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論　文

Nitridation Reaction of Aluminum and Magnesium in 5000 Series Aluminum Alloy*

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The purpose of this study is to investigate the origin of nitride inclusions, Aluminum Nitride (AlN) in the aluminum casting process. The oxidation and nitridation behaviors of aluminum and magnesium under several melting conditions were experimentally researched. The results indicated that the sequential occurrence of the oxidation and nitridation reactions during the melting process was a key factor for producing nitride inclusions. The experimental results were consistent with the thermodynamic stability according to the standard Gibbs free energies of the formation of several oxides and nitrides, AlN and Mg_3N_2 . The method of preventing the formation of the nitride inclusions was both experimentally and theoretically derived. The point is that not having Mg_3N_2 generated in the magnesium ingot melting process in the furnace is very important to prevent generating the AlN inclusions since the existence of Mg_3N_2 in the aluminum melt causes the aluminum nitridation.

Keywords: *melting process, casting process, nitride inclusion, AlN, Mg_3N_2, 5000 series aluminum alloy*

1. Introduction

Nitride inclusions are sometimes found inside of an aluminum rolled sheet. These inclusions consist of Al, N, a trace of Mg and O. The nitride inclusion, AlN, is harder than the aluminum matrix and a pin-hole defect can occur during the rolling process if the inclusion size is larger than sheet thickness. AlN is often found in Al-Mg alloys, like the 5000 series alloy, and Mg is detected close to the AlN (**Fig. 1**). Therefore, the origin of AlN seems to be related to the existence of Mg.

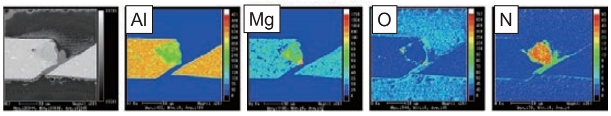

Fig. 1 EPMA image of AlN inclusions found in an Al-Mg alloy sheet.

Many studies have been carried out regarding the nitridation reaction of aluminum and magnesium. The formation of AlN by bringing N_2 gas directly into the liquid aluminum has been experimentally tested. The formation temperature of AlN, however, was reported to be 700℃[1], 720℃ - 740℃[2], 820℃[3], or 1200℃[4], thus it varies between the different experimental methods. In other words, a unified view of the AlN generation has not been obtained. Meanwhile, it was confirmed that AlN can be generated by adding Mg_3N_2 solid powder to the molten Mg-Al alloy or Al-Mg alloy[5, 6]. Moreover, Ye et al. reported that the key mechanism is as described by the following two reactions which occurred when N_2 gas is added to the molten Mg-Al alloy[7].

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$Mg_3N_2 + 2Al \rightarrow 2AlN + 3Mg$$

Thus, it has already been proved that the generation of AlN has something to do with the Mg element, but it has not been fully understood as to what happens during the aluminum melting process and how nitrogen reacts with the aluminum via magnesium.

In the practical aluminum melting process, magnesium ingot is normally added to the aluminum melt in a melting furnace or a holding furnace. The dry air in the furnaces contains 78% nitrogen, 21%

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oxygen, 0.9% argon, 0.04% carbon dioxide, and small amounts of other gases. It is postulated that Mg tends to form MgO if it reacts with the air because MgO is thermodynamically more stable than Mg_3N_2. However, there are the essential elements Al and N for producing AlN in the actual furnaces. The purpose of this study is to clarify the origin of the nitride inclusions, focusing on the magnesium melting process in the aluminum melt.

2. Experimental Procedure

2.1 Preliminary melting experiment of magnesium ingots in aluminum melt

To demonstrate the melting behavior of magnesium in a practical melting furnace, a preliminary experiment that the addition of magnesium ingots to the aluminum melt without stirring was conducted. Two small pieces of magnesium ingot (100 g) were added to the aluminum melt (3 kg), which was melted in advance in a graphite crucible at 800℃. Several stages of magnesium ingot melting process were visually observed, and the temperature was measured.

