Advanced Plasma Nitriding for Aluminum and Aluminum Alloys

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Low hardness and wear resistance of aluminum alloys limit their use in practical application to automotive parts. Formation of hard aluminum nitride (AlN) layer on the surface can prolong the life time of aluminum automotive parts. Plasma nitriding was selected in the present study to form AlN layer on aluminum alloys. This processing is an environmental friendly method because of its low gas and energy consumption. Normal plasma nitriding requires long processing time to successfully form AlN layer. For advancing this surface treatment, refining microstructure and micro-alloying processes are proposed to activate the formation of AlN by plasma nitriding. Bulk Mechanical Alloying is used not only to make grain-size refinement but also to carry out micro alloying with addition of 1 mass% Ti. The formation rate of AlN layer is improved from $4.2 \times 10^{-5}$ μm/s to $20.8 \times 10^{-5}$ μm/s by microstructure refining. In particular, since the co-formed TiN with AlN works as a template in the initial state nitriding, the micro-alloyed aluminum can be nitried even without pre-sputtering.

(Received February 10, 2003; Accepted October 2, 2003)

Keywords: plasma nitriding, aluminum nitride, microstructure refining, enhancement of nitriding.

1. Introduction

How to reduce the environmental burdens is one of the most critical issues in industrial countries. Significant reduction of CO2 emission has become an essential issue in manufacturing of automotive components, since about 80-90% of CO2 emission comes from automobiles in using. Hence, automotive materials have to be carefully selected to reduce the environmental burden through minimizing energy consumption and exhausting CO2 or NOx gas. In the United States, the automotive companies have to reduce the vehicle exhaust emission, improve occupant safety, and enhance fuel economy according to government regulations. In order to meet this requirement, light weight alloys such as aluminum or magnesium alloys must be utilized for automotive parts instead of cast iron and copper. Aluminum alloys with high specific strength can be considered as an ecomaterial aiming to reduce the total weight of automotive. After Japan Aluminum Association (JAA), weight reduction of the automobiles directly leads to high reduction of fuel consumption as shown in Fig. 1. Every 10% weight reduction equals to 5.5% improvement of fuel economy. Recently, aluminum usages in automotive applications have grown by more than 80%. Total weight of aluminum in vehicle, which was only about 110 kg in 1996, is predicted to rise to 250-340 kg by 2015. In particular, aluminum alloys are applied for power-train parts such as engine blocks, piston, cylinder head or transmission and so forth.

Main limitations in the aluminum applications lie on its low hardness and wear resistance. There are many research groups, investigating various methods to increase the wear resistance of aluminum alloys. At present, Al-Si alloys having higher wear resistance than other alloys are used for power train or engine parts. The primary silicon and eutectic silicon must be controlled to be small-sized with spherical morphology in order to achieve high wear resistance without loss of machinability or high tensile strength. Otherwise hard layer must be formed on the top surface of aluminum alloy parts to achieve the sufficient wear resistance. One candidate is a thick oxide layer (Al2O3) formed by the anodizing method. Alumina coating has high surface hardness but the severe wear easily occurs due to its high friction coefficient. Aluminum nitride (AIN) is selected as an alternative candidate material to be formed on the top surface of aluminum because of its outstanding properties. It has high hardness (1400 HV), high thermal conductivity ($k = 319$ W/mK, theoretically at room temperature) as well as high electrical resistivity. AIN layer can be formed on aluminum by several methods: ion implantation, plasma immerse ion implantation (PIII), ball milling and other nitriding methods as listed in Table 1. More effective processing is necessary as an industrial reliable surface treatment for aluminum automotive parts.

In this present study, plasma nitriding was selected to form AIN layer on the surface of aluminum, making full use of its advantages: low gas and energy consumption, non toxicity and high possibility to extend its capability from laboratory scale to real industrial processing. In the normal plasma nitriding, however, long processing time is necessary including the long pre-sputtering time. From industrial point of view, the growth rate of AIN layer must be increased. The
refined microstructure contains large amount of grain boundaries, which act as a high diffusion path. Microstructure refining is firstly chosen as a method to enhance the AlN formation rate. Micro alloying of aluminum is also prepared to enhance the AlN formation even without the presputtering process. Bulk Mechanical Alloying (BMA) is employed for refining the microstructure and homogenizing the alloying element. Enhancement of inner nitriding in aluminum and aluminum alloys becomes the first breakthrough technique to improve the normal nitriding.

