Interaction of Boron with Copper and Its Influence on Matrix of Spheroidal Graphite Cast Iron

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High strength steel, which often contains a few tens of ppm B, has been used in the automobile industry due to weight reduction for energy savings. If this steel scrap is recycled for producing high strength spheroidal graphite iron castings, the alloying element, B, changes the matrix from pearlite to ferrite. In this research, the influence of B on the matrix of the high strength spheroidal graphite iron castings and the means of counteracting its bad effects were investigated.

The result of the study on the ferritization effect of B on the matrix showed that the ferrite volume fraction increased with the addition of B. Meanwhile, the smoothness of the spheroidal graphite surface was damaged.

In order to investigate the counteracting measures to the ferritization effect of B, N or Ti was added to the parent alloy to form BN or TiB₂. It was found that the addition of N or Ti reduced the ferrite volume fraction slightly, and the effect of Ti was more obvious.

Some tests were carried out to discuss the interaction of Cu with B. The existence of a thin Cu film on the spheroidal graphite surface was observed in the B-free Cu-added sample; nevertheless, it could not be confirmed in the B-added sample. When Cu was replaced by Mn, there was no difference in the ferrite fraction with the B addition. Therefore, it could be confirmed that the ferritization effect of B exists only in the presence of Cu in spheroidal graphite cast iron.

KEY WORDS: spheroidal graphite; high strength cast iron; high strength steel; boron; ferrite; copper.

1. Introduction

It is widely accepted that the matrix is critical to the comprehensive properties of spheroidal graphite cast iron. For high strength spheroidal graphite cast iron, pearlite is the ideal matrix, and then Cu is an element that facilitating cast iron with higher tensile strength without chill formation. In the past, much research work¹⁻⁴⁾ has been done on the effect of Cu on the matrix structure and the graphite morphology, and researchers have come to realize that Cu has an appealing feature of pearlite stabilization in the spheroidal graphite cast iron. Nowadays, the high strength steel scrap, recycled from the automobile industry, which often contains a few tens of ppm of B, is usually used in the casting industry, and the existence of B induces the tensile strength reduction for the high strength spheroidal graphite iron castings.^{5,6)}

According to the study done by Izui *et al.*,⁵⁾ even a few tens of ppm B has an adverse impact on the matrix in the high-strength spheroidal graphite cast iron alloyed with Cu, in that B could increase the ferrite fraction of the cast iron. If the B content is more than 50 ppm, carbide appears in the matrix.^{5,6)} Izui⁵⁾ reported that B segregates around the spheroidal graphite to form Fe₂₃(CB)₆ in the samples alloyed with Cu, which dramatically lowers the carbon content in

the matrix near the spheroidal graphite and leads to the ferrite matrix. These phenomena indicated that there could be some interaction between Cu and B, but there was no detailed study either on explaining the mechanism or whether it is a particular phenomenon. On the other hand, in order to increase the pearlite fraction in the matrix for higher tensile strength, one method was proposed in which a strong pearlite-forming element such as Sn was added to the melt.

Umehara *et al.*⁷⁾ showed that the desulfurization treatment of cupola melt could lessen the B content by combining B with O to form B₂O₃; nevertheless, the result was not sufficient. Igarashi *et al.*⁸⁾ observed a secondary graphite precipitated on the spheroidal graphite surface by a SEM, using deep-etched samples alloyed with Cu and B; However, the existence of the Cu film was not clarified. Tsujikawa⁹⁾ also failed in finding the Cu film by a TEM observation. The existence of the thin Cu film around the spheroidal graphite was first confirmed by Ishiguro¹⁰⁾ using an in-lens type FE-SEM. However, the segregation mechanism of Cu has not been clarified.

In this research, a treatment to reduce the ferritization effect of B was examined by adding N or Ti to the cast iron melt. Then, in order to identify whether the interaction of B with Cu is a particular phenomenon, the interaction of B with Mn was also studied. Finally, the distribution of B was

investigated using a WDX, and the observation of the Cu film was also carried out to examine the interaction mechanism of B with Cu.

