Feasibility of Plasma Nitriding for Effective Surface Treatment of Pure Aluminum

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Cast aluminum with 99.99% purity was successfully plasma nitrided using nitrogen and hydrogen mixed gas. Pre-sputtering was carried out prior to plasma nitriding in order to eliminate surface oxide film. Sputtering and nitriding durations were varied from 3.6 to 18 ks and 72 ks to 252 ks, respectively. The samples were nitrided at 823 and 873 K to observe the effect of nitriding temperature. The nitrided samples were analyzed by GIXD, XPS, and TEM. Through GIXD and XPS results, formation of AlN was distinctly detected as a nitrided surface. Cross-sectional microstructure of nitrided samples showed that AlN was formed with the thickness up to 3–5 μm. AlN formation is controlled by the diffusion process. The thickness of AlN layer was determined by the nitriding time and temperature. Partial degradation of AlN in the vicinity of the free surface occurred due to its reaction with moisture in air. Partial detachment of AlN layer occurred due to the residual thermal stress, which was caused by the difference in thermal expansion coefficient between AlN and substrate of Al.

Keywords: plasma nitriding, aluminum nitride, aluminum, sputtering

1. Introduction

Aluminum alloys have widely been used in many industrial applications. In the automotive industry, various aluminum alloys are expected to be useful as light-weight structural materials or components because of their intrinsic properties such as high specific strength, high corrosion resistance and formability. In particular, light-weight and high strength has become indispensable to minimize significantly the automotive fuel consumption and to reduce the environmental burden. In fact, selection of structural material for automotive parts has been rapidly changed from cast iron and forged steel to aluminum alloys. Even at the present, most of aluminum applications in automotive parts are limited to non-moving parts such as instrument housing. For its further applications in the power train parts, high qualification is strictly required to significantly increase their hardness and tribological properties. Without effective surface treatment, the practical usage of aluminum alloys is much restricted.

Aluminum nitride (AlN) is a popular ceramic material for its high hardness (1400 HV) and wear resistance as well as its high thermal conductivity ($\kappa = 319 \text{ W/mK}$, theoretically at room temperature) and electric resistivity. $^{2-4}$ The materials coated with AlN are expected to have excellent tribological properties. In the case of aluminum alloys, formation of AlN up to the thickness of 3 μm was reported to significantly increase their wear resistance. $^{5,6}$ From the thermodynamic data, free energy of AlN formation is large and negative approximately $-462 \text{ kJ/g-atom}$ for nitrogen at 773 K. Hence, the formation of AlN is thermodynamically easy, though AlN cannot be formed by the conventional gas nitriding. An obstacle to AlN formation in gas nitriding of aluminum alloys is a highly stable Al$_2$O$_3$ surface film. Dense Al$_2$O$_3$ film retards the nitrogen diffusion, and acts as a barrier to reaction between metallic aluminum surface and nitrogen. $^{5,7}$ Therefore, the most important key to successfully fabricate AlN is to eliminate Al$_2$O$_3$ from the aluminum surface. In fact, many researchers reported that AlN was possible to form on the surface of aluminum alloys only after elimination of Al$_2$O$_3$. Natural Al$_2$O$_3$ film can be eliminated by several methods. Addition of magnesium into aluminum alloy powder in a small amount can reduce Al$_2$O$_3$, or, Al$_2$O$_3$ is mechanically broken by ball milling in nitrogen atmosphere. $^{8,9}$

In this research, plasma nitriding was chosen instead of gas nitriding, since bombardment of positive ions is available to sputter atoms on the specimen surface during plasma nitriding. That is, plasma nitriding can afford to nitride aluminum by removing the Al$_2$O$_3$ on the surface of Al. Furthermore, plasma nitriding process has some merits: less consumption of gas and energy, and safety to be free from toxic gas or salts. $^{10,11}$ In the plasma nitriding process, the bias voltage is directly applied in a controlled atmosphere chamber, in which the nitriding samples are connected to the cathode and the chamber wall is connected to anode as a ground potential. Various exited species are generated in plasma and positive ions are accelerated to the cathode by the cathode fall in corresponding to the applied electrical potential. When the ions bombard the sample surface, its kinetic energy is transferred to sputter natural Al$_2$O$_3$ film by elastic collision, except for heating the specimen. Then the energy transfer during sputtering can be generally expressed by

$$E_{kin} = Q + A + E_d$$

where $E_{kin}$ is the kinetic energy of ion, $Q$, the heat generated and $A$, the detaching energy of surface atom and $E_d$, the kinetic energy of the detached atom. $^{12}$