2. Experimental Procedure

2.1 Preparation of samples

Pure aluminum samples were prepared by three methods: casting, cold pressing and BMA for 1000 cycles. Cast aluminum samples were cut to a disk shape with the thickness of 8 mm and the diameter of 15 mm. The cold pressed samples were prepared from aluminum powders with the mean size of 33 μm and pressed under 870 MPa for 120 s. The cold pressed samples have a disk shape with 2 mm in height and 10 mm in diameter. The refined aluminum samples were prepared by BMA method, where the powder mixture was subjected to severe shear deformation. The standard cyclic loading pass schedule is consisted of two compression and one extrusion modes, as depicted in Fig. 2. In particular, large shear stress is transferred to materials in the forward extrusion mode during BMA, resulting in refinement of particle and grain size. For BMA samples, aluminum powders were mixed with 1 mass% of paraffin as lubricant. After BMA the samples were cold pressed and cut to size of 10 mm × 10 mm × 2 mm. Samples with Al-1 mass%Ti were prepared by cold pressing and BMA. Titanium powders with the mean size of 40 μm were mixed with aluminum powders prior to cold pressing. For BMA samples, the mixture was subjected to BMA in the similar way as the pure aluminum. All cast and BMA samples were polished until 1 μm diamond paste and rinsed in acetone before putting into nitriding chamber.

2.2 Plasma nitriding

Plasma nitriding chamber was evacuated by rotary and mechanical booster pumps to a base pressure less than 2.66 Pa (2 × 10⁻² Torr) in order to minimize the rest oxygen partial pressure in chamber. After that, pure nitrogen was filled into the chamber until the pressure reaches 133.3 Pa (1 Torr). The samples were heated up to the specified temperature by heater and glow discharge, simultaneously. At the specified temperature, glow discharge of nitrogen was generated by applying a bias voltage of 200 V to samples which were set on the table, acting as a cathode in this experiment. Pre-sputtering was employed to eliminate the surface oxide film by nitrogen plasma. N₂⁺ in the nitrogen plasma is an effective species for pre-sputtering. Holding time of pre-sputtering is 10.8 ks for pure aluminum sample. No pre-sputtering was employed for nitriding the Al-Ti alloy. After sputtering, nitrogen and hydrogen was filled into the chamber until the total pressure became 533.2 Pa (4 Torr). The applied bias voltage for glow discharge in plasma nitriding was set up 200 V with the current of 0.2 A. Samples were nitried for 72-252 ks (20-70 h) for pure aluminum, and 72 ks (20 h) for Al-Ti alloy. During nitriding, the gas was evacuated out by rotary pump to keep pressure in chamber constant. After nitriding, samples were cooled down to room temperature in hydrogen atmosphere. The standard nitriding conditions were listed in Table 2.
2.3 Characterization of nitrided sample

Formation of AlN by plasma nitriding was analyzed by the Grazing Incident X-ray Diffraction (GIXD) at the incident angle of 1°. The cross-sectional microstructure of nitrided samples was observed by optical microscope and Scanning Electron Microscope (SEM). Hardness was analyzed by Dynamic Hardness Tester (DHT) with the load of 0.1 g.

3. Results and Discussions

3.1 Normal plasma nitriding

The cast samples were nitrided for 72-252 ks with 10.8 ks pre-sputtering. The cross-sectional microstructure shows that the thickness of AlN layer is around 1-2 µm or less than 3 µm for 252 ks nitriding as shown in Fig. 3. The growth rate of AlN layer is very slow, approximately less than $4.2 \times 10^{-5}$ µm/s. The formation of AlN by normal plasma nitriding is controlled by diffusion process as had been reported in Ref. 16). Refs. 17) and 18) stated that the diffusion coefficient of nitrogen in aluminum at the temperature around 772 to 873 K ranges from $10^{-17}$ to $10^{-19}$ m²/s. Those diffusion coefficients of nitrogen in aluminum are far lower than that for iron, which is around $10^{-11}$ or $10^{-12}$ m²/s. Due to this low diffusion coefficient of nitrogen into aluminum, the growth rate of AlN by normal plasma nitriding becomes also very slow. Long processing time is necessary not only for pre-sputtering but also for nitriding. This nitriding procedure is not preferred to the industrial processing, when compared to the highly reliable and cost-competitive routes such as anodizing.

