Use of KBF₄–Al Mixed Powder to Produce Boron-Bearing 6063 Aluminum Alloys

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In this study, a simple boron addition process for producing 6063 aluminum alloy containing 0.03% B was investigated. KBF₄ (98.0 mass%) and commercial-purity aluminum powder (>99.7 mass%, particle size: 30 μm) were weighed, mixed, wrapped in aluminum foil, and placed in a phosphorizer. The phosphorizer was then immersed in a molten 6063 aluminum alloy at a temperature of 720, 760, 810, or 860°C. The boron recovery rate depends on the amount of aluminum powder in the mixture and the melt temperature. Optimizing these factors gives a 90% boron recovery rate. Excess aluminum powder in the mixture leads to an increase in the specific surface area of the KBF₄ particles and promotes the reaction, 2KBF₄ + 3Al → AlB₂ + 2KAlF₄. The AlB₂ contained within the KAlF₄ migrates into the melt as the KAlF₄ evaporates. Therefore, a mixed powder of KBF₄ and aluminum can be an effective means of adding boron to 6063 aluminum alloy if the amount of aluminum and the temperature are carefully controlled. For the present experimental conditions, it was difficult to find AlB₂ in the alloy by EPMA, because only a small amount of boron was added. Boron seems to form a solid solution with aluminum without forming coarse intermetallic compounds.

Keywords: KBF₄-aluminum mixed powder, 6063 aluminum alloys, boron, excess aluminum, evaporation

1. Introduction

The addition of boron to aluminum alloys has several purposes. One well-known purpose is the refinement of solidification structures. Boron also enhances grain refinement by titanium. Therefore, it is used to obtain aluminum alloy ingots with fine solidification structures. Boron may also be added to introduce a neutron shielding effect. One of the isotopes of boron, 10B, has a large neutron absorption cross section. Boron-bearing aluminum alloys are used as structural materials to maintain subcriticality for spent nuclear fuel storage. Boron also improves the abrasion resistance and fretting resistance of aluminum alloys. In extruded materials, the surface smoothness and glossiness are improved.

A main process for adding boron to aluminum alloys has not been established, and various methods are used. In general, commercially available Al-B master alloys or chemicals such as Potassium tetrafluoroborate (KBF₄) are often used. Master alloys are easier to handle than KBF₄ and are superior in that the desired boron contents are easier to obtain than when they are used. However, since the master alloys are expensive, the manufacturing cost of the material is higher.

The 6063 aluminum alloys are excellent materials with the required mechanical properties, corrosion resistances, and anodizing treatment characteristics for various structural materials. They also have excellent extrudability and hardness, so they are produced in large quantities as extruded materials. In general, boron is not added to 6063 aluminum alloys. However, when an aluminum sash, which requires excellent design properties, is produced through extrusion, a trace amount of boron (approximately 0.03% by mass) may be added to improve the brilliance of its surface. In the production of aluminum sashes, the development of an inexpensive and highly reliable boron addition process is desired.

In this paper, we report that a mixed powder of KBF₄ and aluminum is an effective boron additive for 6063 aluminum alloys.

2. Experimental Procedures

2.1 Use of KBF₄-Al mixed powder

In an Al-B master alloy, AlB₂ is dispersed as fine brown particles. When the master alloy is added to the melt, the AlB₂ particles migrate to and dissolve in the molten aluminum alloy, resulting in boron addition. When only KBF₄ is used as the additive, boron addition occurs via the reduction of boron by aluminum at the interface between [KBF₄] and the molten metal; the brackets indicate that the salt is in a molten state (i.e., flux).

We focused on reaction (*) between solid KBF₄ and aluminum powder, which generates AlB₂ in situ immediately after the addition of KBF₄-Al mixed powder to the molten metal. AlB₂ migrates directly into the molten metal and is dissolved.

\[ 2\text{KBF}_4 + 3\text{Al} \rightarrow \text{AlB}_2 + 2\text{KAlF}_4 \] (*)

In this respect, this boron addition reaction differs from those of the above two processes.

2.2 Boron additives

KBF₄ (98.0 mass%) and aluminum powder (>99.7 mass%, particle diameter of 30 μm) were mixed so as to obtain a predetermined mass ratio. A planetary mill (Fritsch P-6) was used for mixing. Each powder was placed along with aluminum balls (φ 20, 20) in a 500 cm³ aluminum container, which was then capped, and mixed at a rotation speed of 200 rpm for 20 min. In this paper, the mixed powder of KBF₄-Al prepared for boron addition will be referred to as the boron additive.

