Analysis of Graphite Nuclear in Spheroidal Graphite Cast Iron and Mechanism of Nodule Count Increase by Bismuth Oxide^{*1}

Hiroaki Tsuji^{1,*2}, Hiroyuki Chono¹, Nobuya Yamamoto¹, Tokio Kai¹ and Yoshio Igarashi²

¹TOYO DENKA KOGYO CO., LTD., Kochi 781-9525, Japan

²Micro Analysis Center, Shimotsuke 329-0434, Japan

In order to elucidate the mechanism of nodule count increase by Bi, we analyzed spheroidal graphite cast iron with increased nodule count by Bi addition. In the Scanning Electron Microscope - Energy Dispersive X-ray Spectrometry (SEM-EDS) analysis, Bi was identified to be present near the center of the spheroidal graphite. The center of this spherical graphite was pretreated by Focused Ion Beam (FIB) micro sampling method to prepare analytical sample and analyzed by Transmission Electron Microscope - Energy Dispersive X-ray Spectrometry (TEM-EDS). As a result, it was found that Bi exists as Bi-La-Ce-Sb oxide on the outer periphery of the graphite core centered on (MgCa) S.

To verify the effect of the Bi-La-Ce-Sb oxide on the increase in nodule count, we first used mechanical alloying to prototype a Bi-La-Ce-Sb oxide having the same composition as that observed via TEM-EDS. This oxide was then added to the molten spheroidal graphite cast iron. As a result, nodule count did not increase with the addition of the prototype Bi-La-Ce-Sb oxide alone, but when the prototype Bi-La-Ce-Sb oxide and Fe-Si inoculants were mixed and added, the nodule count increased more than when only the Fe-Si inoculants was added.

From these results, it is considered that the effect of increasing nodule count by Bi addition is that Bi acts on graphite nucleus as an oxide.
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1. Introduction

In spheroidal graphite cast iron, increasing the nodule count provides material strengthening^{1,2)} and defect reduction by suppressing chill, shrinkage, and chunky graphite.³⁻⁵⁾ As a method of increasing nodule count, inoculation treatment is generally performed in the production of spheroidal graphite cast iron.^{6,7)} Various inoculants are used in the inoculation process, and most of them are based on Fe-Si alloys made by alloying Al, Ca, Sr, Ba, Ce, La, Zr, Bi, etc.⁶⁻⁸⁾ In particular, although Bi is considered to be a spheroidizing inhibitor,^{9,10)} it can also significantly increase nodule count.^{11,12)} According to the study conducted by Horie *et al.*,^{13,14)} the addition of a small amount of Bi significantly increases the nodule count, and the addition of Bi₂O₃ and Bi₂S₃ has the same effect. In this study, the graphite sample containing Bi was analyzed by energy dispersive spectroscopy (EDS), and Bi was detected in the center of the graphite.

From these research reports, the effect of Bi in increasing the nodule count is clear; however, the related mechanism and the form of Bi present in graphite have not been clarified yet. Therefore, in this study, to determine the mechanism by which the use of Bi increases the nodule count in spheroidal graphite cast iron, Bi was added to spheroidal graphite, and the internal structure of the graphite was then observed. This was performed using Igarashi's advanced electron microscopy method,^{15,16)} and the crystallized graphite nucleus was then analyzed. The analysis results showed that Bi could be observed in the Bi, La, Ce, and Sb oxides on the outer circumference of the graphite nucleus. Additionally, the observed oxides were produced and directly added to the molten metal to verify their effect on increasing the nodule count.

2. Observation and Analysis of Graphite Nucleus

2.1 Preparation of graphite nucleus observation sample

Samples for observing the graphite nuclei were prepared under the following conditions. The molten metal of cast iron with a eutectic composition was spheroidized with an Fe-Si-Mg-Ca-RE alloy, with and without addition of the Fe-Si-Bi alloy. A t 25-mm Y block and a mushroom-shaped mold were used for the optical emission spectrometer. To confirm the phenomenon of increase in the nodule count due to Bi, the nodule count in the t 25-mm Y block was measured. The microstructures are shown in Fig. 1. The t 25-mm Y block sample with and without Fe-Si-Bi alloy had 436 and 172 graphite grains/mm², respectively. Thus, the increase in the nodule count due to the addition of Bi alloy was confirmed.

