Plasma Nitriding of Cold-pressed and BMA-forged Al Compacts

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SYNOPSIS

Aluminum powder compacts were successfully plasma-nitrided under nitrogen-hydrogen mixture gas for various holding temperatures from 723 K to 823 K for 36 ks (10 h) to 144 ks (40 h). Two kinds of specimens were prepared for pure aluminum and Al-1 mass% Ti alloy: the cold-pressed aluminum powder compact, and the refined aluminum powder compact via Bulk Mechanical Alloying (BMA). Before nitriding, the samples were sputtered to in situ eliminate surface oxide film by nitrogen plasma for varying the holding time from 0 s to 15 ks (5 h). Glancing angle X-ray Diffraction (GIXD) at 1° incident angle and X-ray Photoelectron Spectroscope (XPS) were used for qualitative analysis of the nitrided surface. Aluminum nitride (AIN) was formed with the thickness up to 15 μm. The refined microstructure by BMA enhanced the formation of AIN by increasing the fraction of high diffusion paths through the grain boundary. Degradation of AIN film adjacent to surface can be caused by its reaction with moisture. Detachment of AIN layer was partially observed in several samples. Detachment of nitrided layer might be introduced by the residual thermal stress in AIN layer during cooling down from the nitriding temperature.

KEY WORDS

plasma nitriding, aluminum alloys, cold pressing, bulk mechanical alloying, aluminum nitride

1 Introduction

Aluminum alloy is widely utilized in industries because of its intrinsic properties: high specific strength, high corrosion resistance and high thermal conductivity. In particular, aluminum alloys are applied to various automotive parts such as piston and housing in order to reduce total vehicle weight and energy consumption. On the other hand, aluminum alloys still have disadvantageous feature: low hardness and wear resistance\textsuperscript{5}. In addition to increase of the surface hardness of aluminum alloys, formation of hard aluminum nitride (AIN) layer is also preferable to improve their wear resistance\textsuperscript{5}, since AIN is a ceramic material with high hardness of 1400 Hv.

AIN cannot be formed by the conventional gas nitriding because natural surface oxide film (Al\textsubscript{2}O\textsubscript{3}) acts as an obstacle to nitrogen diffusion. The fresh surface of aluminum cannot react with nitrogen unless the oxide film is eliminated\textsuperscript{1,4}. Many researches were done on the formation of AlN layer by different methods. For aluminum alloy powders, addition of magnesium has succeeded in reduction of the surface oxide film and fabrication of AlN film up to maximum thickness of 1 μm\textsuperscript{5}. Amorphous AIN powders can be prepared by ball milling in N\textsubscript{2} atmosphere\textsuperscript{6}. Plasma nitriding with sputtering was used to fabricate AlN layer, where the bias voltage was applied to specimens that act as a cathode to generate plasma. In this process, Al\textsubscript{2}O\textsubscript{3} was eliminated by sputtering prior to nitriding. Normally argon plasma was employed for sputtering. The sputtering rate of aluminum is approximately the same as Al\textsubscript{2}O\textsubscript{3} by argon plasma; consequently, surface damage easily occurs after all of Al\textsubscript{2}O\textsubscript{3} was sputtered\textsuperscript{6}.

The refined microstructure of aluminum that contain large fraction of grain boundary, might increase the diffusion rate of nitrogen in aluminum matrix. The refined microstructure can be prepared via Bulk Mechanical Alloying (BMA). During BMA, large amount of plastic deformation was transferred to powder, resulting in elongation and fracture of particles\textsuperscript{7}. In this experiment the BMA process was employed to fabricate the refined microstructure of aluminum and Al-1 mass% Ti alloy to be compared with the conventional cold-pressed samples. Titanium was added to the alloys because it has high affinity to nitrogen, and should accelerate the formation of AlN. All samples were plasma nitrided for several hours to understand the formation mechanism of AlN layer and effect of refined microstructure via BMA.
2 Experimental procedure

2.1 Sample preparation and powder compaction

Pure aluminum powder with the purity of 99.9% and the mean size of 30 μm, was used as starting materials for this experiment. Two kinds of powder compact samples were prepared by cold pressing and BMA. In particular, BMA process was employed to reduce the size of powder and to homogeneously mix and refine titanium in Al-Ti alloy due to large amount of plastic deformation. Cyclic loading was applied to sample powder compact in the inert atmosphere (Ar gas) by repeated compression and extrusion modes in the closed die. One processing cycle of BMA consists of two compressions and one extrusion. The whole processing procedure was listed Table 1. The powder was pressed under 870 MPa for 120 s (2 min) to yield a cold-pressed sample. BMA sample was produced by applying the cyclic loading 1000 times and forging under 830 MPa with preheating at 723 K for 180 s (3 min). These samples were polished by the diamond paste with the size of 1 μm. For Al-1 mass% Ti alloys, Ti powder which has the mean size of 40 μm with purity of 99.7% was mixed with aluminum powder before being cold-pressed or BMA.