In the conventional approach, $^{5-7}$ argon plasma is employed to sputter Al$_2$O$_3$ from aluminum alloy surface. Disadvantage of argon plasma first lies in degradation of surface morphology. In argon pre-sputtering, both aluminum and Al$_2$O$_3$ suffer from nearly the same damage as experienced by excessive sputtering. In addition, perfect evacuation of argon after pre-sputtering requires longer time; otherwise, residual argon atoms remain on the surface to significantly disturb the following nitriding. In order to diminish the
surface damage and to make efficient nitriding, the nitrogen plasma is employed as a new candidate for pre-sputtering instead of argon plasma. Among various kinds of species, \( \text{N}_2^+ \) acts as an effective sputtering species.

In this study, high purity aluminum cast was chosen to study the possibility of AlN formation by plasma nitriding. No additive elements like magnesium were required in this approach. Pre-sputtering was first applied by pure nitrogen plasma to eliminate \( \text{Al}_2\text{O}_3 \) from surface. Duration times were varied to investigate the effect of sputtering time. Subsequently, the operation mode from sputtering to nitriding was changed in the same experimental set-up only by introduction of hydrogen gas. Through the feasibility test, the plasma nitriding with pre-sputtering was demonstrated to be an effective surface treatment for aluminum and aluminum alloys.

2. Experimental Procedure

2.1 Preparation of samples

Cast aluminum billet with the purity of 99.99% was cut to a disk specimen with 15 mm in diameter and 8 mm in height. All samples were polished by SiC paper with the mesh number of 600, 800, 1000, 1500 and 4000 in series. Further, these samples were mirror polished by 1 \( \mu \)m diamond paste. The polished samples were rinsed in acetone by ultrasonic cleaner for 600 s before nitriding.

2.2 Plasma nitriding

Plasma nitriding apparatus was illustrated in Fig. 1. First, nitriding chamber was evacuated by a rotary pump to base pressure around 2.66–4.00 Pa (\( \frac{2}{24} \times 10^2 \) Torr) in order to minimize the residual oxygen partial pressure in chamber. Secondly, pure nitrogen gas for pre-sputtering was introduced into the chamber until the pressure reaches 133.3 Pa (1 Torr). The samples were heated up to 823 K by an external resistive heater and glow discharge, simultaneously. The sample temperature was monitored by a thermocouple, which was inserted into a dummy specimen located on the same cathode neighboring to the sample. At the specified temperature, glow discharge of nitrogen was ignited by applying the bias voltage of 200 V to samples. Sample acts as a cathode in this experiment. Holding time of sputtering was varied for 3.6, 10.8 and 18 ks (1, 3 and 5 h) respectively. After pre-sputtering, nitrogen and hydrogen was filled into the chamber until the total pressure became 533.3 Pa (4 Torr). The ratio of hydrogen to nitrogen was fixed at 3 to 1 in pressure. The applied bias voltage for glow discharge in plasma nitriding was 200 V with the direct current of 0.2 A. Samples were nitrided for 72, 144 and 252 ks (20, 40 and 70 h). During nitriding, the gas was evacuated out by rotary pump to keep constant pressure in the chamber. The pressure in nitriding chamber was monitored by an absolute pressure gauge. The nitriding conditions were listed in Table 1.

2.3 Characterization of nitrided samples

After nitriding, samples were cooled down to room temperature in hydrogen gas flow. Formation of AlN was analyzed by the grazing incident X-ray diffraction (GIXD) at the incident angle of 1° and by the X-ray photoelectron spectroscope (XPS). The surface and cross-sectional microstructure of nitrided samples was observed by an optical microscope and a scanning electron microscope (SEM). Transmission electron microscope (TEM) was used for analysis of AlN layer in order to precisely observe the microstructure. The sample for TEM observation was prepared by the powder suspension method.