2.2 Heating experiment of magnesium and holding experiment of magnesium in aluminum melt

Separating into the burning process of magnesium and the melting process of magnesium in aluminum melt to comprehend oxidation and nitridation reactions in detail, the heating experiment of magnesium without aluminum melt was firstly conducted. Small pieces of magnesium ingot (20 g) were heated in graphite crucibles under several conditions and identified the compounds generated by the magnesium burning. These crucibles were hold at 800°C in a small scaled electric furnace. Two atmospheric conditions which were 'Air' and 'N_2 purged', and two holding times which were 1 hour and 3 hours were set up as shown in **Table 1**. The oxygen level was analyzed by gas detection tubes before inserting the magnesium ingots into the crucibles. The oxygen levels were 19.0% in the 'Air' and 2.3% in the 'N_2 purged' atmospheres. The compositions of each Mg sample after reaction were analyzed by X-ray diffraction (XRD) after the cooling.

Table 1 Heating conditions of the magnesium ingot in several atmospheres.

	Atmosphere	Oxigen level	Holding time
A1	Air	19.0%	1 hour
A2	Air	19.0%	3 hours
A3	N_2 purged	2.3%	1 hour
A4	N_2 purged	2.3%	3 hours

Table 2 Holding conditions of the pre-burned magnesium in the aluminum melt.

	Heating condition	Atmosphere	Holding time
B1	A2 (Air)	Air	1 hour
B2	A2 (Air)	Air	3 hours
B3	A4 (N_2 purged)	Air	1 hour
B4	A4 (N_2 purged)	Air	3 hours

In order to investigate what happens by adding the burned magnesium ingot to the aluminum melt, each of the was then added to the pure aluminum melt which was maintained at 800℃, and each of the liquids with the residues was stirred by a graphite stick. After stirring, these liquids were held under air at four isothermal conditions as shown in **Table 2** and quenched with a small iron mold. These cast samples were polished and observed by a scanning electron microscope (SEM) and a electron probe microanalyer (EPMA).

3. Results and Discussion

3.1 Melting of magnesium ingots in aluminum melt

Photographs of several melting stages of magnesium ingot in aluminum melt are shown in **Fig. 2**. Magnesium ingots melting sequence is as follows:

1) Small pieces of magnesium ingot were added to the aluminum melt of 800℃.
2) The magnesium pieces floated and started to dissolve on the aluminum melt surface.
3) The magnesium pieces got burned and the highest temperature measured by a thermo-couple was 1193℃.
4) Flashings like fireworks (1223℃) were observed and white smoke was emitted from the flashing fires.
5) The fire extinguished and the already-burned surface swelled up like a cauliflower, radiating a red color (840℃).
6) The grown surface changed color from red to black when the reaction ended.

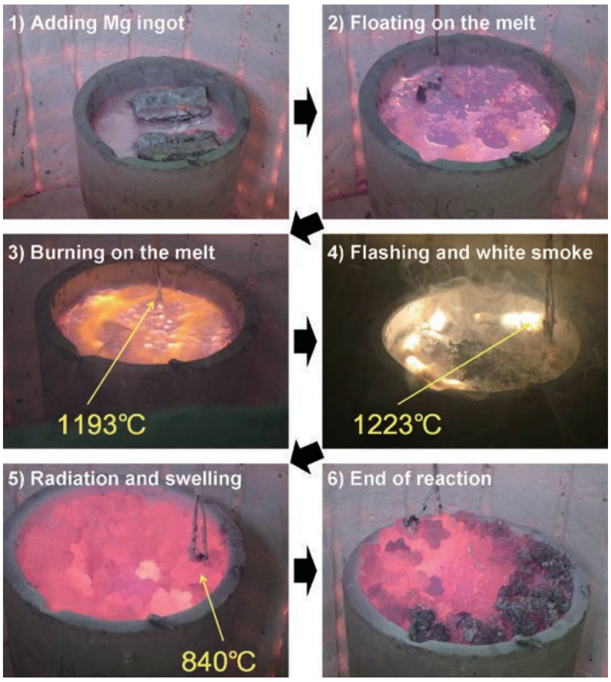


Fig. 2 Photographs of the melting stages of the magnesium ingot in the aluminum melt.

