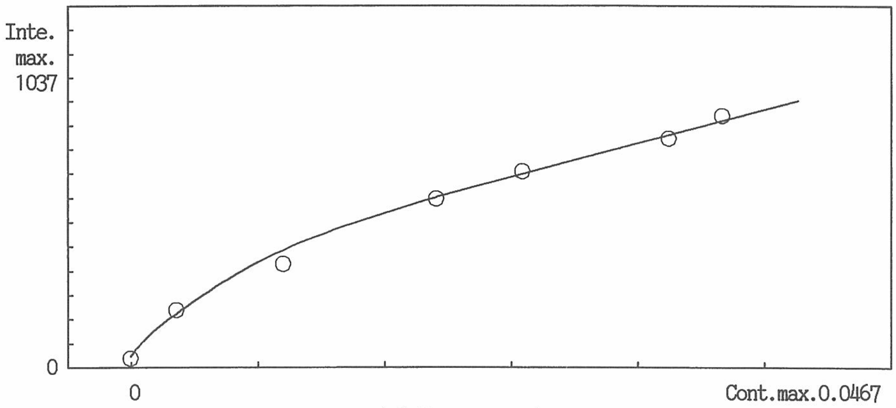
The other chilled samples taken from the same heat were analysed using an emission spectrometer in conjunction with a PDA system.[3,4] Several trials were conducted to check the relationship between the chemical analysis value and the spectrum intensity on total and free magnesium. Therefore, the middle value as illustrated in Fig. 1 was selected as the variable for total magnesium. On the other hand, the frequency distribution detected free magnesium was integrated and the area was used as the variable for free magnesium. To eliminate the influence of the contamination during the sample preparation, pre-discharge was conducted for every analysis. The sequence for the magnesium state analysis established in the emission spectrometer is shown in Fig. 4. The voltage for discharge and the wave length for detecting the luminous spectrum of magnesium were set at 330 V and 280.2 nm, respectively.

Tensile properties in the 50 mm Y-block test castings poured at each magnesium level were examined from the test bars removed as shown in Fig. 5. The microstructure and brinell hardness tests were conducted on at the grip section of every tensile test piece.

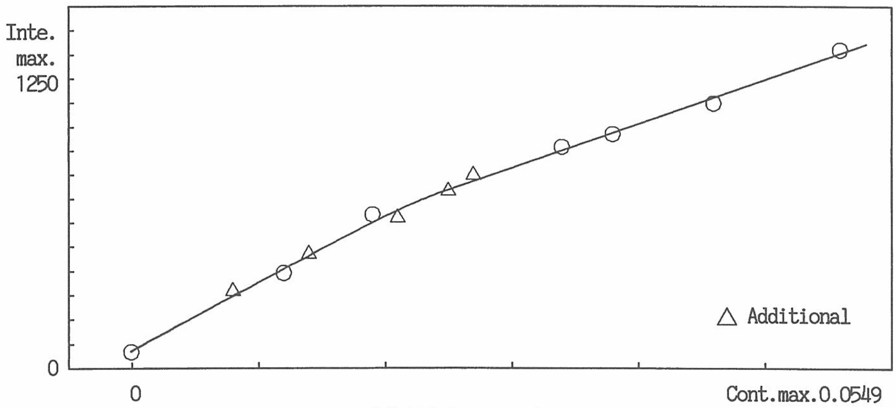
Results

Sampling

The chemical composition, including free oxygen, in magnesium treated liquid irons is shown in Table 1. The total magnesium content could be controlled at the aimed-for level for every heat. The sulfur and free oxygen content decreased in every heat after liquid treatment. The chemical composition, including free oxygen, of base iron for heat No. 5 is shown in Table 1, as an example. Except for sample No. 1, the content of free oxygen was almost the same among all magnesium treated liquid irons. This means that the deoxidation was saturated when total magnesium reached a certain level.