The mushroom-shaped mold was used for composition analysis by an optical emission spectrometer and for scanning electron microscope (SEM)/transmission electron microscope (TEM) observations. The material cast in the quenching mold was used for SEM/TEM observations such as to facilitate the observation of the nuclear material of the graphite nucleus. This is because the molten metal is rapidly cooled and solidified at the micrographite stage in the early stages of graphite formation. Table 1 shows the compositions after the addition of the Fe-Si-Bi alloy. Bi was not detected in the optical emission spectrometer in the molten metal before the addition of the Fe-Si-Bi alloy; however, the concentration of Bi in the molten metal was 22 ppm after the addition of the Fe-Si-Bi alloy, confirming that the prepared sample contained Bi.

2.2 SEM-EDS observation of graphite nucleus

Next, to observe the graphite nucleus of the sample by SEM and TEM, the sample was prepared as shown in Fig. 2. Figure 3 shows the SEM and EDS analysis results of the nuclear material of spheroidal graphite. Characteristic X-ray peaks of Bi, Mg, Si, S, and La can be observed in the white

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^{*2}Corresponding author, E-mail: h-tsuji@toyodenka.co.jp

Fig. 1 Microstructure of 25 mm thickness Y block.

Table 1 Chemical composition of molten metals.

	mass %					
	C	Si	Mn	P	S	Mg
No addition	3.6	2.12	0.21	0.01	0.010	0.035
Bi addition	3.6	2.75	0.30	0.02	0.010	0.052

	mass ppm				
	Ca	Sb	La	Ce	Bi
No addition	23	37	48	88	-
Bi addition	20	57	55	95	22

Fig. 2 Procedure of preparation of specimen for observing graphite.

part in the reflected electron image of the central part of graphite, which seems to be the graphite nucleus. From this result, it is considered that the added Bi exists near the graphite nucleus. The structure of the graphite nucleus is not

Fig. 3 Observation and analysis of graphite nucleus by SEM-EDS.

clear because the graphite nucleus is buried in graphite on the sample surface, as observed by SEM-EDS. To clarify the morphology in which Bi exists, the part analyzed by SEM-EDS was analyzed by TEM-EDS. As shown in Fig. 2, the sample was prepared by processing the sample observation site after SEM-EDS analysis into thin sections using the focused ion beam microsampling method.

2.3 Microstructure analysis of nuclear material by TEM

Figure 4 shows the results of the mapping analysis by TEM-EDS at the points where the characteristic X-ray peak of Bi was confirmed by SEM-EDS analysis. The graphite core had a diameter of approximately 1–2 µm and a roughly spherical shape. The compositions of the graphite core were (MgCa) S in the center, (LaCe) S in the surface layer, and (BiRESb) O and MgOS. Figure 5 shows a composition distribution map of the graphite nucleus traced from the information obtained by the mapping analysis.

Similarly, when another graphite was subjected to TEM-EDS analysis, a graphite nucleus consisting of (BiRESb) O containing Bi was observed in the surface layer centered on (MgCa) S, as in the previous analysis results. Figure 6 shows the results of the mapping analysis, and Fig. 7 shows the composition distribution map of the graphite nucleus traced from the information obtained by the mapping analysis.

Table 2 shows the results of the TEM-EDS analysis of the phase containing Bi. The Bi-containing phase observed in the graphite nucleus had a composition of 45.6% of Bi₂O₃,

Fig. 4 Mapping analysis results of graphite nucleus by TEM-EDS (1).

Fig. 5 Composition distribution chart of graphite nucleus (1).

38.7% of La_2O_3 , 10.7% of CeO_2 , and 5.0% of Sb_2O_3 as measured by four points.

From these results, it is considered that Bi increases the nodule count because the Bi added to the molten metal becomes an oxide containing Bi and La, Ce, and Sb, and this oxide acts on the graphite nucleus. Next, a Bi–La–Ce–Sb oxide with the same composition as the result analyzed by this TEM-EDS analysis was produced, and an experiment was conducted to determine whether the nodule count increased by adding it directly to the molten metal.