3.2 Accelerated AlN formation by microstructure refining

Particle and grain sizes were compared among three methods in Table 3: cast, cold pressed and BMA samples. The aluminum powder particle size was reduced from 30-40 µm to 15 µm by BMA. The grain size of BMA sample is around 1 µm which is much smaller than that of cast sample, 40 µm. As mentioned before, the shear stress was transferred to materials during BMA. This shear stress is high enough to cause elongation and fracture of powder particles. In this step, the refining of powder particles takes place together with agglomeration of the refined powder particles in the die during BMA. Although the particle size of agglomerated powder is still large for BMA powder, its grain size could be refined to have sufficient amount of grain boundary enhancing the nitrogen diffusion.

The GIXD profiles of nitrided pure aluminum are compared among three samples in Fig. 4. AlN was formed on the surface of all samples. However, the relative intensity of AlN peaks in the BMA sample is much higher than those in both cold pressed and cast samples. This means that the volume fraction of AlN formed on BMA sample is much larger than those in the cold-pressed and cast samples. The cross-sectional observation in Fig. 5 depicts that AlN layer thickness by the normal nitriding is around 3 µm in the cold pressed and cast samples. On the other hand, the thickness of
AlN layer formed on pure aluminum in BMA sample is more than 15 μm, even using the same pre-sputtering and nitriding condition. These results confirmed that the refined microstructure can enhance AlN formation. The refined microstructure contains high fraction of grain boundaries which act as a nitrogen high diffusion path.

In case of the small-grained materials, like BMA sample, the volume fraction of grain boundary becomes large by refining process. When the grain size is reduced, the increase of volume fraction of grain boundary becomes large by equations 1 to 4.

$$C = \frac{3\Delta}{d},$$

where C is the volume fraction of grain boundary, Δ, the average grain boundary thickness, and, d, the average grain size. Owning to Table 3, d = 1 μm for BMA sample and d = 40 μm for cast sample. The average grain boundary thickness both for cast and BMA samples is assumed to be the same. Then, the volume fraction of grain boundary for BMA sample is forty times higher than that of cast sample. In the BMA sample, the nitrogen diffusion along grain boundary dominates the growth of AlN while the volume diffusion of nitrogen plays an important role on the growth of AlN in the cast sample. Since the grain boundary is considered as a high diffusion path, the diffusion of nitrogen in BMA sample should be higher than the cast sample. The effective diffusion coefficient \(D_{eff}\) of materials with different fraction of grain boundary in any plane can be calculated by:

$$D_{eff} = D_l \frac{A_l}{A} + D_b \frac{A_b}{A},$$

where \(D_l\) is the diffusion coefficient of intra granular area, \(D_b\), the diffusion coefficient along the grain boundary, \(A\), the total area, \(A_l\), the intragranular area, and, \(A_b\), the grain boundary area. For material that is composed of only one phase, e.g. pure aluminum in this experiment, then \(A_b + A_l = A\). By substituting \(\frac{A_l}{A}\) by \(1 - \frac{A_b}{A}\) in the equation 2, then we can obtain

$$D_{eff} - D_l = \frac{A_b}{A} (D_b - D_l).$$

Assuming that \(X = \frac{A_b}{A}\) for the cast sample, the BMA sample has \(\frac{A_b}{A} = 40\%\). Based on the fact that \(D_l \ll D_b\), \(D_l\) in equation 3 can be neglected. By substituting value of \(\frac{A_b}{A}\) into equation 3, \(D_{eff}\) BMA sample becomes larger than \(D_{eff}\) cast sample by forty times. After Wagner’s theory or Ref. 21, the square of nitride layer thickness \((E^2)\) is proportional to \(D_{eff} \times t\), assuming that the dissolved nitrogen and solute atom concentrations are constant and other nitriding properties are indifferent to the diffusion paths. Here, \(t\) is the nitriding time. Then the ratio of nitride layer thickness for two samples is given by

$$\frac{E^{BMA}}{E^{Cast}} = \left(\frac{D_{eff}^{BMA}}{D_{eff}^{Cast}}\right)^{\frac{1}{2}},$$

at the same nitriding time. Since \(E^{Cast} \approx 3\ μm\), and, \(D_{eff}^{BMA}/D_{eff}^{Cast} = 40\), \(E^{BMA}\) is estimated around 19 μm. From Fig. 5(c), \(E^{BMA}\) was measured: \(E^{BMA} \geq 15\ μm\). Hence, high effective diffusion coefficient is attained in the refined microstructure by BMA by large amount of high diffusion paths, resulting in the formation of thicker AlN layer.

