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Plasma nitriding of Al 99.5

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Abstract

Aluminium nitride (AlN) is a very interesting ceramic because of its combination of properties such as high thermal stability, high hardness and an unusual combination of high thermal and low electrical conductivity. But it is very difficult to obtain an AlN layer on the aluminium substrates by thermochemical nitriding process. Since a thin film of aluminium oxide existing on the surface of every aluminium substrate prevents the nitrogen atoms from diffusing into the aluminium lattice. However, it is possible to sputter the oxide film away from the aluminium surface in a glow discharge with the use of plasma nitriding technique and to allow the formation of AlN layer on the aluminium bulk.

In the present work specimen of aluminium Al 99.5 has been plasma nitrided in a modified plasma nitriding unit, in which a diffusion pump was used to obtain an especially low partial pressure of oxygen in the vacuum chamber. The sputter-cleaning prior to the nitriding was conducted with the variation of the applied voltage and the sputtering time. The plasma nitriding after sputtering was carried out in a glow discharge of pure nitrogen. The metallurgical properties of the AlN-Al-composites were characterized in detail. The results show that shiny black AlN layers with thickness up to a few micrometers have been created on the surface of aluminium and so the enhancement of wear and corrosion resistances of the substrate can be obtained.

1. Introduction

Nitriding of steel is a widespread thermochemical heat treatment process used in manufacturing industries. Important advantages of plasma nitriding, compared to other nitriding processes are as follows: possibility to depassivate the surfaces with a plasma assisted pre-treatment; shorter cycle times and lower treatment temperature; lower energy and gas consumption; no environmental pollution. Investigations have shown that not only ferrous metals, but also non-ferrous metals like titanium alloys or nickel alloys can be successfully plasma nitrided. On the other hand, plasma nitriding of aluminium alloys without pre-treatment fails because of the thin layer of aluminium oxide (Al_2O_3), which exists on the surface of every aluminium material and prevents the nitrogen atoms from diffusing into the aluminium bulk. Plasma nitriding of aluminium is therefore only possible, as shown by Arai *et al.* /1/, if the Al_2O_3 layer is removed by a sputtering process prior to plasma nitriding.

Because of their low specific gravities and good machinabilities compared with those of ferrous materials, aluminium alloys have attracted great interests in the industrial applications. But their practical uses are restricted for lack of appropriate surface hardening processes. Therefore, one of the salient points derived from a world-wide survey of about 2000 plasma heat treatment shops was that how the plasma nitriding of aluminium could be made easier, since a enormous market was assumed from the commercial realization of plasma nitriding of aluminium /2, 3/. In spite of this prospect, however, few detailed knowledge of AlN layers on the aluminium substrates produced by plasma nitriding has been drawn and so that further experiments must be made, before this technique be accepted for industrial applications. For these reasons, the authors studied at present work the plasma nitriding of aluminium. The efforts were put mainly on the metallurgical characterization of the surface morphology after sputtering and the microstructure of the AlN layers after plasma nitriding. The tribological and corrosive behaviours of the AlN layers on the aluminium substrate were also analysed.

2. Experimental details

A pure aluminium Al 99.5 (1050) with chemical composition of 0.25Si, 0.4Fe, 0.05Cu, 0.05Mn, 0.05Mg, 0.07Zn, 0.05Ti (wt.-%) was used as substrate. Specimens were machined to the size of $\varnothing 49.5 \times 12$ mm. Before treatment they were ground with SiC paper, polished with 1-3 μm diamond powder polish solution and then cleaned with ethanol.

Experiments were carried out using a commercial 20 kW (1 kV \times 20 A) plasma nitriding unit with pulsating DC glow discharge (Fig. 1a). In the experiment, the pulse and pause interval were varied from 20 to 200 μs . The size of the vacuum chamber is about $\varnothing 0.6 \times 1.0$ m. An auxiliary heating ($\varnothing 0.4 \times 0.3$ m, maximum power 4 kW) allows to heat the specimen up to the range of 200-250 $^{\circ}\text{C}$. An oil diffusion pump was used to evacuate the chamber prior to the pre-treatment, so that a base pressure of 10^{-3} to 10^{-4} Pa and therefore very low partial pressures of O_2 and H_2O in the chamber could be achieved. Highly purified gases (N_2 , H_2 and Ar) with qualities of 99.996-99.999% were used. The substrate temperatures were controlled with an electrically isolated thermocouple.