2. Experimental Procedure and the Alloy Compositions

In an Ar atmosphere, carbon steel rods (Fe–0.25%C–0.14%Si–0.18%Mn–0.017%P–0.021%S), graphite electrode and ferro-manganese were melted in a high-frequency induction furnace. After that, metallic silicon and pure copper were added to the melt. High purity ferro-boron (14.6%B) was added to the melt to study the influence of B on the matrix. Ferro-manganese nitride (4.66%N) and sponge titanium (98%Ti) were also added to the melt to study the effect of N and Ti, respectively. Thermal analysis was done during the melting using a CE-cup, and the carbon equivalent was adjusted to 4.4%. An inoculant (22%Fe–75%Si–3%Ca) and a spheroidizer (48%Fe–45.4%Si–1.54%Ca–3.67%Mg–1.71%RE) were added in a ladle, and the melt was then cast into knock-off type keel blocks of 25 mm diameter. The chemical compositions of B-added, B-N-added, and B-Ti-added alloys used in this study are shown in **Tables 1, 2 and 3**, respectively.

The samples were polished and then etched with 3% nital for about ten seconds until the metallic luster was lost. The

macro- and microstructures of the samples were then observed by an optical microscope and a SEM. In order to observe the graphite surface morphology with the SEM, the samples were deeply etched in 10% nital for about 25 minutes.

For the observation of the Cu film on the graphite surface, the Fe in the matrix should be etched without the dissolution of Cu. Therefore, a special corrosion method was introduced into this research using a degassed HCl aqueous solution. Firstly, pure water was degassed for 1 hour by vacuum treatment. After that, HCl was added into the water at 7% and degassed for another 1 hour. Because of the difference in ionization tendency of Fe and Cu without oxygen in the solution, the Fe in the matrix was corroded, while the Cu film on the graphite surface remained with this etching method.¹¹⁾ The ferrite volume fraction was measured using the 3% nital-etched samples with a microcomputer equipped with an optical microscope.

3. Results and Discussion

3.1. Influence of B, N and Ti on the Matrix

3.1.1. Influence of B

The microstructures of the matrix of the 1%Cu spheroidal graphite cast iron at different B contents are shown in **Fig. 1**. The figure reveals that the pearlite volume fraction decreases with the increase in the B content. Where is the precipitated carbon with the ferrite formation? To study this problem, the three-dimensional shape of the spheroidal graphite surface was observed using the SEM, and the result was the same as that in **Fig. 2**.⁸⁾ The spheroidal graphite surface was covered with a special kind of graphite, like the D-type graphite in flake graphite, because the precipitation of the carbon in austenite formed a secondary graphite. Since there was no Cu film, the precipitated secondary graphite formed a layer around the crystallized spheroidal graphite, as pointed out by the arrows in **Fig. 3**. We can eas-

Table 1. Chemical composition of B-added samples. (mass%)

Number of sample	C	Si	Cu	B	Mn
1	3.62	2.52	1.09	<5 ppm*	0.44
2	3.65	2.64	0.95	5 ppm	0.43
3	3.61	2.53	1.08	10 ppm	0.41
4	3.57	2.50	1.07	15 ppm	0.44
5	3.66	2.56	1.14	31 ppm	0.44

*: 5 ppm B is the lower limit of this chemical analysis.

Table 2. Chemical composition of N-added samples. (mass%)

Number of sample	C	Si	Cu	B	N	Mn
6	3.62	2.52	1.09	<5 ppm*	84 ppm	0.62
7	3.65	2.64	0.95	4 ppm	81 ppm	0.66
8	3.61	2.53	1.08	10 ppm	95 ppm	0.66
9	3.57	2.50	1.07	15 ppm	85 ppm	0.67
10	3.66	2.56	1.14	38 ppm	89 ppm	0.61

Table 3. Chemical composition of Ti-added samples. (mass%).