(a) Free magnesium



(b) Total magnesium

Fig. 7 Relationship between chemical analysis value and spectrum intensity detected by emission spectrometer; a) Intensity vs free magnesium content b) Intensity vs total magnesium content

ICP analysis

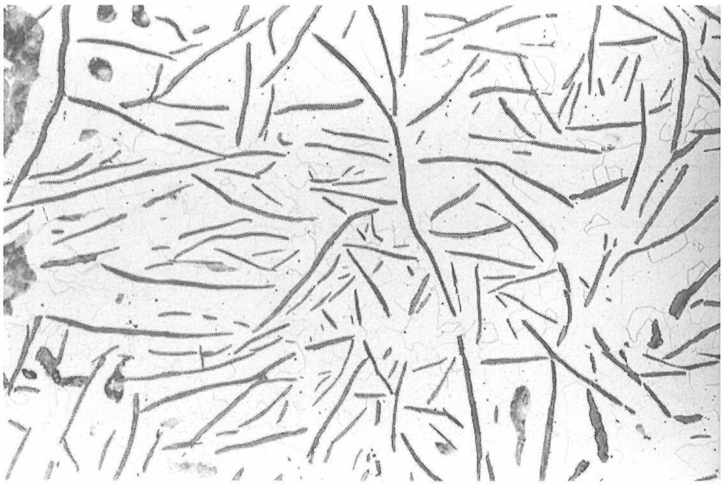
Most of inclusions in the chilled matrix were the size of 0.5–5 μm. Inclusions larger than about 20 μ were rarely observed. Screening collected the inclusions through a filter with 0.2 μm pores. Although magnesium treated liquid iron test specimens were poured into a metal mould, the precipitation of sphere graphite was still observed at the analysed surface; the diameter was 3–5 μm. Even if some sphere graphite had inclusion contained within its body, it is certain that such inclusion would also be resoluted by acid, since the extract including sphere graphite was well ground after filtering.

The result of ICP analysis on total and inclusive magnesium are shown in Table 2. The calculated free magnesium is also shown in Table 2. The inclusive magnesium content was almost the same among the chilled samples, although the total magnesium content was different. On the other hand, the free and total magnesium were linked together, through varying content. The deoxidation degree was nearly the same among the series of magnesium treated liquid irons, shown in Table 1. Similar conditions are also shown on the degree of desulfurisation.

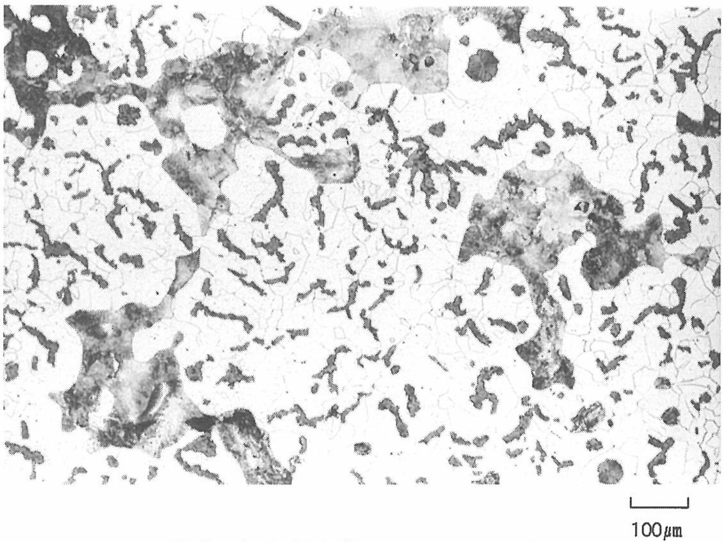
Emission spectrum analysis

An example of the pulse profile on magnesium in sample No. 6 is shown in Fig. 6. There was a big difference between free and inclusive magnesium on the spectrum intensity, as expected. The intensity from free magnesium was nearly all at the same level, and about half of the maximum intensity from inclusive magnesium. This pulse profile suggested that the accurate state analysis on magnesium would be a possibility.