As shown in Fig. 1b, the whole process of plasma nitriding was carried out in following steps: 1) Evacuation and pre-heating with auxiliary heating up to 200-250 $^{\circ}\text{C}$. 2) Heating with the help of glow discharge up to desired substrate temperature. The heating rate was controlled within 3-4 $^{\circ}\text{C}/\text{min}$. 3) Pre-treatment with pure Ar (1.4-2 l_n/min) or gas mixture of Ar (1.4-2 l_n/min) and H_2 (0.4-0.6 l_n/min) at a pressure of $0.4\text{-}2.0 \cdot 10^2$ Pa (0.4-2.0 mbar) with applied voltage of 400-800 V and sputtering time of 0.5-2 h. 4) Plasma nitriding with pure nitrogen at a pressure of $2\text{-}3 \cdot 10^2$ Pa with applied voltages of 600 ± 50 V, the temperatures for nitriding were controlled within 480 ± 5 $^{\circ}\text{C}$. 5) After nitriding, the specimens cooled down in the evacuated chamber.

The specimens were analysed with XRD (Cr- K_{α}), SEM, ESCA, light metallography (LM) and Vickers hardness measurement with a load of 10 g (HV 0.01). Two methodes were used for the testing of the tribological behaviour: 1) Scratch test with following conditions: $r_{\text{diamond}} = 0.2$ mm, $v_{\text{load}} = 0.1$ N/s, $v_{\text{scratch}} = 0.1$ mm/s, $F = 0\text{-}10$ N, no lubricante was used. 2) Pin-on-disc test with the use of untreated and plasma nitrided specimens as discs and with following condition: 100Cr 6 (DIN) coated with TiN were selected as pins with $r_{\text{pin}} = 5$ mm, $F = 1.8$ N, $v_{\text{pin}} = 3.8$ m/min and no lubricante was used; the volume loss on the discs after the wear test was calculated from the width and depth of the wear scars. Finally, the corrosion resistance of the specimens was tested with dipping-method in an acid medium, 1n-HCl solution, at ambient atmosphere and temperature.

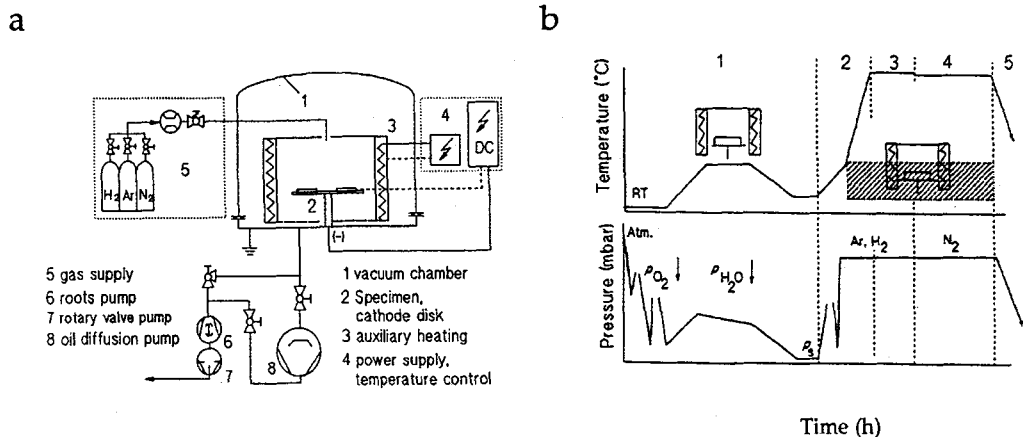


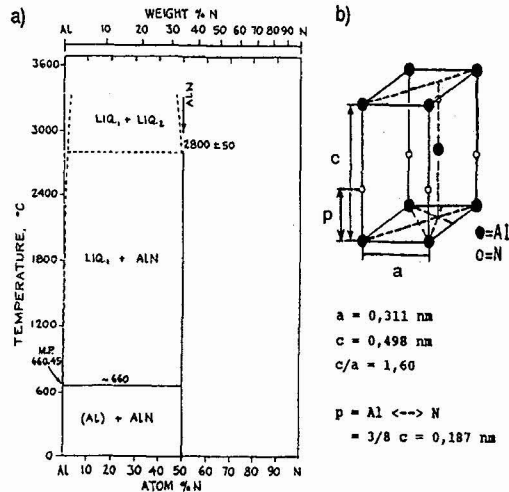
Fig. 1: Schematic diagram of the experimental apparatus (a) and the plasma nitriding process (b)