3. Trial Production of Bi–La–Ce–Sb Oxide

The oxide to be produced should have the same composition as that obtained by TEM-EDS quantitative

analysis and the particle size should be as small as possible, equivalent to that of the graphite nucleus, as it is assumed to act on the graphite nucleus. A Bi–La–Ce–Sb oxide was produced according to the procedure shown in Fig. 8 to meet this condition. Bi_2O_3 , La_2O_3 , CeO_2 , and Sb_2O_3 were used as raw materials with a purity of more than 99% and a particle size of less than 200 nm, and were weighed and mixed to obtain the composition shown in Table 2. The mixture was placed in an alumina pot containing zirconia balls to obtain a uniform composition, and crushed and mixed with a planetary ball mill at a rotation speed of 260 rpm for 5 h.

The analysis was performed via SEM-EDS and X-ray diffraction (XRD) to confirm the mixed state of the prototype sample. Figure 9 shows the analysis results of SEM-EDS. Before crushing and mixing, each oxide was segregated. However, after crushing and mixing, it was observed that each oxide was uniformly dispersed and mixed.

The XRD analysis results are shown in Fig. 10. The diffraction intensities of Bi_2O_3 , La_2O_3 , CeO_2 , and Sb_2O_3 are smaller and broader than those of the raw materials before the crushing and mixing treatment. This indicates that the crystal size of the prototype oxide is small. From this analysis result, it is considered that the prototype oxide is equivalent to the oxide observed in the TEM-EDS analysis, thus, a direct addition experiment to the molten metal was conducted.

4. Experimental Method and Results

4.1 Bi–La–Ce–Sb oxide addition method

The Bi–La–Ce–Sb oxide prepared by crushing and mixing was directly added to the molten spheroidal graphite cast iron under various conditions, and the effect of the oxide on the increasing nodule count was verified. The oxide addition conditions were the two conditions shown in Table 3.

In condition 1, four levels of oxide addition rate were set. The RE addition rate in the graphite spheroidization

Fig. 6 Mapping analysis results of graphite nucleus by TEM-EDS (2).

Fig. 7 Composition distribution chart of graphite nucleus (2).

Table 2 Quantitative analysis result of Bi containing phases by TEM-EDS.

	mass %			
	Bi ₂ O ₃	La ₂ O ₃	CeO ₂	Sb ₂ O ₃
a	47.3	35.6	14.1	3.0
b	48.2	35.5	11.4	4.9
c	41.6	42.9	9.0	6.5
d	45.4	40.7	8.4	5.5
AVG	45.6	38.7	10.7	5.0

treatment was also included in the experimental level to separately evaluate the effect of La₂O₃ and CeO₂ contained in the prototype oxide and the effect of Ce and La added to the graphite spheroidization treatment.

Condition 2 corresponded to a mixed addition of Bi–La–Ce–Sb oxide and inoculants, because it is difficult for the oxide alone to invade the molten metal.¹⁷⁾ In addition, the

Fig. 8 Production condition of Bi–La–Ce–Sb oxide.

Fig. 9 EDS analysis results of prototyped Bi-La-Ce-Sb oxide.

Fig. 10 X-ray diffraction results of prototyped Bi-La-Ce-Sb oxide.

Table 3 Bi-La-Ce-Sb oxide addition conditions.

Condition 1	RE addition rate in graphite spheroidization treatment (mass%)	<0.001, 0.023
	Bi · Sb · La · Ce oxide addition rate (%)	0, 0.01, 0.05, 0.1
Condition 2	RE addition rate in graphite spheroidization treatment (mass%)	<0.001, 0.023
	Inoculant type	Fe-Si-Ba, Fe-Si-RE Fe-Si-Zr, non
	Bi · Sb · La · Ce oxide addition rate (%)	0, 0.01

oxide may aggregate, float, and separate, which can hinder its action on the molten metal. The types of inoculants mixed with oxides were set to four levels, including those not mixed with inoculants, and the oxide addition rate was set to two levels. The RE addition rate of the graphite spheroidization treatment was included as a factor for the same reason as in condition 1.