2.2 Plasma nitriding and analysis

Plasma nitriding has been carried out by using the dc plasma nitriding technique under nitrogen and hydrogen mixture with the total pressure of 533.3 Pa (4 torr). Sputtering process aiming for surface cleaning prior to nitriding, was carried out by 133.3 Pa (1 torr) in nitrogen. The base pressure in chamber before nitriding was reduced from 13.33 Pa (10⁻¹ torr) to 0.1333 Pa (10⁻³ torr) when nitriding at lower temperature. During plasma nitriding, the nitriding chamber was evacuated by rotary and mechanical booster pumps to preserve constant pressure.

Specimens were heated up simultaneously by both the heater and the glow discharge. Temperature of specimens was monitored and controlled by the thermocouple, which was inserted in a dummy specimen and placed adjacent to nitriding specimens. The nitriding apparatus was illustrated in Fig. 1. Al-1 mass% Ti samples were plasma nitrided at 823 K (500 °C) for 144 ks (40 h) without sputtering. Pure aluminum samples were plasma nitrided at 773 and 823 K (450 and 500 °C) for 72 ks (20 h) with various sputtering time. The applied bias voltage used in plasma nitriding, is 200 V and the electric current was fixed around 0.2 A. All of nitriding conditions were listed in Table 2.

![Fig. 1 Schematic view of nitriding apparatus.](image)

Table 1 Experimental procedure via BMA process to yield BMA samples.

<table>
<thead>
<tr>
<th>Process and details</th>
<th>Figures and details</th>
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<tbody>
<tr>
<td>Powder</td>
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<tr>
<td>BMA</td>
<td>![BMA Figure]</td>
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<td>Preformed Al</td>
<td>![Preformed Al Figure]</td>
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<td>Cut to sample</td>
<td>![Cut to Sample Figure]</td>
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Table 2 Nitriding conditions in this experiment.

<table>
<thead>
<tr>
<th>No</th>
<th>Materials</th>
<th>Fabrication method</th>
<th>Sputtering condition</th>
<th>Nitriding condition</th>
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<tr>
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<td>72 ks, 723 K</td>
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<tr>
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<td>7</td>
<td>Al-1 mass% Ti</td>
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The nitrided samples were characterized by Glancing angle Incident X-ray Diffraction (GIXD) at 1° incident angle and X-ray Photoelectron Spectroscope (XPS). The cross-sectional and surface microstructures were observed by optical microstructure and Scanning electron Microscope (SEM).

3 Results and discussion
3.1 Formation of AlN and effect of sputtering parameters

The color of sample surface after nitriding changes from metallic aluminum phase to dark gray or shiny black color, depending on the thickness of formed AlN layer. The shiny black color is typical to the hexagonal AlN (JCPDS no. 25-1133). Outside view of the samples before and after nitriding were shown in Fig. 2.

The surface microstructure of the cold-pressed aluminum compact after nitriding was shown in Fig. 3 (a). The entire surface of the cold compacted sample was not homogeneously covered by AlN. The dark area is a flat surface covered with AlN, while the white area is a cleavage area, which is still covered with Al₂O₃ and no AlN was formed. In this experiment, the cold-pressed samples were nitrided without surface polishing. There cleavage areas are corresponding to the valleys between powders particles after compaction. This cleavage area is difficult to make effective sputtering in the similar way to the flat surface. In this cleavage area, the sputtered atom redeposits on the surface again with large fraction, as illustrated in Fig. 3 (b) in Ref. (8). Therefore, all of Al₂O₃ cannot be eliminated from the surface of cleavage area. AlN is not possible to form on the surface of cleavage areas since Al₂O₃ still covers these areas.

The GIXD profiles of the cold-pressed aluminum samples after nitriding for 72 ks (20 h) with 3.6 ks (1 h), 10.8 ks (3 h) and 18 ks (5 h) sputtering, were shown in Fig. 4. AlN can be formed on the surface of all nitrided samples since AlN peaks can be detected. In case of longer sputtering time, the relative intensity of AlN peaks remarkably increased; this implies that volume fraction of AlN is enhanced with prolongation of sputtering time. Sputtering is a time dependent process in the present study; therefore, the longer sputtering time, the larger amount of Al₂O₃ was eliminated and the larger amount of AlN can be formed. Then, the sputtering process plays an essential role on elimination of Al₂O₃. It is the most important key

Fig. 2  Aluminum sample: (a) cold pressed and (b) 1000-cycle BMA.