3. Results and discussions

A. The phase system of Al-N

Only a stable aluminium nitride (AlN) exists in the Al-N binary phase diagram, as shown in Fig. 2a after Moffatt /4/. The AlN lattice was confirmed to have a hexagonal ZnS (wurtzite)-type (Fig. 2b), as given in a detail summary by Wriedt /5/.

Fig. 2: The Al-N phase diagram (a) and the hexagonal structure of AlN lattice (b)



B. Sputtering prior to plasma nitriding

The sputtered aluminium surface shows in Fig. 3-4 a very high roughness. Not only temperature and time, but also applied voltages and pressure play an important role by sputtering. At a lower temperature, longer sputtering time was needed to achieve a similar sputtering effect on the surface. The sputtering of aluminium in a glow discharge of argon is essentially a destroy process for the surface quality. In order to take the aluminium oxide away from the surface but at the same time to reduce this undesirable surface destruction effect, following sputtering conditions were selected: A gas mixture of Ar-50±10vol.%H₂ with gas flow rate of 2-2.5 l_n/min were used. The other parameters were voltage $U=600\pm 50 \text{ V}$, time $t=1\pm 0.5 \text{ h}$ (within temperatures of $480\pm 20 \text{ }^\circ\text{C}$).

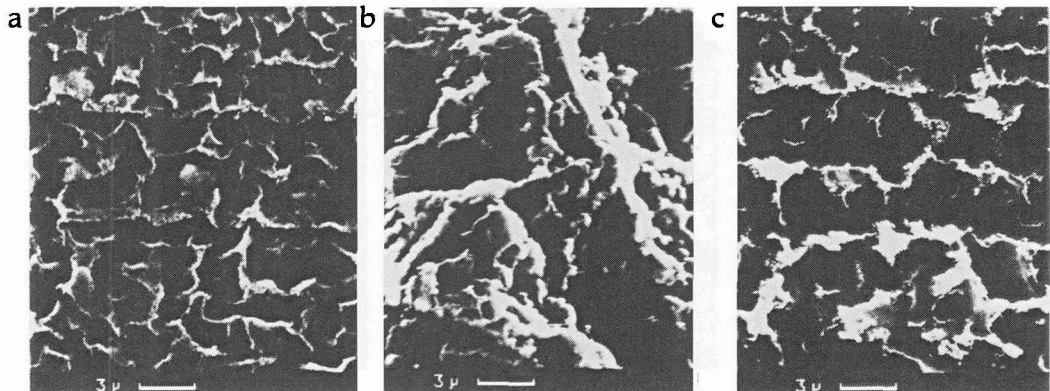


Fig. 3: SEM-photographs, the specimens were sputtered with pure Argon at 500 °C for 1 h with applied voltages/pressure (V/mbar) of 400/1 (a), 600/0.8 (b) and 800/0.4 (c)

