

A Novel Method for The Production of AlN Film with High Adhesion on Al Substrate

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In this study, a new nitriding technique is suggested to produce aluminum nitride film with high adhesion on aluminum substrate. Bilayer aluminum nitride can be produced on aluminum substrate using barrel nitriding and plasma nitriding. Furthermore, plasma nitriding parameters are also investigated. It is suggested that the aluminum nitride film thickness strongly depends on the gas mixture ratio and the treatment time, and the surface morphology of the film has close relation to the gas pressure.

Keywords: plasma nitriding, barrel nitriding, adhesion, hardness, aluminum nitride, aluminum

1. Introduction

Aluminum and aluminum alloys have numerous industrial applications due to their outstanding properties such as light weight, high specific strength, good machinability and so on. However, various surface treatments are indispensable to improve mechanical properties, such as hardness and wear resistance. Aluminum nitride is attractive as a protective coating film for automotive and electrical aluminum alloy parts, and the properties of aluminum nitride such as high hardness, wear resistance, chemical corrosion resistance, high thermal conductivity and electrical resistivity are very attractive for advanced technological applications¹⁻²⁾. The formation of aluminum nitride surfaces on aluminum alloys components is a well-known technology for improving the surface properties of aluminum. The formation of aluminum nitride on aluminum has been reported by many researchers using different methods such as plasma nitriding, ion implantation, physical vapor deposition (PVD), chemical vapor deposition (CVD), and thermal spraying²⁻⁴⁾. However, these processes have a problem in terms of the delamination of the film caused by thermal stress. Delamination of the film strongly depends on the coating method⁵⁻⁶⁾.

In this study, a new nitriding technique is suggested to produce aluminum nitride film with high adhesion on aluminum substrate. In order to improve the surface properties of aluminum, aluminum nitride layer was deposited by using barrel nitriding in nitrogen gas. Duplex coating was performed with plasma nitriding in nitrogen and argon gas after barrel nitriding. Using this process, no crack or delamination of the aluminum nitride film can be

observed, and the aluminum nitride film with good adhesion can be formed on the aluminum surface. The bilayer aluminum nitride is formed by these processes. The first layer deposited was aluminum rich aluminum nitride layer to improve the adhesion and the last one was nitrogen rich aluminum nitride layer to improve the surface hardness. Furthermore, the aim of this study is also the investigation of plasma nitriding parameters including gas mixture ratio, treatment time, and gas pressure at constant temperature. The aluminum nitride film thickness strongly depends on the gas mixture ratio and treatment time, and the surface morphology of the film has close relation to the gas pressure.

2. Experiment Procedures

Aluminums with the purity 99% were used a sample for nitriding. The chemical composition of the sample is shown in Table 1. Pure aluminums were cut into 20 x 20 x 5mm³ with wire-electrical discharge machining. The samples were ground using 500 to 2400 grit SiC papers, and were polished using 0.5μm Al₂O₃ slurry before nitriding. The polished samples were ultrasonically cleaned in acetone.

Table 1 Chemical composition of pure aluminum (wt%)

Si	Fe	Cu	Mg	Ti	V	Al
0.06	0.30	0.01	0.01	0.02	0.01	bal

Barrel nitriding⁷⁻⁸⁾ was performed as pretreatment before plasma nitriding. Barrel nitriding apparatus is shown in Fig. 1. Al₂O₃ powder and Al-50mass%Mg powder were used as the filling powders of the barrel. Nitrogen gas was introduced into the barrel and the flow rate was adjusted with a mass flow controller. After introduction of nitrogen gas, the substrate was heated to 903K and was nitrided

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during oscillating movements of the barrel. Nitrogen flow rate is 1500cc/min, and treatment time is 18ks.

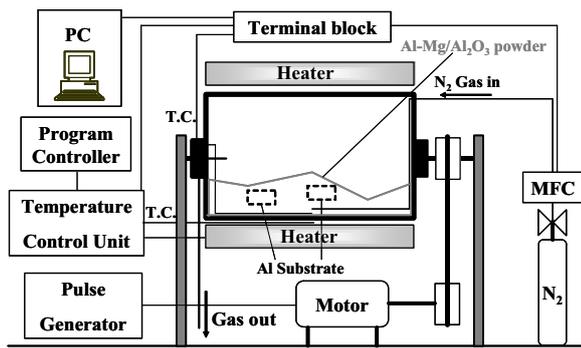


Fig. 1 Schematic diagram of experimental apparatus.