Fig. 3  Surface microstructure of the cold-pressed aluminum sample after nitriding (a) uncovered valley among AlN-covering area and (b) schematic view to illustrate the ineffective sputtering area.
on AlN formation by plasma nitriding. In order to increase the sputtering yield, there are many candidate methods. For example, the argon-plasma sputtering might be one way but it can easily cause surface damage. Increasing bias voltage may need the extremely low pressure $1.33 \times 10^{-3}$ Pa ($1 \times 10^{-5}$ torr) to prevent arc plasma. Reducing residual oxygen in nitriding chamber reduces the possibility of redeposit Al$_2$O$_3$. However, the possibility to adapt the apparatus in laboratory scale to the real industrials must be concerned. In this experiment, we achieve the effective sputtering by reducing the base pressure before sputtering from 13.33 Pa (0.1 torr) to 0.1333 Pa (0.001 torr), by adding another mechanical booster pump to the nitriding apparatus. GIXD profile in Fig. 5 showed the different results of different base pressure before nitriding. It can be clearly seen that when reducing the base pressure, the larger volume fraction of AlN can be achieved. The cross-sectional microstructures of cold-pressed samples with different base pressure (13.33 and 0.1333 Pa) were shown in Fig. 6 when nitriding with base pressure of 13.33 Pa, AlN layer is too thin to be observed. On the other hand, AlN layer with thickness up to 3 µm can be observed after reducing the base pressure to 0.1333 Pa. These cross-sectional microstructures correspond well with the GIXD profiles in Fig. 6, and confirm that the reducing base pressure before nitriding can achieve the thicker AlN layer due to the effective elimination of Al$_2$O$_3$.

### 3.2 Effect of PM routes on AlN formation

The powder particle size of aluminum and titanium before and after BMA was listed in Table 3. The powder size was reduced from 30–40 µm to 15 µm by BMA. The

<table>
<thead>
<tr>
<th>Materials</th>
<th>Powder size (µm)</th>
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<tr>
<td></td>
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<tr>
<td>Al</td>
<td>30</td>
</tr>
<tr>
<td>Ti</td>
<td>40</td>
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</table>

Fig. 6 Cross-sectional microstructure of nitrided cold-pressed aluminum samples with base pressure $10^1$ torr (a) $10^4$ torr (b).
plastic deformation during BMA was transferred to materials, resulting in elongation and fracture of powder particles. In this step, the refining of deformed powder takes place together with agglomeration of refined powder in the die during BMA. Although the particle size of agglomerated powder is still large for BMA powders, its crystal size could be refined to have sufficiently amount of grain boundary to enhance the nitrogen diffusion.

Fig. 7 showed the cross-sectional microstructure of pure aluminum sample after nitriding. AlN layer was formed with thickness around 3 µm on the surface of cold-pressed sample. The AlN layer on the BMA sample with the refined microstructure can be observed to have thickness up to 15 µm. The refined microstructure via BMA increases the fraction of grain boundary, leading to enhancement of nitrogen diffusion. Due to high diffusion rate of nitrogen in the refined microstructure, AlN formation is assisted.

The BMA sample was surface polished by 1 µm diamond paste. The sputtering on BMA sample surface might be more effective than cold-pressed sample. The AlN layer formed on BMA sample might be more homogeneous than AlN formed on cold-pressed sample. This enhancement of AlN formation cannot be performed by surface morphology change. The formation of AlN can be confirmed by GIXD at 1° incident angle as shown in Fig. 8. The AlN peaks can be detected coexisting with aluminum peaks. The relative intensity of AlN of BMA sample is much higher than that for the cold-pressed sample. This is just corresponding to thicker AlN layer of BMA sample in the cross-sectional microstructure. The explanation of coexistence of aluminum peaks is that the AlN layer is thinner than the depth penetration of X-ray, which is around 5 µm by calculation. Another reason is that the AlN layer does not cover the entire surface because of ineffective sputtering area such as cleavage area on the surface of cold-pressed sample or the detachment of AlN layer on BMA sample during cooling down period, this point will be explained in the later section.

In case of Al-1 mass% Ti alloys, the cross-sectional microstructure of nitrided sample was shown in Fig. 9. The AlN layer was successfully fabricated with the thickness up to 3 µm in BMA sample. There is no observation of AlN layer on the cold-pressed surface. The GIXD profiles confirm the formation of AlN on Al-Ti surface as shown in Fig. 10. The higher relative intensity of AlN in BMA sample assures the larger volume fraction of AlN which corresponds well with the large thickness of AlN layer observed in cross-sectional microstructure. Titanium that added to aluminum matrix was also nitrided to TiN because of its high affinity to nitrogen. TiN peaks can be detected in GIXD profiles with those of AlN and Al.

