

## **Influence of Magnesium on Formation and Growth of Nitride Layer on Aluminum Substrate**

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The aluminum nitride layer is formed on pure aluminum and aluminum alloy (Al-Mg) substrates by the nitriding process using magnesium and alumina powders. This nitriding process, barrel nitriding, has been developed by authors. The influence of magnesium on formation and growth of aluminum nitride on the aluminum substrate is examined by the barrel nitriding. The size and the kind of the magnesium powder influence the growth of the aluminum nitride layer, and the microstructure also influences the formation and the growth of the aluminum nitride layer. When the Mg and Al-50mass%Mg powders are used as activation, the high thick aluminum nitride layer is formed on the pure aluminum substrate. The melting point and the exothermic reaction of activation powders influence the growth of the aluminum nitride on the aluminum substrate. In the aluminum alloy which includes magnesium, the high thick nitride layer is formed for the short time. The formation and the growth of the aluminum nitride also influence microstructure as a grain boundary.

**Keywords:** *Aluminum, Aluminum nitride, Magnesium, Surface modification, nitriding*

### **1. Introduction**

Aluminum alloys are one of the most promising materials for sliding parts in automotive power trains. However, the tribological properties of the aluminum alloys are poorer than that of the steels used for the machine parts. Therefore, the properties of the aluminum surfaces need improvement in order to use it in the sliding parts [1]. A novel aluminum nitriding process is developed by authors [2-4]. A nitride layer can be formed on the aluminum surfaces in a barrel where the aluminum surface is activated with the movement of alumina powders physically and the reduction by magnesium (Mg) powders chemically. This nitriding process can obtain the aluminum nitride layers with the high thickness on the aluminum surfaces. A barrel processing is applied to the aluminum nitriding, so we call this method a barrel nitriding. Alumina powders and various Mg powders, Al-50mass%Mg, Mg powders and Mg chips, with aluminum substrates are inserted into the barrel furnace. The aluminum substrates are heated and are nitrided during oscillating movement of the barrel furnace. The aluminum nitride layer with thickness of several hundred micrometers can be obtained on the aluminum substrate using our proposed process. We examined the influence of magnesium on the formation and the growth of the aluminum nitride on the aluminum substrate using the barrel nitriding process in this article. Furthermore, we also examined the influence of the nitride growth on microstructure of the aluminum sample.

### **2. Experimental Procedures**

Barrel which is usually used for plating or abrader was applied for aluminum nitriding. Aluminum oxide powders ( $Al_2O_3$ ) with average diameter  $100\mu m$  were used as the filling powders. The aluminum oxide powders polished the aluminum surface, and the aluminum oxide layer on the aluminum surface was removed. Magnesium (Mg) powder was also inserted into the barrel as the filling powders. Each Mg powder used is shown in Table 1. Mg powders chemically remove the

oxide layer on the aluminum substrate, and the traces of oxide in the furnace are also removed by Mg powders. The furnace temperature was adjusted with a temperature control unit. After the nitrogen gas was introduced into the barrel, the specimen was heated to 600°C and was nitrided during oscillating movements of the barrel. Flow rate of nitrogen was 1500cc/min. A schematic diagram of the barrel nitriding apparatus is shown in Fig. 1[2].

Table 1 Each Mg powder used as the filling powders.

Material	Al-50mass%Mg	Mg	Mg
Shape	Powder	Powder	Chip
Size	Average diameter 200 $\mu$ m	Average diameter 180 $\mu$ m	Thickness=250 $\mu$ m Width=1mm, Length=several millimeters
Pure		99.5%	99.9%

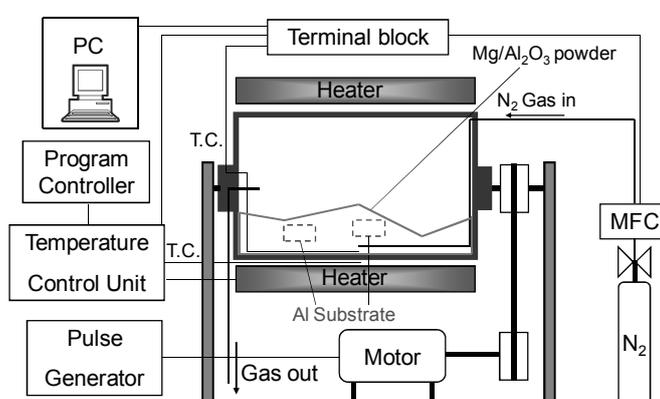


Fig. 1 A schematic diagram of the barrel nitriding apparatus.