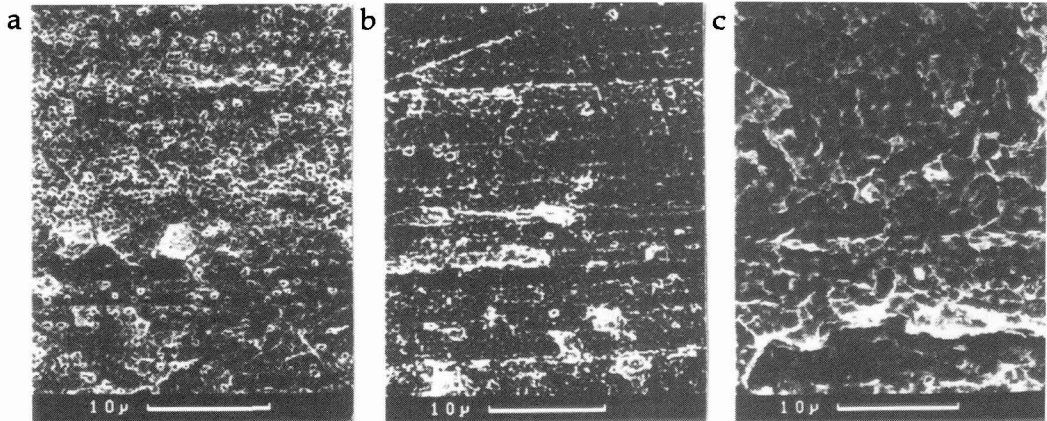


Fig. 4: SEM-photographs, the specimens were sputtered with pure Argon and with applied voltages of 600 V at 400 °C for 0.5 h (a), 1 h (b) and 2 h (c)

C. Plasma nitriding and metallurgical analysis

The surface of the aluminium specimen after plasma nitriding shows visually a shiny black colour. The microhardness of the layers measured on the micrograph was in the range of 600-1000 HV. Fig. 5-6 present the surface morphologies and the microstructure of specimens after sputtering and nitriding. It can be seen that after 2 h of nitriding the AlN layer is not yet compact whereas after 3 h of nitriding a homogeneous layer has developed. This is probably because the diffusion of nitrogen in an aluminium bulk is not homogeneously, since the diffusivity of nitrogen atoms is greater along the grain boundaries as in the aluminium grains. Therefore it takes some time to obtain a continuous AlN layer. It was also found that the temperature played an important role during plasma nitriding of aluminium. Partial melting on the surface occurred easily at a too high temperature, due to the low melting point of aluminium. On the other hand, an AlN layer with good macroscopical uniformity could be hardly achieved if the nitriding be carried out at too low temperature. It is confirmed that the suitable nitriding temperature for Al 99.5 was in the range of 480 ± 20 °C.

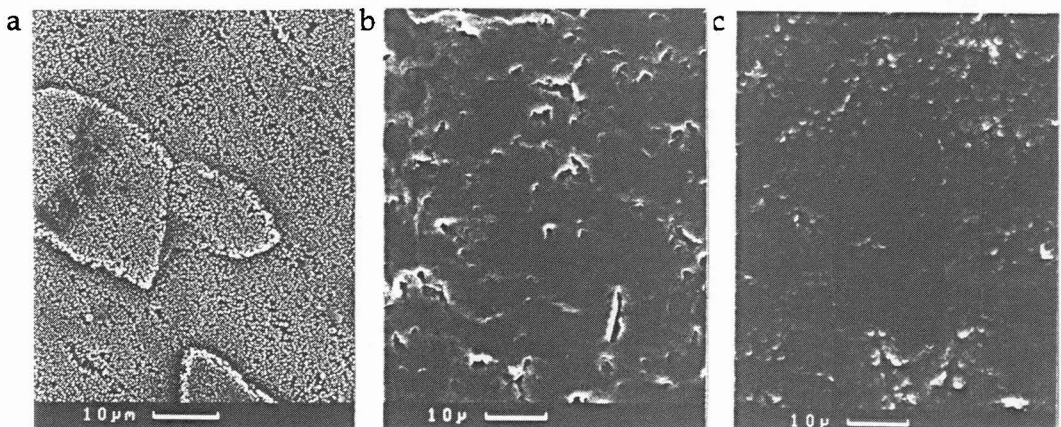


Fig. 5: SEM-photographs, the specimens were sputtered for 1 h with a gas mixture of Ar and H₂ (a), and then plasma nitrided for 2 h (b) and 3 h (c) at 480 °C