Number of sample	C	Si	Cu	B	Ti	Mn
11	3.62	2.52	1.09	<5 ppm*	588 ppm	0.63
12	3.65	2.64	0.95	8 ppm	516 ppm	0.65
13	3.61	2.53	1.08	11 ppm	613 ppm	0.67
14	3.57	2.50	1.07	21 ppm	486 ppm	0.67
15	3.66	2.56	1.14	37 ppm	601 ppm	0.61

Fig. 1. Influence of B on the matrix structure of 1%Cu spheroidal graphite cast iron.

Fig. 2.⁸⁾ Spheroidal graphite surface of 31 ppm-B sample observed by SEM.

Fig. 3. All-ferrite matrix and secondary graphite precipitated spheroidal graphite iron.

Fig. 4. Influence of added elements on ferrite fraction.

ily confirm the secondary graphite in all-ferrite-matrix spheroidal graphite iron due to its significant volume.

3.1.2. Counteracting Effect of N and Ti

To investigate the counteraction to the damaging effect of B on the matrix, the addition of N or Ti was studied. Approximately 85 ppm N or 550 ppm Ti was added to the alloys for controlling the ferrite volume fraction. The ferrite volume fraction decreased in the N-treated and the Ti-treated samples as shown in Fig. 4. As for the effect of the pearlite formation, Ti is much more effective than N in restraining the ferrite formation and retaining the smoothness of the spheroidal graphite surface.

3.1.3. Mechanism of Influence of N and Ti

As indicated above, the precipitated carbon from the austenite matrix during the cooling forms the D-type-like graphite at the spheroidal graphite surface of the B-added samples. If N or Ti is added to the samples, B reacts with N or Ti to form BN or TiB₂, thus decreasing the dissolved B concentration in the austenite and weakening the ferrite formation tendency. The reason why Ti is much more effective than N could be explained by the chemical reaction and the free energy change shown in Eqs. (1) and (2).¹²⁾

A thermodynamic calculation was done using these two equations; the results are shown in Fig. 5, via the influence of temperature on the boride formation energy ΔG_0 . From Fig. 5, it is clear that at the eutectoid temperature, the formation energy of TiB₂ is much lower than that of BN.

Fig. 5. Formation energy of BN and TiB₂ at different temperatures.

Fig. 6. Changes in ferrite fraction with B content in the samples alloyed with Cu or Mn.

The difference in the formation energy of BN and TiB₂ demonstrates that it is easier to form TiB₂ than BN at the eutectoid temperature. Accordingly, Ti is much more effective than N in reducing the dissolved B concentration in the matrix and neutralizing the ferrite-forming effect of B.

3.2. The Interaction of B with Mn and Cu

To investigate the interaction of B with Mn, 1.8%Mn was added to the Fe-3.58%C-2.54%Si parent alloy at different contents of B. The effects of Mn and Cu on the ferrite formation are compared in Fig. 6. It shows that there is little ferritization effect of B on the Mn-added samples, and the secondary graphite was not found on the spheroidal graphite surface, and Mn segregation at the grain boundary of the eutectic cell was confirmed with the Mn mapping in the matrix by the WDX, as shown in Fig. 7.

When 1.0%Cu was added to the same parent alloy, the ferrite fraction increased dramatically with the increase in B, as already shown in Fig. 1. Nevertheless, the ferrite fraction hardly changed in the Mn-added samples. Therefore, it could be concluded that the interaction between B and Cu is a peculiar phenomenon.

3.3. Cu Film Observation

It is estimated by many researchers that the pearlite-forming effect of Cu is due to the precipitation of a thin Cu film

Fig. 7. Mn mapping in the matrix of the spheroidal graphite cast iron by the WDX.

Fig. 8. Precipitation of thin Cu film around spheroidal graphite in the B-free sample.

Fig. 9. Mapping of Cu film around spheroidal graphite in the B-free sample by the EPMA analysis.

around the spheroidal graphite, which prevents the diffusion of carbon from the matrix to the spheroidal graphite.¹³⁾ Nevertheless, nobody except Ishiguro¹⁰⁾ could find the film. Therefore, we tried to find the film with the special etching technique, as already mentioned.