Nitrogen gas ( $N_2$ ) was introduced into the barrel and the  $N_2$  flow rate was adjusted with a mass flow controller. The furnace temperature was adjusted with a temperature control unit. After  $N_2$  was introduced into the barrel, the specimen was heated and nitrided during oscillating movements of the barrel. At the end of treatment, the introduction of  $N_2$  and the oscillating movement of the barrel were stopped and the barrel was cooled to room temperature.

Pure aluminums (JIS-A1050) and aluminum alloys (JIS-A5083, JIS-A5056) were used in this study. The samples were ground using 500 to 2400 grit SiC papers, and were polished using 0.5 $\mu$ m  $Al_2O_3$  slurry before the barrel nitriding. The polished samples were ultrasonically cleaned in acetone.

### 3. Results and Discussion

#### 3.1 Formation of Aluminum Nitride on Aluminum Substrate by Barrel Nitriding

Aluminum nitride layers were formed by the barrel nitriding on the pure aluminum surfaces. Al-50mass%Mg and Mg powders, and Mg chips were used as filling powders. Figure 2 shows optical micrographs of the cross section. The AlN layer with high thickness was formed using the Al-50mass%Mg and Mg powders. No crack and delamination in the formed AlN layer can be found, and the AlN layer formed by barrel nitriding was achieving good adhesion.

Figure 3 shows the relation between the thickness of AlN layer and the ratio of Mg and Al<sub>2</sub>O<sub>3</sub> powders. When the Al-50mass%Mg and Mg powders were used, the thickness of the aluminum nitride layers increases with the increase of the Mg/Al<sub>2</sub>O<sub>3</sub> ratio. The thickness of the AlN layer shows a sharp increase when Al-50mass% Mg was used as activation powders.

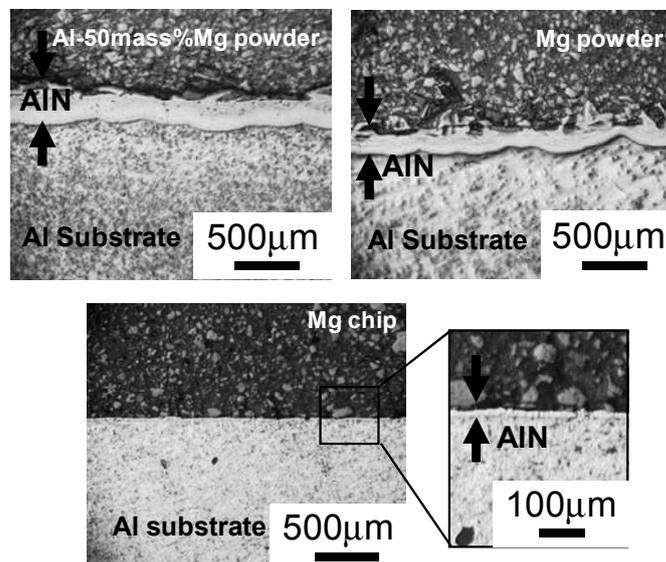


Fig. 2 Cross section micrographs after the barrel nitriding.

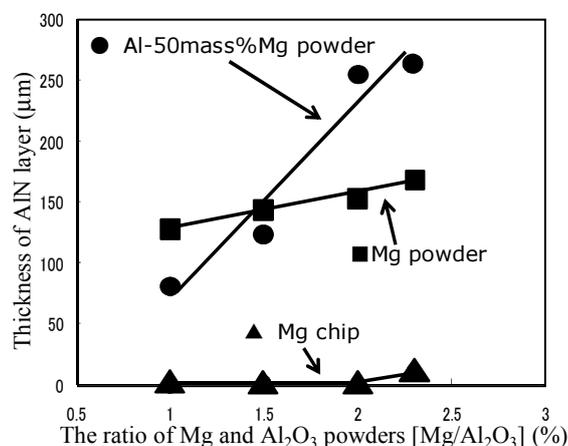


Fig. 3 The relation between thickness layer of AlN and ratio of Mg and Al<sub>2</sub>O<sub>3</sub> powders.

The thermal analysis of Al-50mass%Mg and Mg powders using DTA was performed to identify the melting points. Figure 4 shows the thermal analysis results of Al-50mass%Mg and Mg powder. The melting points of Al-50mass%Mg and Mg powders was 460°C and 650°C, respectively. The Al-50mass%Mg powders are fully melting during the nitriding. Ikeda revealed that the nitride layer was formed after Mg elements diffused in the aluminum surface. When Mg elements was not contain in the surface, the aluminum nitride layer in the aluminum surface was not formed [1]. The molten Al-50mass%Mg powders adhere to the aluminum surface, and the magnesium diffusion is accelerated. The molten Al-Mg adhered to the aluminum surface easily absorb the nitrogen. Therefore, the high thick aluminum nitride layer is formed when the Al-50mass%Mg powder is used.