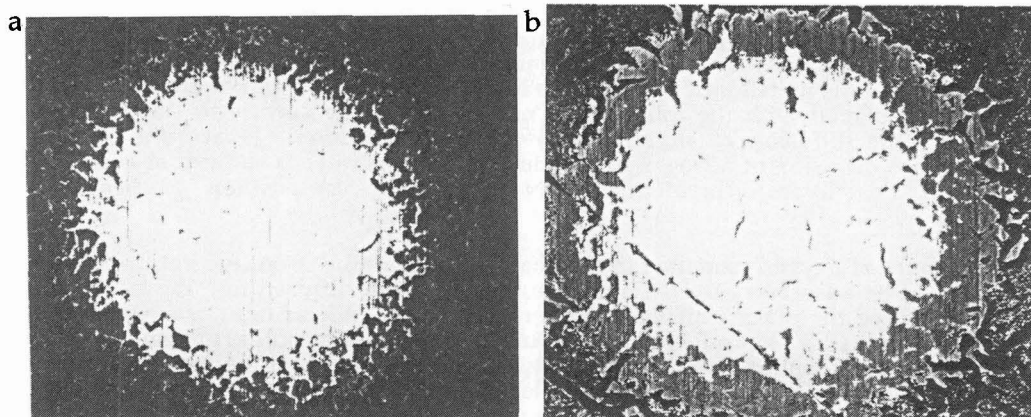


Fig. 6: LM-fotographs (spherical section), the specimens were plasma nitrided for 2 h (a) and 3 h (b) at 480 °C

100 μm

The XRD pattern of the plasma nitrided specimen in Fig. 7 shows not only the reflexes of fcc aluminium substrate, but also the additional reflexes caused by aluminium nitride compound corresponding to the hexagonal AlN lattice. This result coincide well with the fact shown in Fig. 2 according to Moffatt /4/ and Wriedt /5/, i. e. in the Al-N binary phase diagram only the existence of a stable AlN compound has been proved.

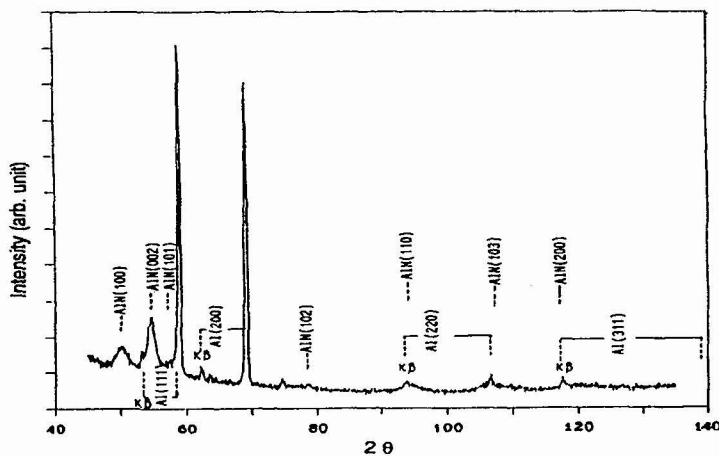


Fig. 7: XRD pattern of a plasma nitrided specimen with a 3 μm AlN layer

A sharp boundary between the dark aluminium nitride layer and the bright aluminium substrate in Fig. 8 indicates that there is no existence of diffusion zone beneath the AlN layer. But an interesting phenomenon revealed from the ESCA analysis of this specimen in Fig. 9a shows that two forms of aluminium coexist in the AlN layer. One is the free aluminium with a binding energy (E_b) of 72.5 eV and the other is the aluminium combined with nitrogen, i. e. AlN, with a E_b of 73.9 eV. Additionally, the nitrogen exists in form of AlN with a E_b of 396.9 eV shows in Fig. 9b. This finding here make a distinguish difference in comparison with that of Meletis and Yan at a similar study /6/,

in which the existence of another type of Aluminium nitride in form of a fcc- Al_3N has been assumed. Quantitative ESCA profile analysis, made also on this specimen and illustrated in Fig. 10, shows the existence of composition gradient and hypostoichiometry in the AlN layer. This metallurgical phenomenon indicates that the growth of the AlN layer must be accompanied with the diffusion of nitrogen from the surface to the interior material and the diffusion of aluminium in the other direction. On account of the inhomogeneous diffusion of nitrogen in the aluminium substrate, as showed above, the existence of this hypostoichiometrical AlN layer with composition gradient is explainable.