In the B-free sample, the existence of the Cu film was successfully detected as shown in the SEM image of Fig. 8. As can be seen clearly, the interface of the matrix/graphite was significantly etched, and the Cu film on the smooth spheroidal graphite surface was confirmed with the EPMA analysis, as in shown in Fig. 9. The matrix in Fig. 8 was fully pearlite and the spheroidal graphite surface was smooth. The reason why we could find the thin Cu film around the spheroidal graphite in the B-free sample is schematically demonstrated in Fig. 10. The Cu film acted as a barrier

Fig. 10. Model of Cu film confirmed around spheroidal graphite in the B-free sample.

Fig. 11. Precipitation of secondary graphite on spheroidal graphite surface.

restraining the diffusion of carbon to the spheroidal graphite surface.¹³⁾ Hence, this maintained the high carbon concentration in the matrix and prevented the formation of the secondary graphite on the surface to form the all-pearlite matrix.

The observation of the Cu film in the sample with B was also done in the same way. However, we could not find any Cu film. The precipitated D-type-like graphite (secondary graphite) on the spheroidal graphite surface and the ferrite matrix around were confirmed, as shown in Fig. 11. Meanwhile, the graphite surface was quite coarse, which was of the identical phenomenon with that in Igarashi's report.⁸⁾

In order to investigate the distribution of Cu in the matrix, a mapping and point analysis with the WDX were done near the spheroidal graphite. In the sample with B, very little Cu was detected on the spheroidal graphite surface, which indicated the absence of the Cu segregation. In this case, it was easier for the carbon to diffuse from the matrix to the spheroidal graphite surface to form the D-type-like graphite. Therefore, the matrix was ferrite and the precipitated secondary graphite was observed on the spheroidal graphite surface.

3.4. Distribution of B

If the idea that B reacts with Cu is correct, B should exist within the area of the Cu film. In order to confirm the distribution of B, a mapping analysis was done using the WDX to detect B near the spheroidal graphite in the 31 ppm-B sample (polished, not etched). B was detected near the surface area of the spheroidal graphite, and there was no Cu film, as the interaction of B with Cu destroyed the continuity of the Cu film. Therefore, it is possible for the carbon to diffuse from the matrix to the spheroidal graphite. When the carbon concentration in the matrix near the spheroidal graphite becomes low enough, the matrix will change from pearlite to ferrite.

Fig. 12. Influence of temperature on solubility limit of Cu in Fe-C-Cu ternary phase diagram.

3.5. Precipitation of Cu

For the confirmation of the Cu film formation, a ternary phase diagram of Fe-C-Cu was calculated^{3,14)} and is shown in Fig. 12. The solubility limit of Cu decreases with the temperature and the dissolved Cu is precipitated at 750°C if the iron contains 1%Cu and at 710°C for the 0.5%Cu sample, as can be estimated in the figure. It is well known that the growth of the spheroidal graphite is controlled by the diffusion of carbon through the austenite shell. If the spheroidal graphite is covered with a Cu film, the diffusion rate is significantly low, and the carbon is enriched in the austenite to form the pearlite. This is believed to be the reason why Cu promotes the pearlite formation in the spheroidal graphite iron in the eutectoid transformation.

4. Conclusions

The influence of B on the matrix, the counteraction method using N and Ti to reduce the damaging effect of B, the comparison of the interaction of B with Cu and B with Mn, the distribution of B and the segregation mechanism of Cu were investigated in this research. The following points have been established in this study.

- (1) B could increase the ferrite fraction in the matrix, coarsen the spheroidal graphite surface, and promote the formation of the secondary graphite on the spheroidal graphite iron alloyed with Cu.
- (2) The addition of N and Ti could neutralize the ferritization effect of B, while Ti is much more effective.
- (3) The ferrite-forming effect of B only exists in the spheroidal graphite iron alloyed with Cu.
- (4) The Cu film around the spheroidal graphite was successfully observed in this research using FE-SEM with a special etching method of degassed HCl aqueous solution, and is believed to act as a barrier to the carbon diffusion, maintaining the pearlite morphology in the matrix. The formation of it is the result of the solubility limit of Cu in the Fe-C-Cu ternary alloy.
- (5) In the samples alloyed with Cu, B is distributed on the spheroidal graphite surface.

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