Table 4 Spheronizing agents and inoculant composition.

mass %				
Spheronizing agent	Si	Mg	Ca	RE
Fe-Si-Mg-Ca-RE	45	4.7	2.5	1.9
Fe-Si-Mg-Ca	44	4.8	2.1	< 0.05

mass %		
Inoculant	Si	Ca
Fe-Si-Al	74	0.8

Next, the procedure for adding Bi-La-Ce-Sb oxide is described. The base molten metal was dissolved by adding 50% of crude iron and 46% of iron scrap, and the remaining 4% were adjusted by adding electrode scrap, Fe-Si, and Fe-S. This molten metal was subjected to graphite spheroidization treatment using spheroidizing agents and ladle inoculants, as shown in Table 4, using the sandwich method. As shown in Fig. 11, the oxide was added to the molten metal by placing Bi-La-Ce-Sb oxide in a shell cup with a diameter of 30 mm and a height of 50 mm, and the molten metal was

Fig. 11 Method of adding Bi-La-Ce-Sb oxide and nodule count measurement place.

Table 5 Inoculants composition mixed with oxide.

Inoculant	Si	Ca	Al	Ba	RE	Zr
Fe-Si-Ba	72	1.3	1.8	0.8	-	-
Fe-Si-RE	72	1.6	0.9	-	3.9	-
Fe-Si-Zr	70	2.3	1.2	-	-	1.6

poured into it. Under the condition that the oxide and the inoculants (particle size $<0.25\text{ }\mu\text{m}$) were mixed and added, the inoculants of the compositions in Table 5 were used, and the addition rate of the inoculants was 0.1%. As shown in Fig. 11, the nodule count measurement point was cut 15 mm from the bottom of the sample to create five fields of view between the central and outer peripheral surfaces. The nodule count was measured by image analysis, and graphite with a diameter of less than $5\text{ }\mu\text{m}$ was excluded.

4.2 Bi-La-Ce-Sb oxide addition experimental results

Figure 12 shows the results for condition 1. When only Bi-La-Ce-Sb oxide was added, the nodule count did not increase regardless of the RE addition rate or the oxide addition rate.

Figure 13 shows the results when the Bi-La-Ce-Sb oxide under condition 2 and the inoculants were mixed and added. When Bi-La-Ce-Sb oxide and an inoculant were mixed and added, the nodule count increased compared to the case

when only the inoculum was added, regardless of the RE addition rate and the type of inoculant to be mixed. Figure 14 shows the microstructure of the sample with the largest increase in nodule count in this test. The higher nodule count was obtained under the conditions of Fe-Si-Mg-Ca-RE alloy treatment and mixed addition of Bi-La-Ce-Sb oxide and Fe-Si-Zr inoculants.

5. Consideration

5.1 Analysis results of graphite nucleus of Bi-added spheroidal graphite cast iron

In the observation of graphite nuclei by SEM/TEM, Bi added to the spheroidal graphite cast iron molten metal was observed as a composite oxide of $\text{Bi}_2\text{O}_3\text{-La}_2\text{O}_3\text{-CeO}_2\text{-Sb}_2\text{O}_3$ to cover the graphite nucleus. Thus, it is considered that the observed oxide was a liquid in the molten metal. Bi added to the molten metal became Bi_2O_3 , mixed with other oxides such as La_2O_3 , CeO_2 , and Sb_2O_3 , and spherically covered the graphite nucleus as a liquid phase mainly composed of (MgCa) S. Therefore, it is considered to effectively act as a nucleus of spheroidal graphite.

5.2 Effect of the direct addition of Bi-La-Ce-Sb oxide

The oxide with the same composition as the composite oxide of $\text{Bi}_2\text{O}_3\text{-La}_2\text{O}_3\text{-CeO}_2\text{-Sb}_2\text{O}_3$ obtained by TEM-EDS measurement was produced and directly added to the molten

Fig. 12 Relationship between the addition rate of Bi-La-Ce-Sb oxide and nodule count.