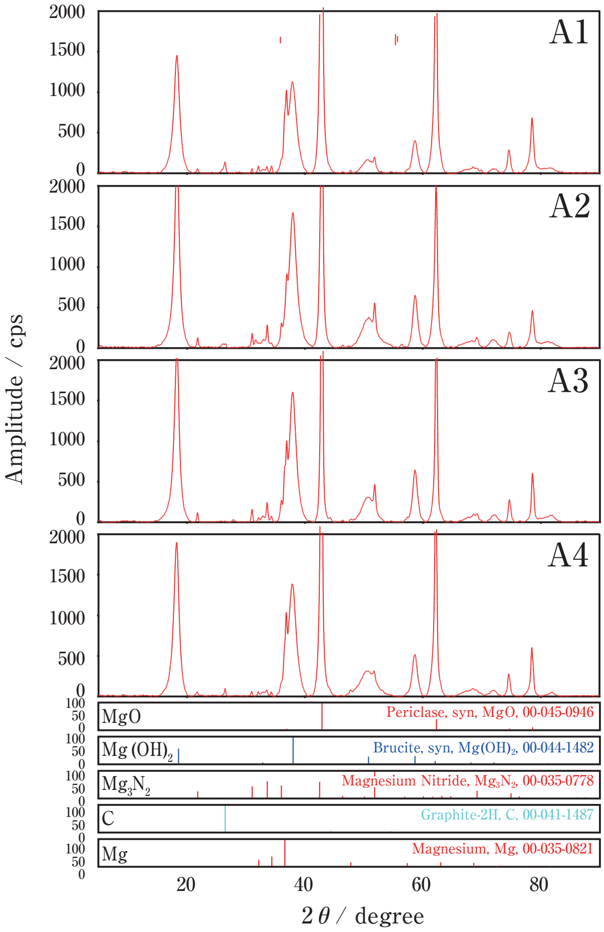


Fig. 3 X-ray analysis of the compounds generated by Mg burning under the four heating conditions (A1-A4 in Table 1).

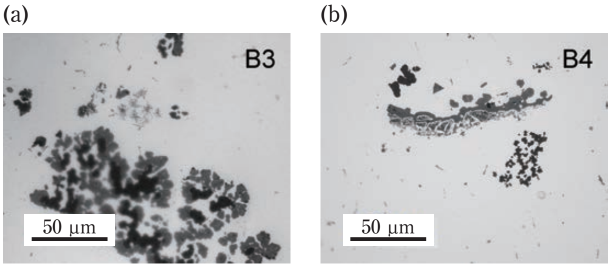


Fig. 4 SEM image of the inclusions in (a) B3 and (b) B4.

The preliminary experiment proved the following. When the magnesium ingot was added to the aluminum melt, it floated on the aluminum surface because its density is 1.65 g/cm^3 (at 650℃) and much lower than that of the liquid aluminum, i.e. 2.38 g/cm^3. The ignition point of pure magnesium is about 580°C and lower than its melting point of 650°C[8]. Thus, the magnesium ingot could burn during floating on the aluminum melt before melted. There were some high temperature spots, above 1200℃, in the furnace when the magnesium ingot was added. Therefore, it is found to be needed to consider the magnesium burning situation just after magnesium ingot adding to the aluminum melt in order to investigate the oxidation and nitridation process of magnesium in the aluminum melt thoroughly.

3.2 Compounds generated by heating magnesium

The results of the X-ray analysis of the compounds generated by magnesium burning under the four heating conditions are shown in **Fig. 3**. MgO, $Mg(OH)_2$, Mg_3N_2, Mg and graphite were detected in all four heating conditions. This result indicates that pure Mg forms nitrides even in a high O_2 atmosphere like the ʻAirʼ and it takes only one hour. Therefore, Mg_3N_2 tends to be formed when it burns while floating on the aluminum melt. The reason why $Mg(OH)_2$ was detected is thought to be that the residues were analyzed 24 hours after this experiment and H_2O in the air was postulated to combine with the MgO.