Plasma nitriding was performed on barrel nitrided aluminum. The schematic diagram of the nitriding apparatus with an electron beam excited plasma (EBEP) source is shown in Fig. 2. Figure shows schematic diagram of the nitriding apparatus with EBEP source. The EBEP source is a unique electron beam source that can produce amperes of beam current with a beam kinetic energy less than 100eV, which is lower by several orders of magnitude than the energy of electron beams produced by other ordinary beam sources¹⁰. The vacuum chamber was evacuated below 10^{-4} Pa before processing. After elevating the sample temperature to a holding temperature, plasma of Ar was generated for pretreatment to eliminate the surface contaminants or oxides. Nitrogen and argon gas were introduced to the chamber. Table 2 lists typical processing conditions for pretreatment and nitriding.

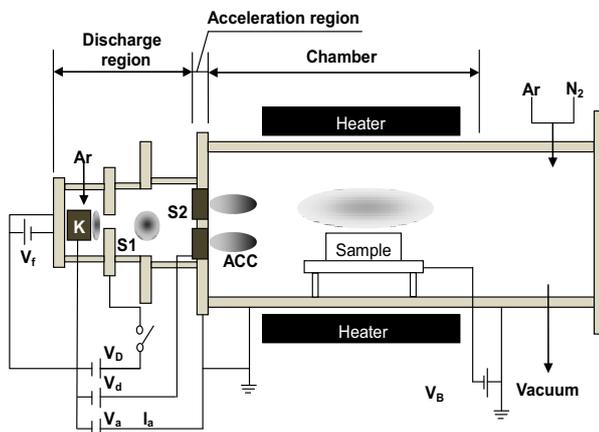


Fig. 2 Schematic diagram of the nitriding apparatus with electron beam excited plasma (EBEP) source.

X-ray diffraction (XRD) using Cu $K\alpha$ X-ray source was employed to analyze the nitrided surface of aluminum. The evolution of surface morphology was performed by using scanning electron microscope (SEM). For characterizing the mechanical properties, indentation test on the cross sectional surface was conducted at a load 0.19N using Vickers diamond indenter. The dwell time at maximum load was 5 second.

Table 2 Experimental condition of plasma nitriding

	Pretreatment	Nitriding
Temperature in furnace (K)	853	853
Treatment time (ks)	7.2	3.6 - 21.6
Total pressure (Pa)	0.25	0.38 - 0.76
Flow rate of Ar (cc/min)	30	30
Flow rate of N ₂ (cc/min)	-	20
Acceleration voltage (V)	130	130
Electron beam current (A)	8	8

3. Results and Discussion

3.1 Surface Modification of Aluminum

The aluminum nitride is produced using barrel nitriding and plasma nitriding technique. Figure 3 (a) shows SEM micrograph of the barrel and plasma nitrided surface. The aluminum nitride layers formed by barrel nitriding and by plasma nitriding are defined as AlN/B and AlN/P, respectively. Uniform aluminum nitride layer, AlN/P, was formed on the surface using barrel nitriding and plasma nitriding, as shown in Fig. 3 (a). On the Al substrate, the crack or delamination of the AlN/P layer can be found from surface observation as shown in Fig. 3 (b). On the AlN/B on Al substrate formed by barrel nitriding, no crack or delamination of the AlN/P layer can be found from surface observation, and the AlN/P film formed duplex coating has good adhesion.

It is widely known that the AlN films formed by using plasma nitriding often exhibit a large compressive stress, and the AlN films occur to the crack or delamination. The difference between physical properties of Al substrate and of AlN films is one of the major reasons of the compressive stress with films. There is clearly a major gap when one compares the hardness of AlN/P (1400Hv) and that of Al (25Hv). The hardness of AlN/P and AlN/B is 1400Hv and 250Hv - 450Hv, respectively. The AlN/B has the middle properties between AlN/P and Al substrate. Therefore, the AlN/B would play a role as the interlayer of AlN/P and Al substrate as shown in Fig. 3 (a), so the AlN/P with high adhesion can be obtained by using this process.