The temperature change of each Mg powder was also examined. Figure 5 shows the temperature change of Mg powders and Mg chip. Al-50mass% Mg powders cause to exothermic reaction after the

melting. The thickness of the AlN layer formed using Al-50mass%Mg powders shows a sharp increase. The exact reasons for the tendency are not clear, but the difference of the melting point of Al-50mass%Mg and Mg powders and the exothermic reaction which Al-50mass%Mg causes greatly influences the growth of the aluminum nitride layer. Nevertheless to draw a certain conclusion, further investigations are required in the future.

When Mg chip was used, the growth of the aluminum nitride layer was sluggish. The each powder size and chip size is shown in Table 1, and the size of the Al<sub>2</sub>O<sub>3</sub> powders is average diameter 100μm. The barrel furnace was made using an acrylic board to be confirmed by direct visualization of the movements of the powders, the chips and the aluminum substrates during the nitriding. Figure 6 shows the results of the visualization. The aluminum substrate was constantly located on the top layer in the Al<sub>2</sub>O<sub>3</sub> powders. Mg powders (Al-50mass%Mg, Mg powders) and Al<sub>2</sub>O<sub>3</sub> powders mix freely with each other because there isn't so much of a difference between the size of Mg powders and Al<sub>2</sub>O<sub>3</sub> powders. The Al<sub>2</sub>O<sub>3</sub> powders polish the aluminum surface, and the aluminum oxide layer on the surface is removed. Mg powders chemically remove the aluminum oxide layer on the surface. Therefore, the aluminum substrate mechanically and chemically gets active, and the high thick aluminum nitride layer is formed on the aluminum substrate. On the other hand, the Mg chips were constantly located on the top layer in the Al<sub>2</sub>O<sub>3</sub> powders. The aluminum substrate has little contact with the Mg chips. The Mg diffusion layer at the aluminum surface was poorly formed, so the growth of the aluminum nitride layer was sluggish.

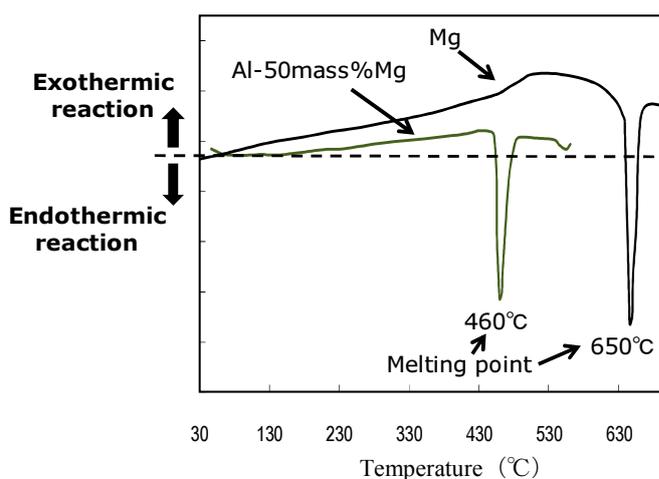


Fig. 4 The thermal analysis results of Al-50mass%Mg and Mg powders.

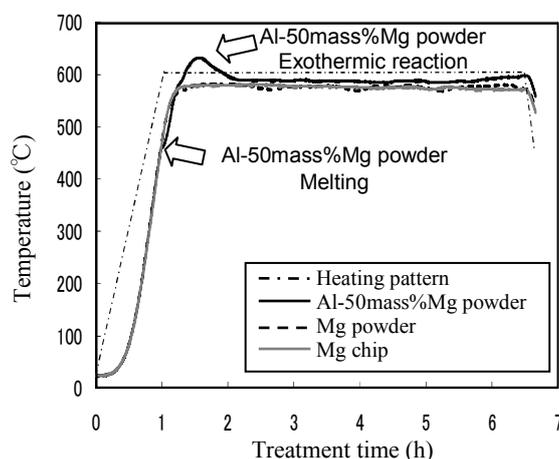


Fig. 5 The temperature change of Mg powders and chip.