3.3 SEM/EMPA analysis of inclusions in aluminum melt after holing experiment

SEM images of the cross section of the cast samples are shown in **Fig. 4**. While a lot of characteristic inclusions were found only in B3 and B4, there were no inclusions in B1 and B2. The analyzed chemical data are shown in **Table 3**. The Mg content indicates that the residue from the 'N$_2$ purged' conditions was dissolved in the melt. When the residues were added to the melts and stirred, the residue from the 'Air' conditions was not soluble because its shell was thermodynamically stable, but the residue from the 'N$_2$ purged' conditions was soluble because its shell was easier to dissolve. It is suggested that the difference in the stability of the shells was caused by the thickness of the MgO layer. The inclusions, which were observed in B3 and B4, have black and gray areas. Especially, the inclusion in the shape of a flower observed in B3 is a good example for such an inclusion with two phases, which are quite adjacent to each other.

Table 3 Magnesium content of each sample.

	Heating condition	Mg content (mass%)
B1	A2 (Air)	<0.01
B2	A2 (Air)	<0.01
B3	A4 (N$_2$ purged)	3.5
B4	A4 (N$_2$ purged)	3.2

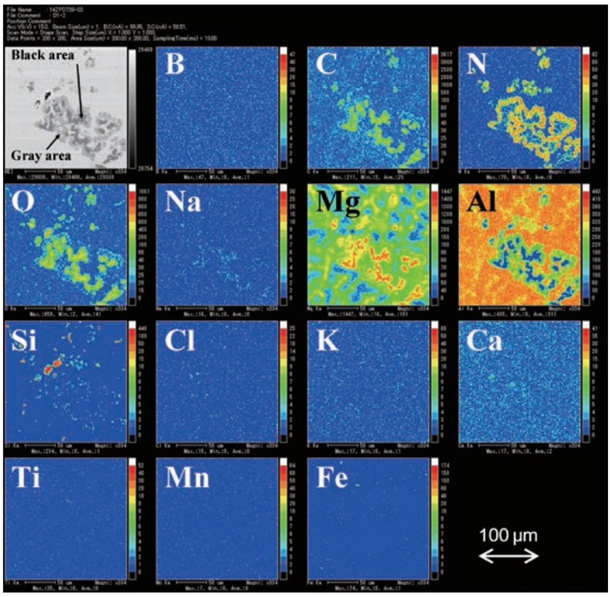


Fig. 5 EPMA analysis of the flower-shaped inclusion observed in B3.

Table 4 Chemical analysis result for each area of the inclusion (mass%).

	C	N	O	Mg	Al
Black area	3.6	—	30	66.3	0.1
Gray area	0.6	19.4	0.9	4.7	74.2

The compositions of these two black and gray areas were analyzed by EPMA. The EPMA results are shown in **Fig. 5** and **Table 4**. The stoichiometric analysis result suggested that the black area is MgO and the gray area is mainly AlN. There was barely Mg_3N_2 in the cast sample of B3.

3.4 Thermodynamic stability of various reactions

To clarify the behavior of Mg_3N_2 in the liquid aluminum, the thermodynamic stability was calculated. The standard Gibbs free energies of six reactions based on the following formulas are shown in **Fig. 6**.

$$Mg + 1/2\ O_2(g) = MgO \tag{1}$$

$$3Mg + N_2(g) = Mg_3N_2 \tag{2}$$

$$3MgO + 2Al = 3Mg + Al_2O_3 \tag{3}$$

$$1/2\ Mg_3N_2 + Al = 3/2\ Mg + AlN \tag{4}$$

$$Mg_3N_2 + 3/2\ O_2(g) = 3MgO + N_2(g) \tag{5}$$

$$2Al + N_2(g) = 2AlN \tag{6}$$

$$2AlN + 3/2\ O_2(g) = Al_2O_3 + N_2(g) \tag{7}$$

Fig. 6 suggests that the reactions (1, 2, 4, 5, 6, 7), which show negative values, are stable when going to