A small amount of oxygen remained in the chamber and coming from the impurities of the gase could be adsorbed onto the aluminium surface and diffused into the lattice of aluminium during the plasma nitriding. As a result, a negligible amount of oxygen has been detected in the ESCA profile in Fig. 10. During the plasma nitriding, there would be a competition of adsorption and diffusion between the nitrogen and the oxygen on the aluminium substrate. To enable a successful plasma nitriding of aluminium, the negative effect of oxygen on the surface of aluminium must be reduced. A very low partial pressure of oxygen in the vacuum chamber had to be ensured for this reason. Otherwise, the oxidation of the aluminium surface would become predominant and no satisfactory AlN layer could be formed, as the case by our pre-experiment performed at a conventional plasma nitriding unit with a relatively high partial pressure of oxygen.

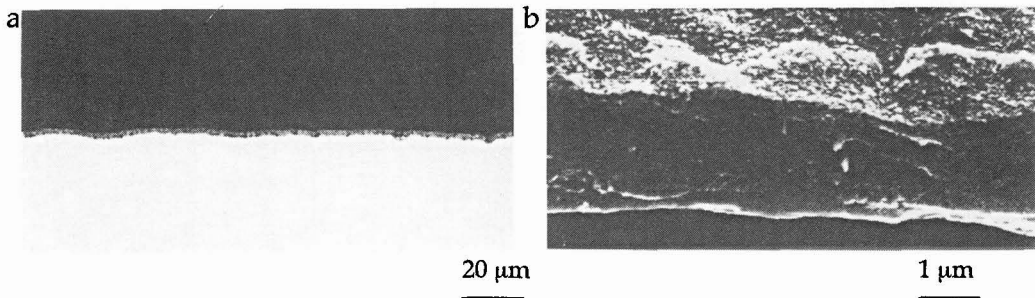
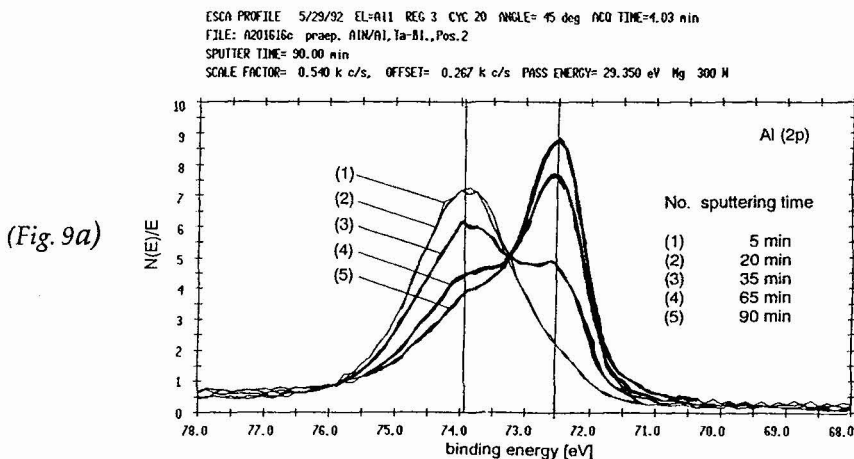


Fig. 8: a) LM-photograph, b) SEM-fractograph, the specimen was nitrided at 480 °C for 3 h