3. Results and Discussions

3.1 Formation and degradation of AlN by plasma nitriding

After nitriding, the surface color of samples changed from metallic-shinning to dark gray or shinny black color. This color is typical to hexagonal AlN (JCPDS no. 25–1133) which is the most stable structure in AlN. An outlook of the sample after plasma nitriding is shown in Fig. 2.

Figure 3 shows the nitrided surface microstructure observed by SEM. Small cracks along the grain boundary might be caused by the high sputtering rate at the grain boundary. In this research, nitrogen plasma was employed for pre-sputtering in order to eliminate \( \text{Al}_2\text{O}_3 \) from aluminum.
surface, instead of argon plasma. In this nitrogen plasma, \( \text{N}_2^+ \) plays an important role in sputtering as an attacking species. The sputtering yield of \( \text{Al}_2\text{O}_3 \) by this nitrogen plasma is lower than that by argon plasma under the same accelerated voltage.

The nitrided surface was analyzed by XPS as shown in Fig. 4. In the vicinity of the surface, Al\( \text{2p} \) peak was detected by XPS at the binding energy of 73.5 eV. This binding energy corresponds to \( \text{Al(OH)}_3 \). Increasing the argon ion etching time to 60 s (1 min), the Al\( \text{2p} \) peak shifted to 74.4 eV for AlN and no \( \text{Al}_2\text{O}_3 \) or \( \text{Al(OH)}_3 \) were observed. This indicates that only the surface of formed AlN is partially oxidized. In particular, \( \text{Al(OH)}_3 \) was formed in the vicinity of the surface by the reaction between AlN and moisture in air.

\[
\text{AlN} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NH}_3. \tag{1}
\]

The degradation reaction is described by eq. (1). This thin layer of hydroxide is possible to retard the diffusion of oxygen and moisture. Consequently, it can act as a protection layer of inner AlN from further oxidation.\textsuperscript{13,14}

Figure 5 shows the electron diffraction patterns of AlN. The observed hexagonal symmetric diffraction pattern is in fairly good agreement with the calculated crystalline structure in \( \langle 0001 \rangle \) orientation. This TEM observation together with GIXD and XPS proved that AlN is formed by plasma nitriding. Figure 6 shows both dark and bright field images of AlN with its electron diffraction pattern. AlN formed by plasma nitriding, has a columnar structure with the aspect ratio of around three to four.

### 3.2 Effect of sputtering time on AlN formation

Figure 7 shows the cross-sectional microstructure of the nitrided cast aluminum. In the series of experiments, the nitriding time was fixed to 72 ks (20 h) for various sputtering time. AlN surface layer with the thickness of 1 to 2 \( \mu \)m was observed even by varying the pre-sputtering time, 10.8 ks (3 h) and 18 ks (5 h). On the other hand, no AlN layer was observed when pre-sputtering time only for 3.6 ks (1 h). The shorter pre-sputtering time results in insufficient elimination of \( \text{Al}_2\text{O}_3 \) so that the formed AlN layer thickness was not visible by an optical microscope. Those facts indicate that the pre-sputtering process is one of the most important factors for AlN formation.

Variation of GIXD profiles with increasing the pre-sputtering time is shown in Fig. 8(a). AlN peaks were observed in all the samples. Even for the specimen with
Fig. 6 TEM analysis of polycrystalline AlN layer: (a) electron diffraction pattern, (b) dark field image and (c) bright field image.

Fig. 7 Cross-sectional microstructure of nitrided aluminum samples for different sputtering time: (a) 3.6 ks and (b) 10.8 ks.

Fig. 8 GIXD analysis of nitrided sample with varying the sputtering time: (a) GIXD at the incident angle of $1^\circ$ and (b) variation of relative peak intensity ration of aluminum and AlN.