A good relationship between the chemical analysis value and the spectrum intensity detected by emission spectrometer was obtained on both free and total magnesium, as shown in Fig. 7. There was a good reappearance during a subsequent repeated analysis. Inclusive



a.Sample 1 (0.0114T·Mg, 0.0038F·Mg)



b.Sample 2 (0.0185T·Mg, 0.0120F·Mg)

Fig. 8 Microstructure of 50 mm Y-block for each magnesium level tested. Magnesium results are given in mass%; T·Mg = total magnesium and F·Mg = free magnesium

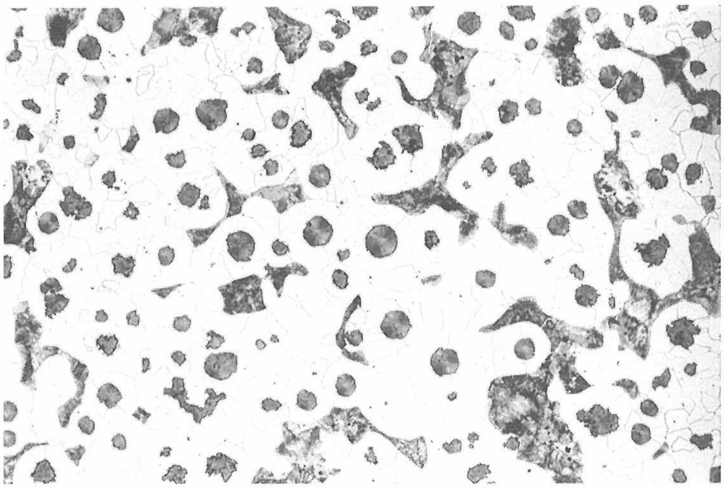
magnesium was almost at the same value among chilled samples. These meant that both chemical and spectrochemical analysis went well and the results were reliable. The curve through the plots would be able to be used as the calibration curve in practice. These curves have been actually used for our foundry practice.

Microstructure and mechanical properties in test samples

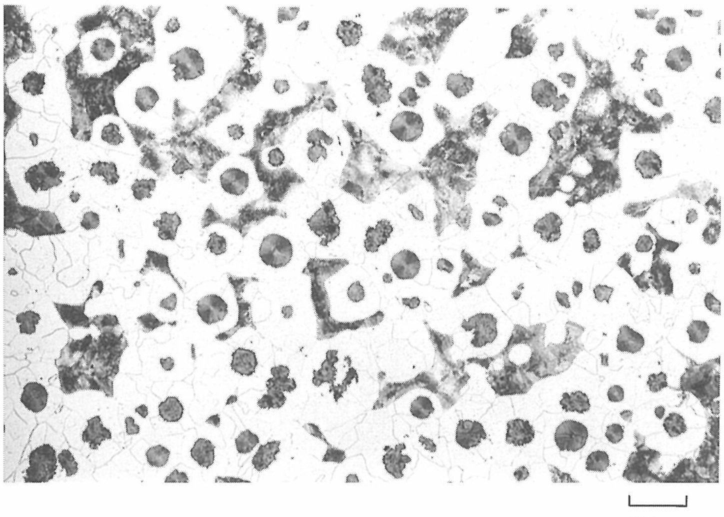
The microstructure of 50 mm Y-block in each magnesium level is shown in Fig. 8a through Fig. 8f, respectively. The nodularity showed a good correlation to the free magnesium content, but the nodule count number did not. The nodularity almost saturated when the free magnesium content was over about 0.0250 mass%. This was also true of the tensile properties, as shown in Fig. 9. All tensile properties showed a good correlation to the free magnesium content. Brinell hardness followed the tensile properties. The inclusive magnesium, however, had no relation to either the nodularity and the nodule count number.

Consideration

Although ledeburite cementite in the chilled samples was also extracted with inclusions, this would not influence the above experimental results. There is the fundamental reason why ledeburite cementite would not influence the result of chemical analysis. The magnesium atom has little possibility to form substitutional and/or interstitial type solid solution in the ledeburite cementite lattice because of the atomic size. The diameter of magnesium atom (3.20 Å[5]) is much larger than that of iron atom (2.48 Å[5]). In fact, the experimental results of emission spectrum analysis suggested that magnesium had no chance to join the ledeburite cementite lattice. The results of emission spectrum analysis corresponded with those of chemical analysis. If magnesium could resolve into the ledeburite cementite lattice, the inclusive magnesium value in chemical analysis might be much higher than that in this study and different among the chilled samples. The precipitation of magnesium carbide cannot occur in chilled samples, since it is unstable over about 660 °C.[6] Magnesium also has almost no solubility in ledeburite



c. Sample 3 (0.0316T·Mg, 0.0241F·Mg)



d. Sample 4 (0.0368T·Mg, 0.0309F·Mg)

Fig. 8 (Continued)

austenite for the same reasons as in ledeburite cementite. T. B. Massalski[6] *et al.* have already verified the solubility of magnesium in austenite.