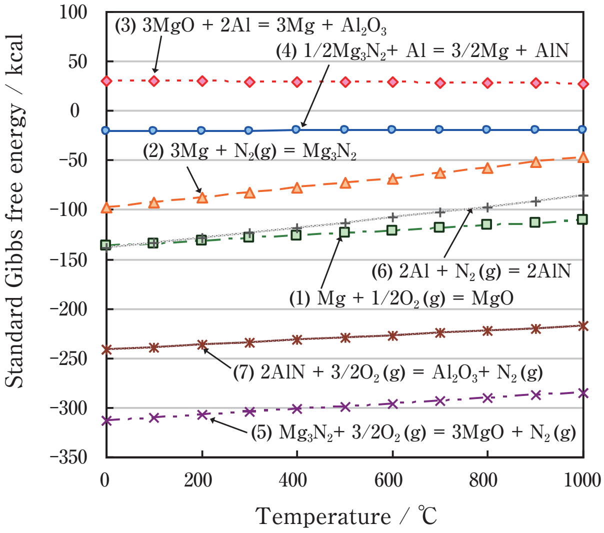


Fig. 6 Standard Gibbs free energies of six reactions between 0°C and 1000°C.

the right in each formula. On the other hand, the reaction (3), which shows positive values, is only stable by going to the left in the formula. Therefore, the following chemical reaction processes are thermodynamically derived from each formula between 0℃ and 1000℃.

(1) MgO can form by combining Mg with O_2.
(2) Mg_3N_2 can form by combining Mg with N_2.
(3) Mg is easier to be oxidized than Al, so MgO is not likely to be deoxidized by Al.
(4) Al is easier to be nitrided than Mg, so AlN and Mg can form by combining Mg_3N_2 with Al.
(5) Mg is easier to be oxidized than to be nitrided, so MgO can form by reacting Mg_3N_2 with O_2.
(6) AlN can form by combining Al with N_2.
(7) Al is easier to be oxidized than to be nitrided, so Al_2O_3 can form by reacting AlN with O_2.

The above thermodynamic theory leads the following hypothesis of generating mechanism of AlN inclusion. Magnesium tends to be more oxidized than nitrided in terms of thermodynamics, but magnesium can become Mg_3N_2 if magnesium directly contacts N_2 gas. Thus, when a magnesium ingot reacts with air at high temperatures, magnesium mostly forms MgO and some Mg_3N_2 due to the locally reduced O_2 content, which originates from reaction (1). MgO is stable in the aluminum melt and if the holding time is long enough, spinel will form, so it is not likely to be deoxidized by aluminum, but Mg_3N_2 changes to magnesium and AlN by displacing Mg with Al. It seems unlikely that N_2 in the air reacts with the aluminum melt even if they are in direct contact because an Al_2O_3 layer, which is more stable than AlN, covers the aluminum melt surface. Therefore, N intrudes into the aluminum melt via Mg_3N_2.

This hypothesis does not conflict with the experimental results that there was barely Mg_3N_2 in the cast samples and that AlN was observed adjacent to MgO in the inclusion. The generating mechanism of AlN inclusion in this experiment is illustrated in **Fig. 7**.

3.5 Condition of generating Mg_3N_2

The ternary phase diagrams of Mg-O-N and the relationship between the $P(N_2)$ and the $P(O_2)$ at atmospheric pressure are shown in **Fig. 8** in which the vertical axis and the horizontal axis represent the partial pressure of N_2 and O_2, respectively. The atmospheric pressure is represented by the red line in Fig. 8 (c), because the $P(N_2)$ and the $P(O_2)$ add up to 1 atm. For simplicity, assuming that the $P(N_2)$ and the $P(O_2)$ are 0.2 atm and 0.8 atm, respectively, the blue point indicates the actual atmospheric pressure in the phase diagram. Therefore, from 800 to 1200℃, Mg_3N_2 is not stable in terms of the thermodynamics. However, the required condition in which Mg_3N_2 stably exists at 800℃ the $P(O_2) <$ 10-39 atm and that at 1200℃ the $P(O_2) <$ 10-28 atm. This suggests that Mg_3N_2 can become more stable at high temperatures, even for a high O_2 level.