3.2 The Influence of Process Parameter on The Growth of The AlN Film

3.2.1 Influence of Treatment Time

The relation between treatment time and nitride layer thickness formed by using plasma nitriding is shown in Fig. 4. The AlN with a uniform thickness is produced on the substrates under each condition. The film is confirmed to have a uniform composition and structure by energy dispersive X-ray spectroscopy (EDS) and hardness test. The film thickness of the AlN/BP proportionately increases with the square root of treatment time. In the diffusion controlled growth, it is noted that the film thickness is proportional to the square root of treatment time^{7,9}. This shows that the AlN/P layer growth on the AlN/B is

diffusion controlled. The diffusion coefficient of nitrogen atoms in AlN is $10^{-18} \text{m}^2/\text{s}$ at $T=823\text{K}$ ¹¹⁾. The direct reaction of $\text{Al} + \text{N} \rightarrow \text{AlN}$ occurs and the AlN/B surface is covered by the AlN/P layer. After the AlN/B is covered by the AlN/P, the AlN/P grows by diffusion of the Al in the AlN/B⁷⁾ or diffusion of N in the AlN/P. Moreover, by extrapolating the relationship to $x = 0$, there exists an incubation time. This can be related to a certain time needed for formation of an AlN nucleation, after which a growth of nitride layer takes places. In this study, an incubation time of around 1.96ks can be obtained. On pure aluminum, an incubation time of around 35.6ks is obtained with the normal plasma nitriding by P. Vissutipitukul¹¹⁾. Although the materials used are different from the pure aluminum, the formation of AlN nucleation with electron beam plasma nitriding is 18 times faster than that of normal plasma nitriding. Electron beam plasma nitriding is proposed as one of the most promising surface treatments for formation of aluminum nitride.

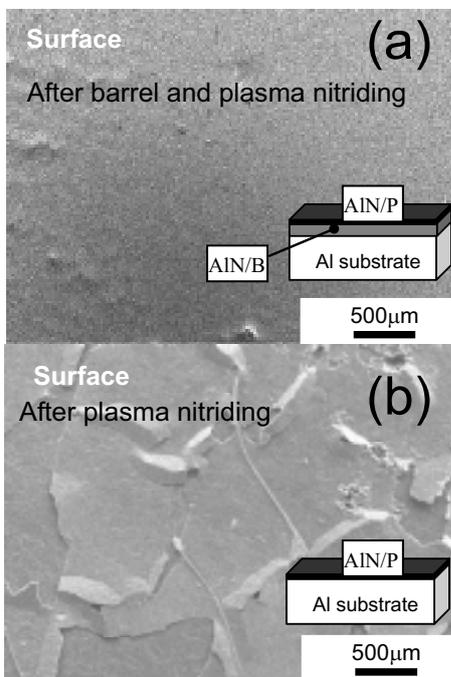


Fig. 3 Scanning electron microscope (SEM) micrograph after nitriding.

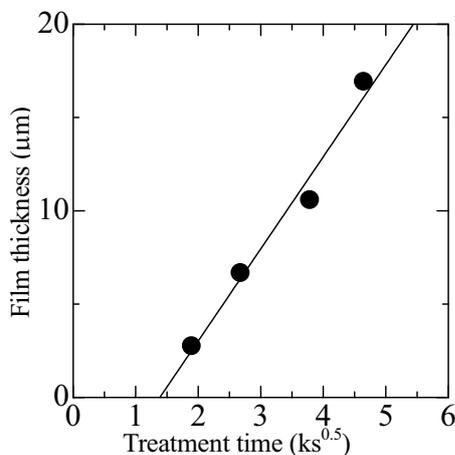


Fig. 4 The relation between treatment time and nitride layer thickness formed by using plasma nitriding.

3.2.2 Influence of N_2/Ar Gas Ratio

To reveal nitriding efficiency, the influence of the gas composition is investigated. The relation between the gas ratio and the film thickness is shown in Fig 5. The AlN growth is greatly affected by the presence of Ar gas. It is shown that the film thickness at the gas ratio 1.0 is the lowest of all. Through energy dispersive X-ray spectrometer (EDS), oxygen was detected on the surface of Ar/ N_2 ratio 1.0. The source of oxygen inside the layer may be the oxygen present in the nitriding gas as an impurity or residual oxygen and water inside the chamber. It is thought that oxygen will always be present in the chamber as a residual gas. The aluminum oxide on Al or AlN is formed by the impurities gas. Therefore, the presence of oxygen may disturb the growth of AlN.