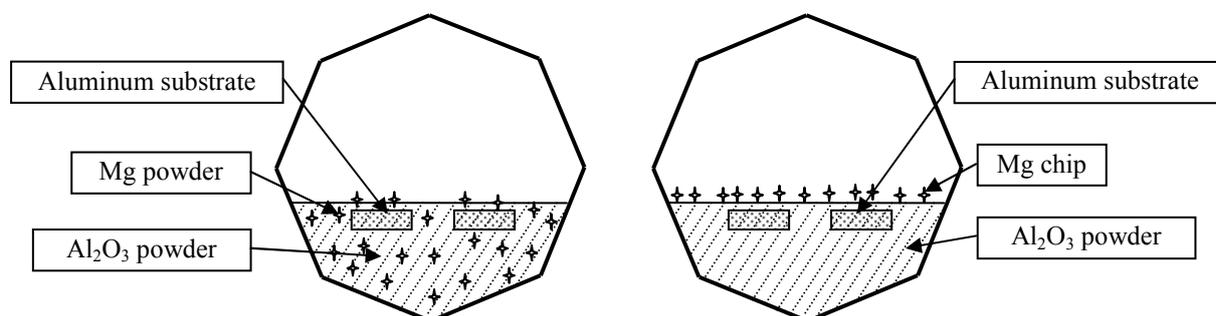


Fig. 6 The movement of the Mg powders, the Mg chips and the aluminum substrate in the barrel furnace.

### 3.2 Influence of Microstructure on Aluminum Nitride Growth

Nitriding was performed at 590 °C for 5 h in Al-Mg alloys (JIS-A5056, JIS-A5083). The Al-50mass%Mg was used as the activation powders. Cross-section optical micrographs of the barrel nitrided substrates are shown in Fig. 6, and the microstructure of the substrate is shown at the lower left. In pure Al as shown in Fig. 3 and 4, the nitride layer thickness is 250 μm and it is uniformity, whereas in Al-Mg alloy it is 750 μm. The growth of the nitride layer is promoted by Mg. Moreover, we found that the growth of the aluminum nitride is susceptible to microstructures of the substrate. A5056 and A5083 substrate has granular texture and fibrous texture, respectively. The aluminum nitride formed in A5056 and A5083 appear granular and fibrous. A grain boundary influences the formation and growth of the aluminum nitride and might grow up fast in a grain boundary.

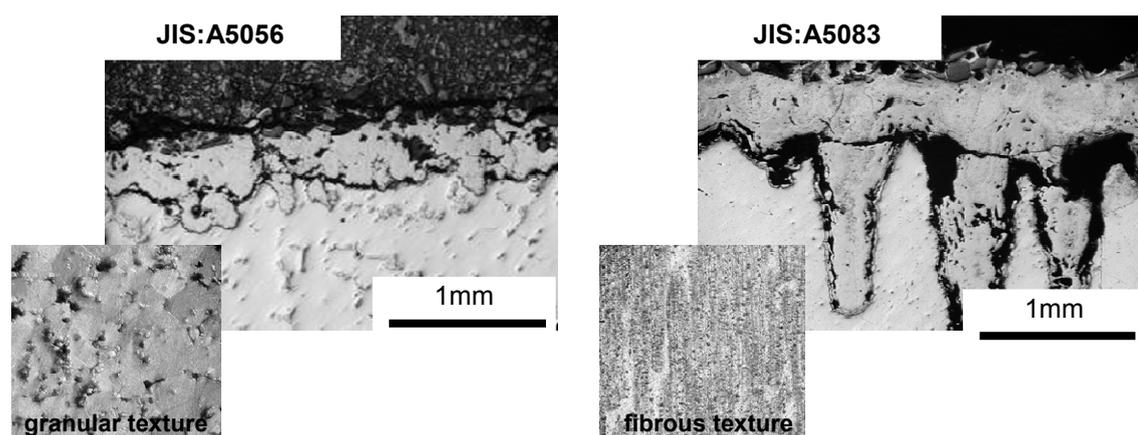


Fig. 6 Cross section micrographs after the barrel nitriding.

## 4. Summary

The influence of magnesium on formation and growth of nitride layer on aluminum substrate were investigated using barrel nitriding.

1. When the Mg and Al-50mass%Mg were used as activation powders, the high thick aluminum nitride layer was formed on the pure aluminum substrate. When the Mg chips were used, the thickness of the aluminum nitride layer was thin, and the top surface showed good conditions.

2. The thickness of the aluminum nitride layer formed using the Al-50mass%Mg powders shows a sharp increase. This might be because the melting point and the exothermic reaction of Al-50mass%Mg.
3. The growth of the nitride layer is promoted by Mg elements. The formation and the growth of the aluminum nitride also influence microstructure as a grain boundary.

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