Several sparking spots with high temperatures above 1200℃ were found during the preliminary experiment (Fig. 2). It seems reasonable to suppose that Mg_3N_2 is generated when the magnesium ingots are floating on the Al melt surface and burning under atmosphere in an actual melting or holding furnace. Exposing magnesium ingots to any atmosphere in the furnace provide time to generate Mg_3N_2 which will be able to form AlN easily in aluminum melt. Therefore, emerging magnesium ingots into aluminum melt immediately after adding magnesium ingot in the furnace is suggested as a practical measure of preventing the formation of AlN inclusions.

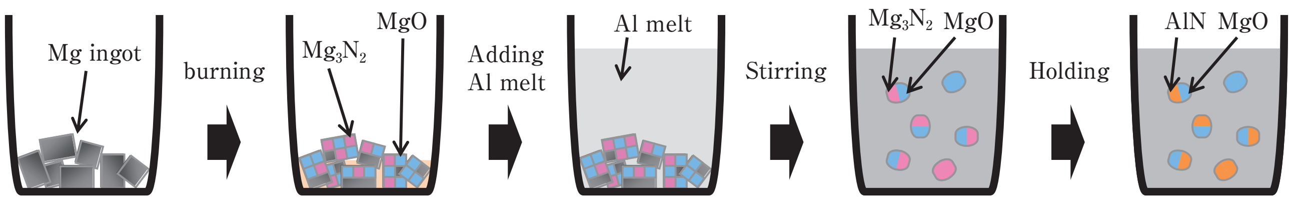
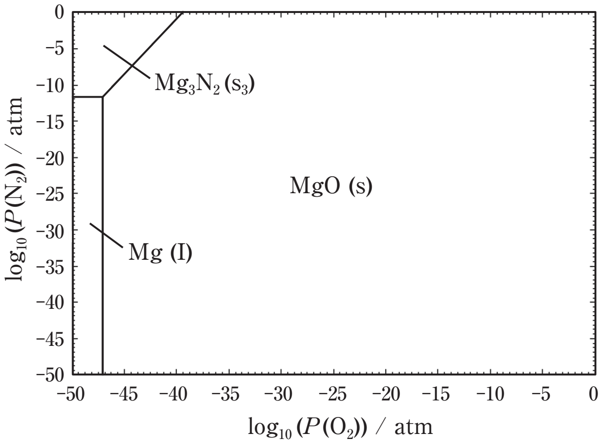
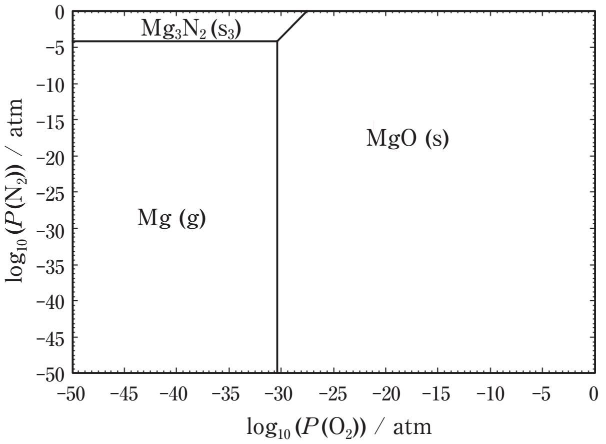


Fig. 7 The generating mechanism of the nitride inclusions in this experiment.