The DHT with low load was selected for hardness measurement in order to restrict the contact area between materials and indentation head in AlN layer. The measured...
hardness values for the aluminum matrix, the AlN layer surface and the inside of AlN layer in the cross-section, were listed in Table 4. The surface hardness of nitrided sample is remarkably higher than that for aluminum matrix. The hardness of the surface is around 1400 to 1500 Hv which is typical to the hexagonal AlN hardness. The surface hardness measured on the top surface is higher than the hardness measured in the cross-sectional AlN layer, especially for cast and cold pressed samples. Since the AlN layer is very thin in the cast and cold pressed samples, the deformation during the hardness measurement on the cross section may not be limited in the AlN area. Areas of both resin and aluminum matrix deformed together in the hardness testing, resulting in lower hardness. In the case of BMA sample, the hardness reaches 1400 Hv both on the top surface and the nitrided layer, since AlN is thick enough to eliminate the effect of resin and aluminum matrix.

The surface roughness plays an important role on homogeneous formation of AlN. The BMA and cast samples were surface polished until 1 μm by using diamond paste. The cold pressed sample was nitrided without this prior-polishing. AlN layer, formed on the BMA and the cast samples, has a more homogeneous surface than that of cold-pressed sample.

### 3.3 Micro alloying effect on AlN formation

In case of Al-1 mass% Ti alloys, GIXD profiles in Fig. 6 shows the coexistence of TiN and AlN on the nitrided sample surface for both cold pressed and BMA samples. The cross-sectional microstructure of 72 ks-nitrided samples was shown in Fig. 7. The nitride layer was successfully synthesized with the thickness up to 3 μm in BMA sample without pre-sputtering. There is no observation of nitrided layer on the cold-pressed surface. Coexistence of TiN with AlN assured that titanium, which was added to aluminum matrix, was also nitrided. The added titanium in aluminum has an effect on activation of AlN formation. After Ref. 21), the role of TiN in activation of the AlN formation is understood in the following. First, TiN is formed due to the high affinity of titanium to nitrogen. Secondly, cubic AlN, which has similar lattice constant to TiN \((a = 0.424 \text{ nm} \text{ for TiN JCPDS 38-1420 and } a = 0.412 \text{ nm} \text{ for cubic AlN JCPDS 25-1495})\), is subsequently formed just around the formed TiN particle. The cubic AlN is formed under the influence of close lattice parameter between cubic AlN and TiN. TEM observation reveals that the cubic AlN has been observed with TiN as a superlattice in (111) and (002). The misfit parameters \((f)\) are calculated from equation 5: \(^{(22)}\)

\[
f = \frac{2|d_1 - d_2|}{d_1 + d_2},
\]

where \(d\) is the interplanar spacing. From this eq. (5), the misfit parameters of TiN and cubic AlN is calculated to be
2.87% for (002) and 2.49% for (111) respectively. As reported in Ref. 23), the misfit parameters of hexagonal AlN grown from TiN are around 3.8% on (0001)AlN/(001)TiN and (1012)AlN/(001)TiN. With the smaller misfit parameter between cubic AlN and TiN, the formed TiN should work as a template for the formation of cubic AlN. Further growth of AlN takes place originating from the TiN. However, the cubic AlN has low stability. Therefore, after long processing time, cubic AlN with the initial coherency with TiN is replaced by the hexagonal AlN (a = 0.311 nm, c = 0.498 nm for hcp AlN) which is the most stable form of AlN.

4. Conclusion

Formation of AlN on aluminum and aluminum alloys is activated by microstructure refining and micro alloying. This enhancement by microstructure refining might be because of the grain boundary diffusion of nitrogen in AlN. The growth rate of nitrided layer is limited by less than $4.2 \times 10^{-5}$ μm/s in the case of normal nitriding for cast and cold pressed aluminum. The formation rate of nitride layer is accelerated up to $20.8 \times 10^{-5}$ μm/s by this microstructure refining. Addition of titanium assisted the inner nitriding of aluminum even without pre-sputtering before nitriding. AlN layer can be formed up to 3 μm in thickness by co-precipitation of TiN with AlN.

Acknowledgements

Authors wish to express their gratitude to Mrs. N. Ise, Research Institute for Applied Science, and Mr. N. Granito, Graduated School of Engineering, The University of Tokyo, for their help in using GIXD and nitriding apparatus. The authors are also indebted to Mr. Nakamura, Department of Metallurgical Engineering, The University of Tokyo, for his help on XPS. This study is financially supported in part by the Grand-in Aid from MEST with the contract number #12305047, and, by the national project on the Barrier-Free Processing.

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