Fig. 13 Increase effect of nodule count by mixing Bi-La-Ce-Sb oxide and inoculants.

Fig. 14 Microstructure of sample mixed with Bi-La-Ce-Sb oxide and Fe-Si-Zr inoculants.

spheroidal graphite cast iron. The nodule count did not increase regardless of the addition rate, but when the oxide and the inoculants were mixed and added, the nodule count increased compared to the case when only the inoculants were added. It is considered that the nodule count does not increase with the addition of Bi-La-Ce-Sb oxide alone, as it does not invade the molten metal. This is because the oxide is nano-sized and has low wettability to the molten metal.¹⁷⁾ This result is considered to be a problem due to the method of adding the oxide to the molten metal.

In the case of mixed addition of Bi-La-Ce-Sb oxide and inoculants, it is considered that the oxide invades the molten metal due to the diffusion of Si in the Fe-Si inoculants, which are mixed and added with the oxide. In the study by Horie *et al.*,¹³⁾ the addition of Bi₂O₃ and Fe-Si-Mg alloy increased the nodule count. It is considered that the oxide easily invaded the molten metal owing to the strong stirring of the molten metal by the reaction with Mg. In addition, when Si in the Fe-Si inoculants was added to the molten metal, it caused an exothermic reaction and the ambient temperature increased, thus it was easier to dissolve the oxide added. As a result, it is considered that the Bi-La-Ce-Sb oxide adheres to the outer periphery of the graphite nucleus and effectively acts as the nucleus for graphite crystallization.

Under the condition of mixed addition of Bi-La-Ce-Sb oxide and inoculants, for all samples, regardless of the type of inoculant to be mixed and the RE addition rate during spheroidizing treatment, the nodule count increased when oxides were mixed and added. Therefore, it is considered that

the Bi-La-Ce-Sb oxide itself has the effect of increasing the nodule count.

5.3 Effect of mixed addition of oxide and Fe-Si-Zr inoculants

The higher increase of nodule count was obtained with the mixed addition of Bi-La-Ce-Sb oxide and Fe-Si-Zr inoculants within the range of this experimental condition. According to Nakae's latest research,¹⁸⁾ Zr refines dendrites; as a result, many regions where graphite crystallizes easily occur between austenites. Thus, Zr has the effect of increasing the nodule count. The results of this experiment are considered to be due to the synergistic effect of the dendrite miniaturization of Zr added from Fe-Si-Zr inoculants and the increase of the nodule count by the action of Bi-La-Ce-Sb oxide on the graphite nucleus.

6. Conclusion

We analyzed the graphite nucleus after addition of Bi, and conducted an experiment in which a produced Bi-La-Ce-Sb oxide was directly added to the molten metal based on the analysis results. The results are summarized below.

- (1) Bi was observed as a composite oxide of Bi₂O₃, La₂O₃, CeO₂, and Sb₂O₃, covering the graphite nucleus mainly composed of (MgCa) S in the analysis of Bi-added spheroidal graphite cast iron;
- (2) Even if only Bi-La-Ce-Sb oxide is directly added to the molten metal, the nodule count does not change. It is considered that the oxide does not invade the molten metal because the wettability between the oxide and the molten metal is low;
- (3) The nodule count increased with the mixed addition of Bi-La-Ce-Sb oxide and Fe-Si inoculants.

It is considered that the oxides invade the molten metal due to the diffusion of Si when the Si in the Fe-Si inoculants dissolves in the molten metal. In addition, the exothermic reaction when Si in the Fe-Si inoculants is added to the molten metal raises the ambient temperature; at the same time, the added oxide becomes easier to dissolve, such that Bi-La-Ce-Sb oxide adheres in a spherical shape and effectively acts on graphite crystallization;

- (4) The higher increase of nodule count was obtained under the mixed addition conditions of Bi–La–Ce–Sb oxide and Fe–Si–Zr inoculants.

This effect of increasing the nodule count is considered to be due to the synergistic effect of the dendrite miniaturization by Zr added from Fe–Si–Zr inoculants and the Bi–La–Ce–Sb oxide on the graphite nucleus.

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