According to the detailed observation recently reported by T. Skaland,[7] the size of magnesium-containing inclusions in 30 mmϕ sample is reported as 0.4–2.0 μm. Y. Igarashi[8] has also reported it was about 1.0 μm. In the present study, it was 0.5–20 μm. These figures are all the result of 2-dimensional (2-D) observation. The measured 2-D diameters (da) can be converted into 3-D values (dv) through formula (2);[9]

$$dv = da \cdot \pi/2 \qquad (2)$$

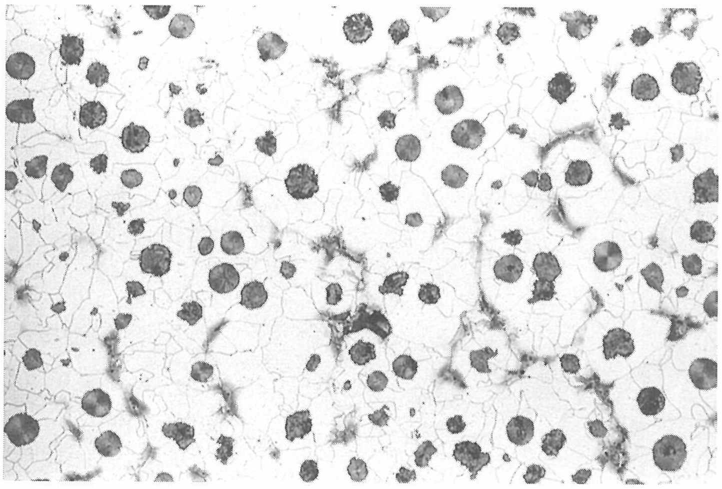
Surely, the extracted inclusion had to be larger than the pore of nuclepore filter (0.2 μm) used in this study. Magnesium-containing inclusions in the chilled samples would be completely extracted and chemically analysed exactly. Emission spectrum analysis well supported this theory, showing good spectrum properties from the inclusions.

The analytical results of free magnesium correlated to the nodularity and mechanical properties closely, but that of inclusive magnesium did not. This means that the free magnesium content is an indispensable factor for the graphite spheroidization, but that of inclusive magnesium is not. The free magnesium content did not have an influence on the nodule quantity of spheroidal graphite. This is the reason why the nodule quantity results from the inoculation effect and the solidification speed.

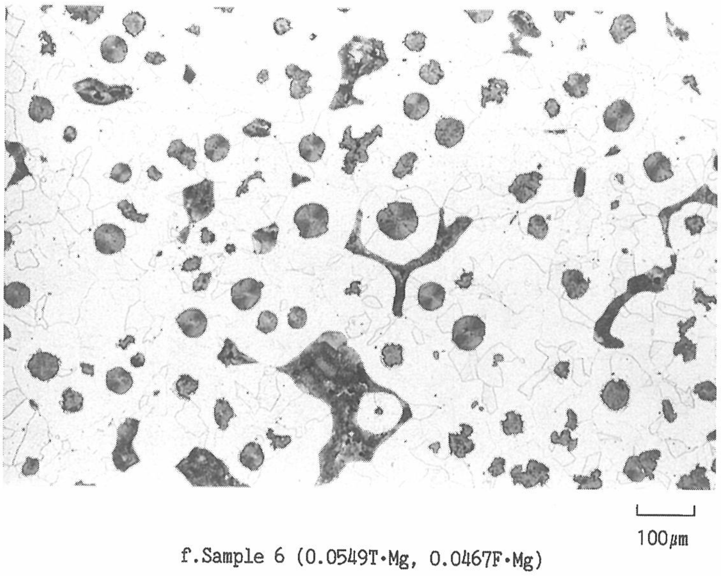
Precise quality control of the nodularity of spheroidal graphite cast iron in practice should be conducted with the free magnesium content. Magnesium is the best element for production of spheroidal graphite cast irons because its practical temperature range matches very well to its physical behaviour in liquid iron.

Most of the free magnesium will exist in the form of a gas bubble in liquid iron, as mentioned in the Introduction. If this is true, free magnesium in the chilled sample will be distributed at the interfacial site between ledeburite cementite and austenite, forming a void as a trace of a gas bubble. This will be examined in later study.