Fig. 9 Cross-sectional microstructure of nitrided aluminum samples for different sputtering time: (a) 3.6 ks and (b) 10.8 ks.
3.6 ks pre-sputtering, although the formed AlN was not visible in Fig. 7. AlN peaks were distinctly detected in Fig. 8(a). Figure 8(b) depicts the variation of the relative peak intensity of AlN (100) to Al (111) with increasing the pre-sputtering time. Monotonous increase of relative peak intensity with the pre-sputtering time, implies that the volume fraction of formed AlN should increase with increasing time. This corresponds to monotonous growth of AlN layer in Fig. 7.

Considering the little change of GIXD profiles in Fig. 8(a), or, the little increase of relative peak intensities in Fig. 8(b) from 10.8 ks (3 h) to 18 ks (5 h), optimum pre-sputtering time is 10.8 ks (3 h) for the following nitriding under 133.3 Pa, 200 V and 0.2 A.

3.3 Effect of nitriding parameters on AlN formation

The pre-sputtering condition was fixed, 10.8 ks (3 h) under 133.3 Pa of nitrogen with the bias voltage of 200 V at 0.2 A. The normal nitriding condition was employed: nitrogen and hydrogen mixture with the total pressure 533.3 Pa and its ratio in pressure by 1 : 3. Only nitriding time was varied from 72 to 252 ks (20–70 h) in this experiment. The nitrided samples were characterized by GIXD at the incident angle of 1°. The GIXD profiles show that AlN layer was formed on the surface of all samples after plasma nitriding. With longer nitriding holding time, the larger amount of AlN is detected in GIXD profiles. Cross-sectional microstructure of the nitrided samples is shown in Fig. 9 by varying the nitriding time from 72 to 252 ks (20 to 70 h). The thickness of AlN layer increased with increasing the nitriding time. This monotonous growth of formed AlN layer might be explained by the diffusion process of nitrogen into pure aluminum. When increasing the nitriding time, the nitriding front further penetrates into aluminum matrix, resulting in the thicker AlN layer. In general, assuming that the single-step reaction of Al+\(\text{N}_2\) results in formation of AlN takes place at the nitriding front, the square of AlN layer thickness \(E^2\) increases proportionally with the nitriding time \(t\) as shown in Fig. 10. According to Ref. 15), the concentration flux \(j\) is proportional to the growth rate of layer by

\[
j = \frac{dE}{dt}.
\]

This flux at the nitriding front varies with \(1/E\) as

\[
j = \frac{k}{E}.
\]

If the concentration at the surface is constant during the nitriding, then the relationship between \(E\) and \(t\) can be obtained by substituting eqs. (2) to (3). After integration,

\[
E^2 = 2kt.
\]

Here, the proportional coefficient or the apparent growth rate of AlN layer, \(2k\) (\(k\) is Tammann constant), is calculated to be \(1.86 \times 10^{-17}\) m² s⁻¹ in this experiment.

In Fig. 10, by extrapolating this \(E^2 - t\) relationship to \(E = 0\), there exists an incubation time, \(t_c\). This implies that the incubation time \(t_c\) is needed to activate the nitrogen diffusion process. At the beginning, direct reaction between aluminum and nitrogen occurs first on the top surface and results in formation of AlN nodules. During \(t_c\), these AlN-nodules grow into a layer and covers the whole surface. After \(t_c\), the growth of AlN layer is controlled by diffusion mechanism. In the present experiment, approximately 36 ks (10 h) is necessary for the formation of AlN layer to cover the entire surface of aluminum or to form a single AlN layer.

The nitriding temperature also plays an important role on AlN formation. When increasing the nitriding temperature to 873 K, the thickness of AlN increased to nearly 5 µm by 72 ks (20 h) nitriding as shown in Fig. 11. The GIXD profiles in Fig. 12 also show higher intensity of AlN peaks with increasing nitriding temperature. In general, since the diffusion coefficient of nitrogen is larger at higher temperature, the nitrogen can diffuse into aluminum matrix at a faster rate. At higher temperature, however, the residual thermal stress induced during cooling also becomes larger enough to generate cracks and to cause detachment of the AlN layer. This residual stress is caused by the difference of linear}

**Fig. 8**  Pure aluminum cast samples nitrided for various nitriding time at 823 K after pre-sputtering for 10.8 ks: (a) 72 ks, (b) 144 ks and (c) 252 ks.