Both aluminum and Al-1 mass% Ti samples show that the refined microstructure by BMA process activates the formation of AlN on aluminum surface by plasma nitriding.
AlN layer formed on the surface of BMA sample is remarkably thicker than AlN layer on the cold-pressed sample in both pure aluminum and Al-1 mass% Ti alloy. The thicker AlN layer achieved in the refined microstructure sample should be because the refined microstructure contains higher fraction of grain boundary that act as high diffusion path. This implies that the diffusion rate of nitrogen along grain boundary or powder surface is higher than the inner grain area.

3.3 Degradation and detachment of AlN

In order to evaluate the stability of AlN, the nitrided samples were left in air for several weeks. After this exposure testing, they were analyzed again by XPS. As shown in Fig. 11, the binding energy of Al2p at the surface corresponds to 75.6 eV of Al2O3, and 73.4 eV of Al(OH)3, respectively. AlN at the adjacent to the surface was degraded to Al2O3 or Al(OH)3 by the reaction between AlN and moisture in air. These degradation reactions were described by Eq. 1 and Eq. 2. The difference in reaction by Eq. 1 or Eq. 2 originates from the reaction temperature.

\[
\begin{align*}
\text{AIN} + \text{H}_2\text{O} & \rightarrow \text{Al}_2\text{O}_3 + \text{NH}_3 \\
\text{AIN} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + \text{NH}_3
\end{align*}
\]

The sample that was baked at 373 K (100°C) in air before analyzed by XPS, is preferable to form Al2O3 on the surface. In the sample, left at room temperature before being analyzed by XPS, formation of Al(OH)3 is detected. AlN layer is possible to react with moisture in air and forms oxide or hydroxide, depending on the ambient temperature. After sputtering both samples for 60 s (1 minute), the Al2p peaks were shift to 74.2 eV, or, no Al2O3 and Al(OH)3 are present except for AlN. This oxide or hydroxide layer is very thin and acts as a protective layer, so that the inner AlN could be free from further oxidation via its reaction with moisture in air.

During cooling the samples from nitriding temperature down to the room temperature, the difference between thermal expansion coefficients of the AlN (\(\alpha_{\text{AlN}}\)) and Al (\(\alpha_{\text{Al}}\)) causes the residual thermal stress in AlN layer. This residual thermal stress can be estimated by

\[
\sigma_{\text{int}} = E_{\text{AlN}} \left( \alpha_{\text{AlN}} - \alpha_{\text{Al}} \right) \left( T - T_R \right) \left( \frac{d_{\text{Al}}}{d_{\text{AlN}} + d_{\text{Al}}} \right)
\]

where the young’s modulus of AlN layer is given by \(E_{\text{AlN}} = 350 \times 10^3 \text{MPa} \), \(\alpha_{\text{AlN}} = 5.7 \times 10^{-6} \text{K}^{-1}\) and \(\alpha_{\text{Al}} = (22 - 25.5) \times 10^{-6} \text{K}^{-1}\). \(T\) is the nitriding temperature, and \(T_R\) the room temperature. \(d_{\text{Al}}\) is the thickness of substrate, and \(d_{\text{AlN}}\) the thickness of AlN. Assuming that thickness of AlN is much less than that of Al, \(d_{\text{Al}}/(d_{\text{AlN}} + d_{\text{Al}})\) is nearly equal to unity and can be neglected. The calculated thermal stress in AlN layer after nitriding at 723 K, is around ~3000 MPa, sufficient to cause cracks and detachment of AlN layer as shown in Fig. 12.
4 Summary

AIN layer on the pure aluminum powder compact can be successfully formed by the dc plasma nitriding technique with the thickness up to 3 μm for the cold-pressed sample and 15 μm for the refined microstructure via BMA. The refined microstructure can activate the formation of AIN. The refined microstructure contains large amount of grain boundary, which acts as a high diffusion path of nitrogen. This excess in the diffusion rate leads to formation of thicker AIN. The most important key on the formation of AIN, is elimination of Al₂O₃ by sputtering. In order to fabricate the thick AIN layer, the base pressure before nitriding must be reduced as low as possible to reduce the residual oxygen in chamber and to achieve the effective sputtering state. AIN adjacent to free surface is possibly to react with moisture in air and become oxide and hydroxide. These oxide/hydroxide layer is very thin but enough to protect the inner AIN layer. Detachment of AIN layer can occur due to the existing residual thermal stress in AIN layer.

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References

1) W.F. Smith: "Structure and Properties of Engineering
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