2.3 Process of adding boron to molten metal

A 6063 aluminum alloy with the composition shown in
Table 1 was used as the experimental material. A graphite crucible was used for the melting process, and 900 g of 6063 aluminum was utilized in each experiment. The target boron content was 0.030 mass%, and the boron addition temperature was 720, 760, 810, or 860°C. The boron additive was wrapped in aluminum foil and placed in a phosphorizer; then, it was pushed into the molten metal and kept there for 5 min. After it was confirmed that all reactants in the phosphorizer had been added, they were stirred for 10–20 s and left to stand for 30 min. Prior to casting, the molten metal was stirred gently and then cast into a cylindrical permanent mold at room temperature (25 ± 2°C). In this paper, the above operation will be referred to as boron addition. The boron concentration in the obtained alloy ingot (φ128 mm × 130 mm) was quantified using inductively coupled plasma emission spectroscopy. Note that the recovery rate of boron \( R \) (%) is defined as \( R = (c_B \times 100)/0.030 \), where \( c_B \) (mass%) is the boron content of the alloy.

3. Results

When only KBF\(_4\) was added to the molten metal at 760°C, the boron concentration was 0.0030 mass%. Meanwhile, when KBF\(_4\)-50 mass% Al mixed powder (hereinafter referred to as KBF\(_4\)-50Al; other compositions will be expressed similarly) was added under the same conditions, the boron concentration was 0.016 mass%. It was found that simply mixing aluminum powder with KBF\(_4\) enhanced the boron recovery remarkably.

Figure 1 shows the relationship between boron addition temperature and boron recovery rate. KBF\(_4\)-50Al was used as the boron additive. The boron recovery rate increased with increasing boron addition temperature and reached 80% (0.024 mass% B) at 860°C. As described above, when the boron addition temperature is increased, boron recovery increases.

Figure 2 shows the relationship between the aluminum powder content in the boron additive and the boron recovery rate. Boron addition temperature is 760°C and 810°C.

Figure 3 shows the changes in the concentrations of the other elements (see Table 1) when boron was added at 810°C. Only magnesium showed a significant concentration change due to boron addition. In this case, the concentration decreased by at least 0.1 mass%, which was lower than the standard value (0.45–0.9 mass%) for 6063 aluminum alloys. The decrease in the magnesium content is considered to be caused by oxidation when boron was added, evaporation due to the boron additive in the aluminum powder, and possibly a chemical reaction between the boron additive and the magnesium in the aluminum alloy.

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mass%)</th>
</tr>
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<tbody>
<tr>
<td>Si</td>
<td>0.52</td>
</tr>
<tr>
<td>Mg</td>
<td>0.50</td>
</tr>
<tr>
<td>Fe</td>
<td>0.18</td>
</tr>
<tr>
<td>Cu</td>
<td>0.032</td>
</tr>
<tr>
<td>Mn</td>
<td>0.031</td>
</tr>
<tr>
<td>Cr</td>
<td>0.026</td>
</tr>
<tr>
<td>Ti</td>
<td>0.012</td>
</tr>
<tr>
<td>Zn</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Fig. 1  Influence of boron addition temperature on recovery rate of boron when KBF\(_4\)-50Al is used as an additive.

Fig. 2  Relationship between the aluminum powder content in the boron additive and the boron recovery rate. Boron addition temperature is 760°C and 810°C.

Fig. 3  Concentration change caused by boron addition (810°C) of each element shown in Table 1. The broken line drawn in the figure shows the value before boron addition.
to being in molten metal, and reaction with the product, [KAIF$_4$]. In contrast, almost no changes were observed in the contents of the other elements. Comparison between Fig. 3 and Fig. 2 revealed that the concentration of each element does not depend on the aluminum powder content.

As mentioned above, increasing the aluminum powder content in the boron additive and the boron addition temperature increases the boron recovery remarkably. It can be said that using KBF$_4$-Al mixed powder is a simple and effective method to add a small amount of boron to 6063 aluminum alloys. However, attention must be paid not to lower the content of magnesium as an alloy element.

4. Discussion

4.1 Reaction behaviors of boron additives

The reaction behaviors of the boron additives will be discussed on the basis of thermogravimetric (TG)/differential thermal analysis (DTA) results. For the analysis, a simultaneous thermogravimetric analyzer (TG/DTA6300, Hitachi High-Tech Science) was used. A 10-mg sample of KBF$_4$-50Al was used for the measurement, and an equal amount of alumina was used as the reference sample. Since the purpose was to determine the actual reaction process that occurs when boron additives are introduced to the molten metal, the heating rate was 50°C/min, which is the upper limit of the analyzer. The measurement temperature range was from room temperature to 1000°C. During the analysis, argon gas (300 cm$^3$/min) was introduced into the sample chamber to prevent sample oxidation.