When argon is added as a sputtering gas, the film thickness increases sharply from $1.6\mu\text{m}$ to $7\mu\text{m}$ and the film thickness became constant at Ar/ N_2 gas ratio 1.5 to 2.0. However, the film thickness decreases at Ar/ N_2 gas ratio 3.0. The argon role in the gas mixture is complex. Ar atom sputters the surface, and the surface is cleaned up and the oxide layer on AlN/B is eliminated. The plasma density was measured to increase from 1.1 to $1.5 \times 10^{10} \text{cm}^{-3}$ with increasing gas ratio from 1 to 3 owing to the addition of Ar gas. Here, Ar^+ ion density most likely increases and then the Ar sputtering accelerates. By bombarding the growing film, Ar sputtering can lead to depth destruction of the already formed AlN film. Therefore, the film thickness became constant from Ar/ N_2 gas ratio 1.5 to 2.0, and decreases at Ar/ N_2 gas ratio 3.0.

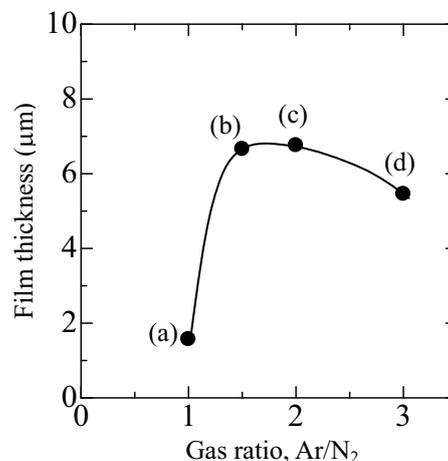


Fig. 5 The influence of gas ratio, Ar/ N_2 , on formation of aluminum nitride. Gas pressure = (a) 0.3, (b) 0.38, (c) 0.5, and (d) 0.62. The N_2 gas flow rate was kept constant. Treatment time = 7.2 ks.

3.2.3 Influence of Gas Pressure

The influence of gas pressure on the nitriding process is shown in Fig. 6. The film thickness is constant at every gas pressure, and doesn't depend on the gas pressure. The plasma density was measured to increase from 1.2 to $1.5 \times 10^{10} \text{cm}^{-3}$ with increasing gas pressure from 0.38 to 0.76 Pa. It is thought that the increase of gas pressure causes the increase of high density nitrogen ion, and the growth rate of the AlN is accelerated. However, since argon ion increases with increasing gas pressure, the already formed AlN film is eliminated by the accelerated argon sputtering

effect. Therefore, the film thickness doesn't strongly depend on the gas pressure.

The SEM micrograph of the substrate plasma nitrided at 0.38Pa and 0.76Pa is shown in Fig. 7. The surface of the substrate plasma nitrided at 0.38Pa shows somewhat larger nodules as compared to the surface of the substrate plasma nitrided at 0.76Pa, that is, the SEM micrographs show that the surface morphology changes into finer structure as the gas pressure increases. A possible reason for the result is the following: The increase of the plasma densities results in increasing the particle density with the high energy and many AlN nucleates occurs on the surface. Therefore, the nucleation density increases with increasing the gas pressure, and the surface morphology may become finer as the gas pressure increases. U. Figueroa *et al.*¹²⁾ and M. Moradshahi *et al.*⁹⁾ has reported the influence of gas pressure. They show that the thickness of nitride layer in surface slightly decreased with increasing the pressure, and the surface roughness increased with gas pressure. Our results are entirely different from their results. It is thought that the AlN film is formed in a completely different way, and gas pressure in plasmas nitriding varies greatly. It is suggested that the AlN growth is not affected by the gas pressure, but the surface morphology changes with fine structure as gas pressure increases. Nevertheless to draw a certain conclusion, further investigations are required in the future.

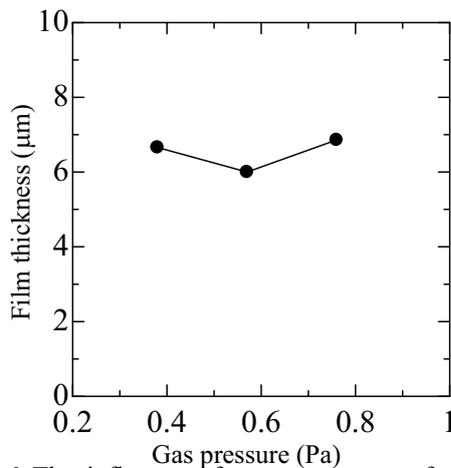


Fig. 6 The influence of gas pressure on formation of aluminum nitride. Gas ratio Ar/N₂ = 0.6. Treatment time = 7.2 ks.