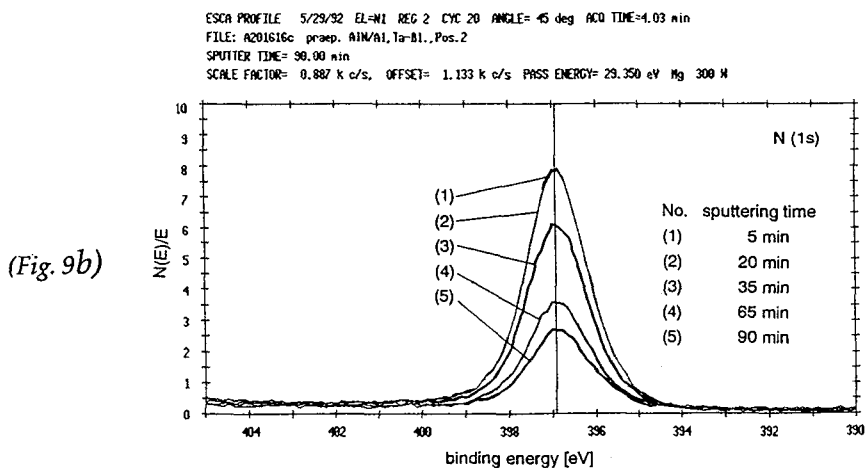


Fig. 9: ESCA analysis made on a specimen plasma nitrided at 480 °C for 3 h, sputtering conditions: Ar^+ -ions, $p = 1$ mbar, $U = 4$ kV, $\varnothing = 45^\circ$,
 a) Relationship between the Al(2p) signal and the sputtering time,
 b) Relationship between the N(1s) signal and the sputtering time

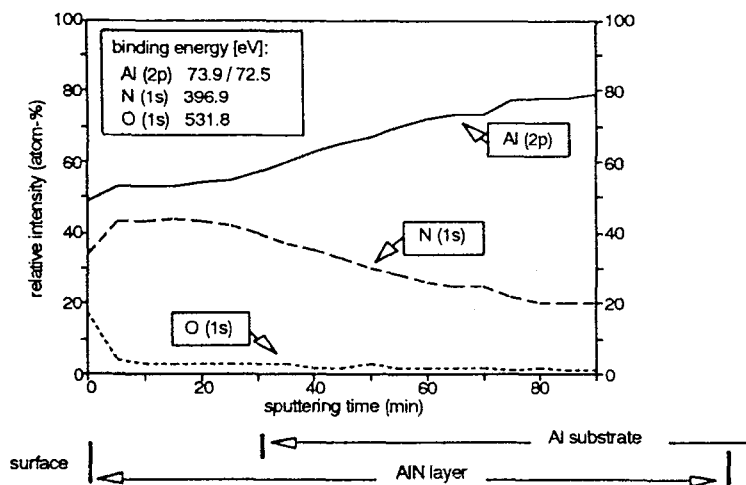


Fig. 10: ESCA profile of a specimen plasma nitrided at 480 °C for 3 h (sputtering conditions were the same as that in Fig. 9)

Scratch test was made on a plasma nitrided specimen with a 3 μ m AlN layer. It has been proved that a critical load (L_c) for the judgement of the adherence of the AlN layer could not be determined with this method. Cracking of the AlN layer occurred almost immediately after the load had been put on the diamond head and the latter began to penetrate into the aluminium substrate through the cracked layer. Fig. 11 show the SEM-

photographs taken from the scratch scar, at which a load of about 2.5-5 N has been applied on the AlN layer. The low ability of the AlN layer to withstand the penetration of the diamond head in the scratch test can be considered due to the extremely soft aluminium substrate underneath the AlN layer as well as the relatively thin AlN layer of only 3 μm .

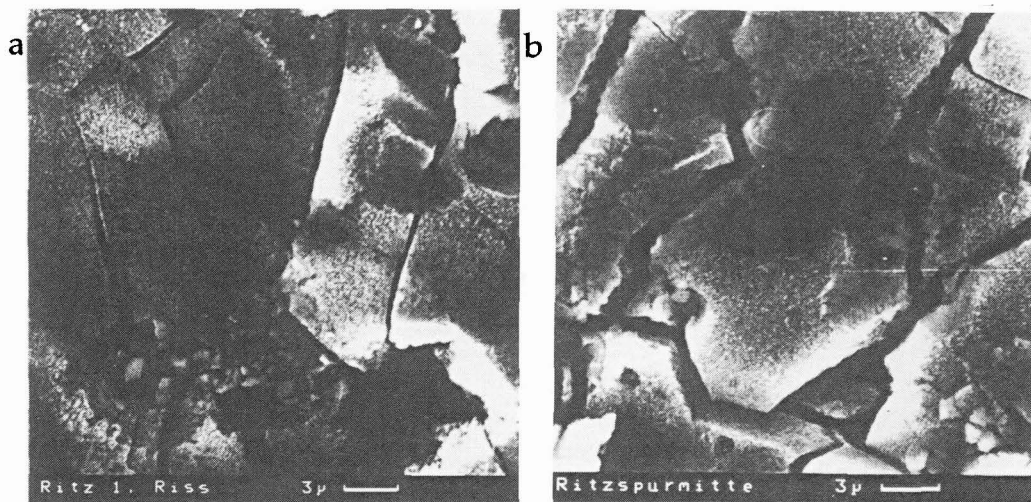


Fig. 11: SEM-photographs made on the scratch scar, the specimen with a 3 μm AlN layer was subjected to a load of 2.5 N (a) and 5 N (b) at the scratch test