Figure 4 shows the TG/DTA curve of KBF$_4$-50Al, which revealed four endothermic reactions (No. 1, 3, 4, and 5) and one exothermic reaction (No. 2). According to the KF-KBF$_4$ phase diagram shown in Fig. 5, KBF$_4$ undergoes a phase transition from a low-temperature phase to a high-temperature phase at 283°C. Therefore, No. 1 is an endotherm accompanying the phase transition of KBF$_4$. Since reaction (*) has been reported to start at around 490°C, No. 2 is attributed to reaction (*). The peak shows a sharp rise at 486°C on the DTA curve, indicating that the reaction progressed in a chain. Therefore, it is assumed that reaction (*) was complete when the peak appeared. The melting point of the product, KAIF$_4$, is 580°C, according to the KF-AlF$_3$ phase diagram shown in Fig. 6. This temperature coincides with the value at which the peak of No. 3 rises. It is considered that No. 3 represents an endotherm due to the melting of KAIF$_4$. The molar masses of KBF$_4$, Al, AlB$_2$, and KAIF$_4$, which are the four species involved in reaction (*), are 125.9, 26.98, 48.60, and 142.0 g/mol, respectively. According to the law of definite proportions, the aluminum powder content required to produce AlB$_2$ is approximately 25 mass% by calculation. Therefore, after reaction (*), the aluminum powder not involved in the reaction, hereinafter referred to as the “excess aluminum powder,” remains as it is. Since the endotherm of No. 4 occurs at the melting point (660°C) of aluminum, it is attributed to the latent heat of melting of the excess aluminum powder.

According to the above, reaction (*) is complete before the temperature reaches the melting point of aluminum. The substances involved in the reaction with the melt will be AlB$_2$ and [KAIF$_4$]. No. 5 covers a wide temperature range,
which corresponds to the change in the TG curve. Since [KAlF₄] is highly volatile,¹¹) the drop in the TG curve is due to the evaporation of [KAlF₄], and No. 5 is the accompanying endotherm. KBF₄ produced in reaction (*) has a mass approximately 1.1 times that of KBF₄. According to Fig. 4, the evaporation of [KBF₄] is complete at 960°C, and the mass reduction rate was approximately 50%. This suggests that almost all KAlF₄ evaporated at 960°C.

4.2 Boron recovery rate

As mentioned in 4.1, the aluminum powder content required to produce AlB₂ in reaction (*) is approximately 25 mass%. However, Fig. 2 shows that excess aluminum powder improves boron recovery. Thus, the boron recovery rates caused by the additions of KBF₄-50Al and KBF₄-65Al were investigated.

Figure 7 shows a scanning electron microscopy (SEM) image of KBF₄-50Al. KBF₄ exists between the round aluminum particles indicated by arrows. It is understood that KBF₄ is an aggregate of fine particles similar in size to aluminum particles. A similar image was also obtained in the case of KBF₄-65Al. The densities of KBF₄ and aluminum at room temperature are 2.50 and 2.70 Mg/m³, respectively. KBF₄-50Al and KBF₄-65Al expressed in terms of volume fractions are KBF₄-48 vol%Al and KBF₄-63 vol%Al, respectively. The boron recovery rate was investigated using KBF₄ aggregate and aluminum powder cubes of the same size and mixed randomly.

The KBF₄ aggregate and aluminum powder are represented in Fig. 8 by □ and ▣, respectively. The distributions are visualized two-dimensionally, and the volume ratio is assumed to be equal to the area ratio in both cases. As shown in Fig. 8, KBF₄ is more widely distributed in KBF₄-65Al than in KBF₄-50Al. After counting the sites where □ and ▣ make contact, the specific surface area of KBF₄-65Al was found to be 1.25 times that of KBF₄-50Al. Excess aluminum powder will promote reaction (*) by increasing the specific surface area of KBF₄ and promote the fine dispersion of the reaction product.

The room-temperature densities of AlB₂ and KAlF₄ are 3.19 and 2.67 Mg/m³, respectively. Therefore, approximately 13% by volume of the reaction product is AlB₂. The melting point of AlB₂ is 1655°C and that of KAlF₄ is 580°C. According to the results in Fig. 4, both solid AlB₂ and [KAlF₄] migrate to molten metal. At this time, the amounts of excess aluminum powder remaining in KBF₄-50Al and KBF₄-65Al were 34 and 54 vol%, respectively. The powder is present between the reaction products and promotes the transfer of the reaction products to the molten metal. In addition, it enables fine dispersion in the melt.