**Fig. 9**  Pure aluminum cast samples nitrided for various nitriding time at 823 K after pre-sputtering for 10.8 ks: (a) 72 ks, (b) 144 ks and (c) 252 ks.

**Fig. 10**  Relation between the nitriding time and the square thickness of AlN.
thermal expansion coefficient between AlN ($\alpha_{\text{AlN}}$) and aluminum ($\alpha_{\text{Al}}$). It can be estimated by

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

where $E_{\text{AlN}}$ is the Young’s modulus of AlN layer, given by $E_{\text{AlN}} = 350 \times 10^3$ MPa, $\alpha_{\text{AlN}} = 5.7 \times 10^{-6}$ K$^{-1}$ and $\alpha_{\text{Al}} = (22 - 25.5) \times 10^{-6}$ K$^{-1}$. $T$ is the nitriding temperature, $T_R$, the room temperature, $d_{\text{Al}}$, the thickness of substrate, and $d_{\text{AlN}}$, the thickness of AlN. The thickness of AlN is much less than that of aluminum, so that $d_{\text{Al}}/(d_{\text{AlN}} + d_{\text{Al}})$ is nearly equal to unity in computation. The calculated stress ranges from $-2000$ to $-3000$ MPa for 623–773 K nitriding temperature. This high stress is enough to cause cracks and detachment of the AlN layer. In fact, the detachment of AlN layer due to residual thermal stress is shown in Fig. 13.

### 3.4 Deposition process during nitriding

In order to study the effect of deposition process on nitriding, an additional nitriding experiment was performed by placing a silicon wafer below the aluminum sample. The silicon wafer after 432 ks (120 h) nitriding was analyzed by GIXD. Figure 14(a) indicates that AlN was formed on the surface. The cross-sectional microstructure in Fig. 14(b) also shows formation of AlN layer with the thickness of around 1 μm. This proves positively that AlN could be formed on the surface of silicon wafer only by deposition process during plasma nitriding. The sputtered aluminum can react with nitrogen and possibly deposit on the silicon wafer as AlN. However, this deposition rate was very low: 432 ks was needed to form AlN with the thickness of 1 μm. This process has nothing to do with the nitriding process.

### 3.5 Mechanism of AlN formation by plasma nitriding

Formation mechanism of AlN by plasma nitriding in this experiment is illustrated in Fig. 15. Aluminum alloy surface is always covered with the natural Al$_2$O$_3$ film, so that no
nitrogen can react with aluminum matrix. Pre-sputtering is ignited by glow discharge of nitrogen plasma. During pre-sputtering, preferable species like \( N_2^+ \) bombard the sample surface to transfer significant amount of energy to detach the atoms from the surface. The oxide film is eliminated at this stage. Nitrogen reacts with a fresh surface of aluminum to form AlN. AlN nodules are formed by direct reaction. During the incubation time, the AlN nodules are combined to a single AlN layer. Subsequently, this AlN layer grows by diffusion mechanism as discussed in section 3.3. AlN deposition during plasma nitriding has a little contribution to AlN formation. After AlN layer was formed on the surface, reaction of this AlN with moisture in air leads to degradation of AlN by formation of \( Al(OH)_3 \) film. This growth rate of \( Al(OH)_3 \) film is very slow, and hence, it protects inner AlN from further oxidation.

4. Conclusion

AlN surface layer with the thickness of 3 to 5 \( \mu \text{m} \) is successfully formed on the pure cast aluminum specimens via DC-plasma nitriding with nitrogen pre-sputtering. This AlN thickness can be controlled by pre-sputtering and nitriding conditions. Different from other surface treatments, the present method is effective to yield homogeneous AlN layer. Detachment or cracking of AlN layer can be eliminated by decreasing the nitriding temperature or by the surface structuring in the aluminum alloys. This process can be utilized as an environmentally benign surface modification for various aluminum alloys.

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