The wear resistance of the AlN layers was examined with a pin-on-disc tester, at which a small load of 1.8 N was used. The result given in Fig. 12 shows a significant enhancement of the wear resistance of a plasma nitrated Al 99.5 specimen. An improvement of the corrosion resistance of Al 99.5 specimen in an acid medium, i. e. 1n-HCl solution, was achieved with the plasma nitriding, too (Fig. 13). These results show that under proper conditions the plasma nitriding can be applied to improve the wear and the corrosion resistances of the Al 99.5 substrate to some extent.

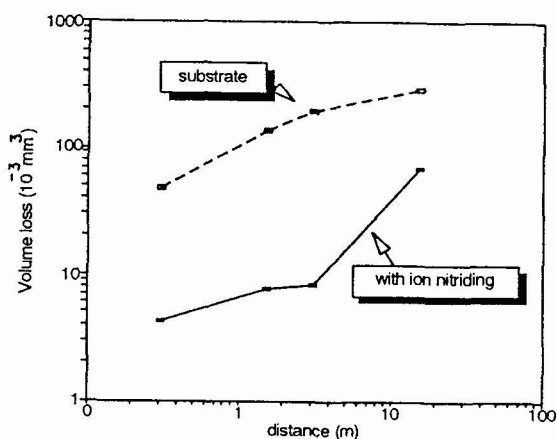


Fig. 12: Pin-on-disc test, relationship between the volume loss and the wear distance, substrate: untreated Al 99.5 and with plasma nitriding at 460 °C for 6 h to obtain a 2 μm AlN layer

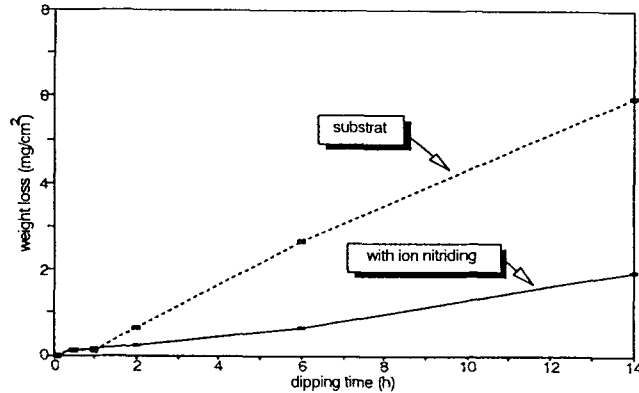


Fig. 13: Corrosion test in 1n-HCl, relationship between dipping time and weight loss, substrate: untreated Al 99.5 and with plasma nitriding at 460 °C for 6 h to obtain a 2 μ m AlN layer

4. Summary

1. AlN thin layers with hexagonal lattice and visually shiny black colour are formed on the Al 99.5 specimens by plasma nitriding performed at a modified plasma nitriding unit. To form an AlN layer on the Al 99.5 substrate successfully, an especially low partial pressure of oxygen in the vacuum chamber must be ensured and this is achieved through the lowering of the basic pressure of the vacuum chamber.

2. A proper combination of process parameters both in the sputtering and in the nitriding, in which the most important aspects are the temperature and time, must be chosen, so that very hard and well adhesive AlN layers with a thickness up to about 3 μ m can be obtained. It is assumed from the existence of the composition gradients of aluminium and nitrogen and the hypostoichiometry in the AlN layers that the growth mechanism of AlN layer in plasma nitriding could be a diffusion controlled process.

3. The AlN layers significantly increase the wear resistance of the aluminium substrate under a small load. An improvement of the corrosion resistance of the Al 99.5 substrate in an acid medium (1n-HCl solution) can be achieved by plasma nitriding as well.

5. Acknowledgements

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6. References

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