It is not clear whether AlB₂ is separated from [KAlF₄] or is contained in [KAlF₄] when it migrates to the molten metal. However, in the former case, the boron recovery rate would not depend on the boron addition temperature, which would contradict the experimental results. In contrast, assuming the latter makes it easier to explain the phenomena shown in the results. AlB₂ will be more likely to migrate to the molten metal side via the evaporation of [KAlF₄]. Figure 1 shows that the evaporation rate of [KAlF₄] increases as the boron addition temperature increases and that AlB₂ coexisting with [KAlF₄] tends to migrate to the molten metal side accordingly. Figure 2 also suggests that excess aluminum powder promotes the fine dispersion of [KAlF₄] droplets with AlB₂ and increases the effective area for the transfer of the reaction products to the molten metal. In addition, it enables fine dispersion in the melt.

The concept of the melt cleaning effect by flux is applied, there are roughly two scenarios for the migration of AlB₂ to the molten metal side, as shown in the conceptual diagram in Fig. 9. Let σₘ/F, σₚ/F, and σₘ/P be the interfacial tensions of "molten metal/flux," "AlB₂/flux," and "molten metal/AlB₂;" respectively. If the relation¹²) σₘ/P > σₘ/F + σₚ/F holds, then the flux enters the interface between AlB₂ and the molten metal and wets AlB₂. In that case, as shown in Fig. 9(a), if the [KAlF₄] droplet surrounding AlB₂

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Fig. 7 SEM micrographs of boron additive (KBF₄-50Al), (a) low magnification and (b) high magnification.

Fig. 8 Schematic representation of mixed powder in which KBF₄ □ and aluminum powder ▣ are randomly distributed, (a) KBF₄-50Al and (b) KBF₄-65Al.
evaporates completely, only AlB₂ remains in the melt. When this relationship does not hold, as shown in Fig. 9(b), as [KAlF₄] evaporates, AlB₂ shifts gradually to the molten metal side. However, it is difficult to judge which scenario these experimental results fall under, and it is necessary to examine them separately.

4.3 Boron in 6063 aluminum alloys

Boron in a 6063 aluminum alloy was examined using an electron beam microanalyzer (EPMA-1720, Shimadzu Corporation). The acceleration voltage was 15 kV, the beam current was 0.17 \(\mu A\), and the spectroscopic crystal used for boron detection was LSA 120.

Figure 10 shows the results of the area analysis of the cast structure (0.27 mass% B). Intermetallic phases containing silicon and magnesium were clearly observed in the structure. On the other hand, it was impossible to clearly confirm the phase where boron was enriched. Using a higher magnification, fine particles (\(~5\ \mu m\)) containing titanium and magnesium were observed, and boron was often detected along with them. However, the number of particles was very low and the amount of boron consumed in their formation was probably small.

Boron tends to form intermetallic compounds with transition elements such as titanium rather than aluminum. Because of its properties, it may be added to improve the electrical conductivity of aluminum.\(^{13,14}\) In this study, we expected that coarse boron compounds could be found easily in the cast structure. However, it was difficult to confirm both such B compounds and undissolved AlB₂, etc., using the electron beam microanalyzer. Although the solubility of AlB₂ in molten metal is unknown, it is presumed based on the above that most of the AlB₂ that was transferred to the molten metal had decomposed (AlB₂ \(\rightarrow\) Al + 2B).

It has been reported that since boron forms AlB₂ in aluminum and polishes its die bearing surface, an extruded material with a smooth and shiny surface can be obtained.\(^{15,16}\) However, the above results suggest that boron is dissolved in the matrix phase. Therefore, it is necessary to investigate the mechanism of the improvement of the surface brilliance caused by a boron content of only approximately 0.03 mass%.

5. Conclusion

In this study, we investigated the addition of boron to 6063 aluminum alloys using KBF₄-Al mixed powder and formed the following conclusions.

(1) When boron is added using KBF₄, the boron recovery rate can be improved by mixing with a predetermined amount of aluminum powder beforehand.

(2) By optimizing the aluminum powder content in the boron additive and the addition temperature, the boron recovery rate can be improved remarkably. For example, adding KBF₄-65Al at 810°C will yield a boron recovery of 90%.

(3) Excess aluminum powder in the boron additive increases the specific surface area of KBF₄, thereby promoting reaction (*). In addition, since excess aluminum powder exists between the reaction products, it simultaneously allows the uniform and fine dispersion of the reaction products as they migrate to the molten metal.

(4) Refining [KAlF₄] droplets that coexist with AlB₂ and increasing the boron addition temperature promote [KAlF₄] evaporation. The evaporation of [KAlF₄] promotes the migration of AlB₂ to the molten metal, and it is considered that most of the AlB₂ that migrates to the molten metal decomposes.

(5) Using KBF₄-Al mixed powder is a simple and effective method to add a small amount of boron to 6063 aluminum alloys. However, the concentration of magnesium, which is one of the constituent elements, decreases.
Acknowledgments

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REFERENCES