In this study, the site theory was verified showing the



e.Sample 5 (0.0500T•Mg, 0.0425F•Mg)



f.Sample 6 (0.0549T•Mg, 0.0467F•Mg)

Fig. 8 (Continued)

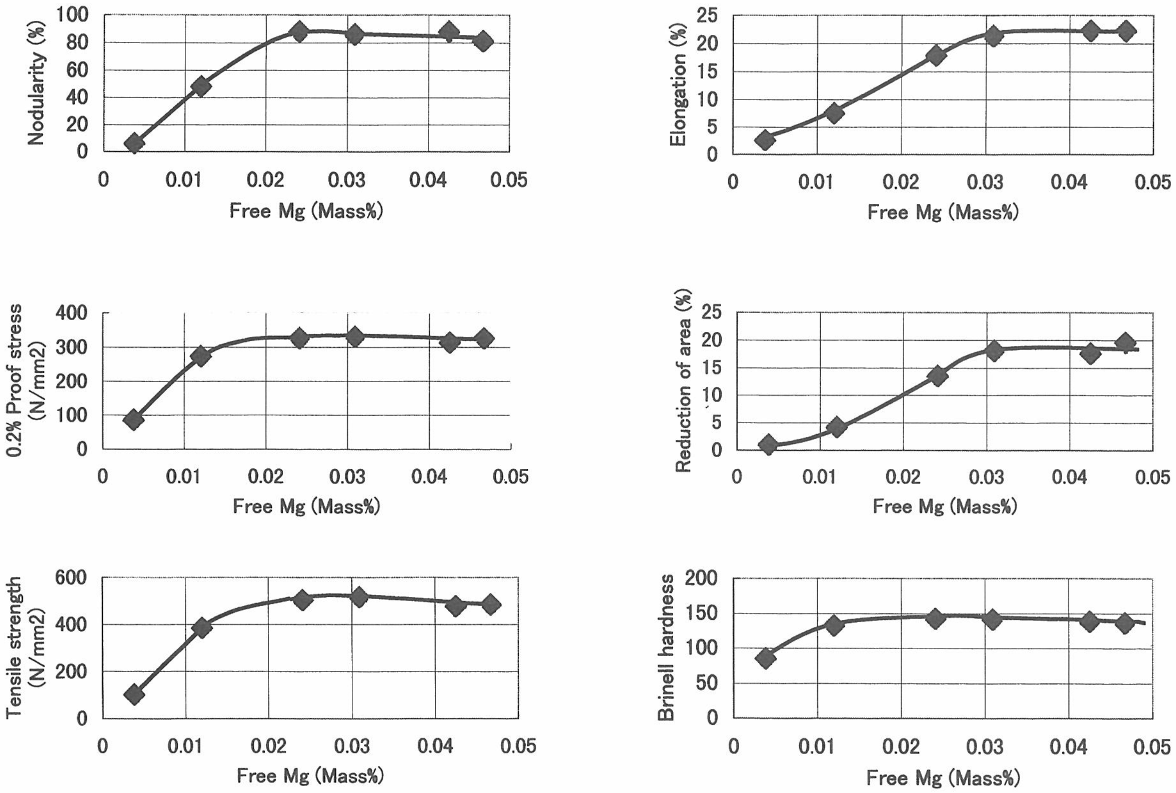


Fig. 9 Influence of varying free magnesium levels on nodularity and mechanical properties in spheroidal graphite iron

existence of free magnesium, and its influence on some properties in spheroidal graphite irons. The method of the verification was quite simple, and is reasonable from the physical, metallurgical and mechanical points of view.

Conclusions

1. The existence of free magnesium in chilled samples can be analytically verified, giving the well-grounded results.
2. The free magnesium and total magnesium were linked together, varying only in content. However, the inclusive magnesium content was nearly the same among the chilled samples.
3. Free magnesium was influential on graphite spheroidization and therefore its content correlated to the nodularity, the tensile properties and the hardness. However, these properties were saturated when the free magnesium content reached about 0.025 mass%.
4. Free magnesium had no influence on the nodule quantity of spheroidal graphite.
5. Inclusive magnesium content influenced nothing.

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