(a) 800˚C



(b) 1200˚C



(c) Curve at $P(O_2)+P(N_2)$ = 1 atm

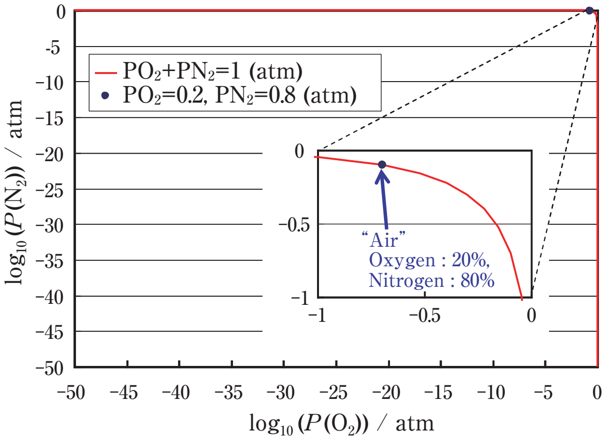


Fig. 8 Ternary diagrams of Mg-O-N at (a) 800°C, (b) 1200°C and (c) the relationship between the $P(N_2)$ and the $P(O_2)$ in the atmospheric pressure.

4. Conclusions

The following generating mechanism of nitride inclusion, AlN, during the actual melting process can be concluded from the experimental results and the thermodynamic theory about magnesium ingot burning in the atmosphere and melting in the aluminum melt as illustrated in **Fig. 9**:

1. The magnesium ingot forms MgO by oxidation when it is burned because magnesium ignition point is lower than its melting point.
2. The magnesium can also form Mg_3N_2 in the locally low O_2 atmosphere at high temperature when the magnesium ingot is burned.
3. The inclusions, which contain MgO and/or Mg_3N_2, be formed on the surface of the aluminum melt.
4. When this inclusion enters the aluminum melt, Al displaces Mg in Mg_3N_2 and AlN forms.
5. The inclusions, which contain MgO and/or AlN, form in the aluminum melt.

The point is that not having Mg_3N_2 generated in the magnesium ingot melting process in the furnace is very important to prevent generating the AlN inclusions since the existence of Mg_3N_2 in aluminum melt is a key factor of causing aluminum nitridation.

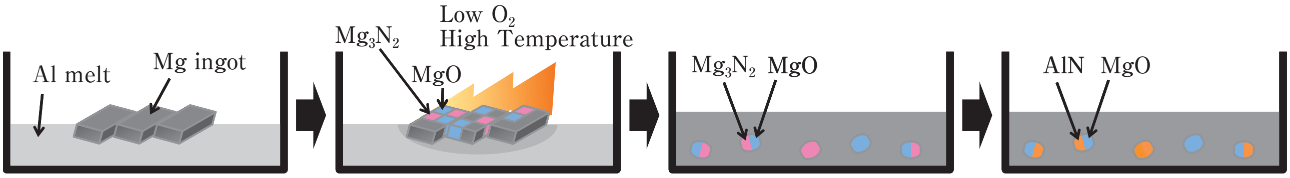


Fig. 9 The generating mechanism of the nitride inclusions in the actual melting process.

References

1) Briegleb F, Geuther A (1862) Ueber das Stickstoffmagnesium und die Affinitäten des Stickgases zu Metallen. Liebigs Ann. **123**, 228-241
2) Fichter F, Spengel A (1913) Die Reaktionen des Aluminiumnitrids. Z. anorg. u. allgem. Chem. **82**, 192-203
3) Wolf J (1913) Zur Darstellung von Aluminiumnitrid aus den Elementen. Z. anorg. u. allgem. Chem. **83**, 159-162
4) Zheng Q, Reddy RG, Wu B (2000) In-situ processing of AlN-Al alloy composites. State Art Cast Met Matrix Compos Next Millennium, 1-12
5) Ye HZ, Liu XY, Luan B (2004) In situ synthesis of AlN particles in Mg–Al alloy by Mg_3N_2 addition. Mater Lett **58**, 2361-2364
6) Kobayashi M, Okayama N, Choh T (1997) Synthesis of AIN/AI Alloy Composites by in situ Reaction between Mg_3N_2 and Aluminum. Mater Trans JIM (Jpn Inst Met) **38**, 260-265
7) Ye HZ, Liu XY, Luan B (2005) In situ synthesis of AlN in Mg-Al alloys by liquid nitridation. J Mater Process Technol **166**, 79-85

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