4. Conclusions

- Using barrel nitriding and plasma nitriding, uniform aluminum nitride layer, AlN/P was formed on the surface by plasma nitriding. The no crack or delamination of the AlN/P layer can be found from surface observation, and the AlN film has good adhesion.
- The film thickness of the AlN/BP proportionately increases with the square root of treatment time, and this shows that the AlN/P layer growth on the AlN/B is diffusion controlled. A certain time is needed for formation of an AlN nucleation, after which a growth of nitride layer takes places. In this study, incubation time of around 1.96ks can be obtained.
- The formation of AlN nucleation with electron beam

plasma nitriding is 18 times faster than that of normal plasma nitriding. Electron beam plasma nitriding is proposed as one of the most promising surface treatments for formation of aluminum nitride.

4. The AlN growth is greatly affected by the presence of Ar gas. When argon is added as a sputtering gas, the film thickness increases sharply. However, the film thickness became constant and decreases with increasing Ar/N₂ gas.

By bombarding the growing film, argon sputtering can lead to depth destruction of the already formed AlN film.

5. The AlN growth is not affected by the gas pressure, but the surface morphology changes with fine structure as gas pressure increases.

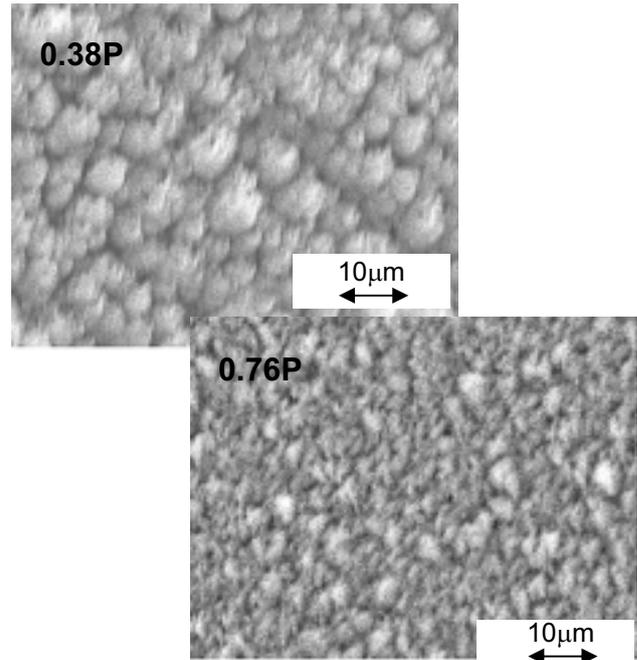


Fig. 7 The SEM micrographs of the substrate plasma nitrided at 0.38Pa and 0.76Pa.

- I. Yonekawa, A. Nikolaev, Y. Melnik and V. Dmitriev, *J. Appl. Phys. Jpn.*, **40**, 426 (2001).
- U. Figueroa, O. Salas and J. Oseguera, *Surf. Coat. Technol.*, **200**, 1768 (2005).
- G. Wang, B. Wang, A. Huang, S. Xu, M. Zhu, B. Wang and H. Yan, *Mater. Lett.*, **58**, 2486 (2004).
- M. Yamada, C. Lee, T. Yasui, M. Fukumoto and K. Takahashi, *J. Vac. Soc. Jpn.*, **50**, 458 (2007).
- Y. Watanabe, N. Kitazawa and Y. Nakamura, *J. Vac. Sci. Technol., A* **18**, 1567 (2000).
- Y. Watanabe, S. Uchiyama and Y. Nakamura, *J. Vac. Sci. Technol., A* **17**, 603 (1999).
- M. Okumiya, H. Ikeda and Y. Tsunekawa, *Solid State Phenomena*, **118**, 137 (2006).
- M. Okumiya, Y. Tsunekawa, H. Sugiyama, Y. Tanaka, N. Takano and M. Tomimoto, *Surf. Coat. Technol.*, **200**, 35 (2005).
- M. Moradshahi, T. Tavakoli, S. Amiri, and S. Shayeganmehr, *Surf. Coat. Technol.*, **201**, 567 (2006).
- T. Hara *et al.*: *J. Vac. Sci. Technol., B* **5**, 366 (1987).
- P. Vissutipitukul, T. Aizawa, *Wear*, **259**, 482 (2005).
- U. Figueroa, O. Salas, and J. Oseguera, *Surf. Coat. Technol.*, **200**, 1786 (2005).