

## Surface modification of aluminium - lithium alloy using prenitriding option and $\text{Si}_x\text{N}_y$ coating deposition

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### Materials

#### ABSTRACT

**Purpose:** EU directive of CO<sub>2</sub> emission reduction causes many applied technologies to become unprofitable considering environmental protection. Due to that, there is an urgent need to create new or modify existing technological solutions - especially in the field of materials engineering. One of the options to reduce CO<sub>2</sub> emission is replacement of parts made of steel by Aluminium -Lithium alloys mainly in such branches like automotive and aircraft industry.

**Design/methodology/approach:** Pre-nitriding option was carried out in low pressure plasma discharge mode, at a substrate temperature below 200°C followed by the deposition of 500 nm thick  $\text{Si}_x\text{N}_y$  coating. Morphology and mechanical properties were compared with substrate without pre-nitriding treatment.

**Findings:** In this paper, first promising results of surface treatment with the use of pre-nitriding option of Al-Li alloy are presented. The results showed that the wear resistance of the Al-Li alloy may be modified by application of plasma enhanced CVD [1-4]. Two different types of surface modification were applied.

**Research limitations/implications:** In case of vehicles' parts, subjected to wear or/and contact fatigue a use of light weight alloys gives rise to many difficulties, caused by their low surface parameters. The aluminium alloys applied for elements operated in wear contact even with the best possible mechanical properties at the moment, it is limited due to still not enough tribological properties. The research in this field may bring another reduction of vehicles total weight.

**Practical implications:** At present, ultra light materials with high durability are elaborated for components, e.g. in automotive industry mainly to realize a light gearbox.

**Originality/value:** Functional Gradient Coatings (FGC) was deposited below temperature which could cause destruction of "tailored" structure of the substrate.

**Keywords:** Aluminium alloy; Pre-nitriding;  $\text{Si}_x\text{N}_y$  coating

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## 1. Introduction

Reducing vehicle weight for limiting energy consumption, in particular mass reduction of engine parts, is one of the most important challenges in the field of modern transport, especially in automotive and aircraft industry [1-4]. Low density materials like titanium, aluminium and magnesium, mentioned above, have a significant and promising potential as a substitute for steel. One of the modern materials ranked among a group of high-advanced ultra light materials is aluminum-lithium alloy. Al-Li is distinguished by reducing density without decreasing strength, toughness, corrosion resistance [5].

However, forming  $Al_2O_3$  on the surface, it is affected by high Al reactivity with oxygen causing wear increase. This phenomenon is generated mainly due to porosity and poor adhesion of  $Al_2O_3$  to the substrate. From scientific literature analysis, it follows that this disadvantage can be overcome by surface modification using such processes like [6]: physical vapour deposition (PVD), plasma assisted chemical vapour deposition (PACVD) [7], magnetron sputtering, ion implantation [8], pulse laser deposition (PLD) [9-11], fluidized bed [15], thermal spraying, [12, 13]. However, only few of them seem to be useful due to structure sensitivity of aluminum alloys to deposition temperature over 200°C.

Independently, a special emphasis is given to plasma nitrided of aluminum alloys reported by [14-17]. Applied ion bombardment could involve sputtering of the substrate to remove  $Al_2O_3$  and accelerate reaction of nitride ions with bare substrate. However, due to close packing of aluminum alloys' unit cell, and from physicochemical point of view, it is very difficult to receive relatively deep concentration profile of nitride solid solution with thin AlN layer on the surface. In contrast to this, mainly AlN layer is formed which could cause discontinuity of mechanical properties between layer and substrate. Additionally, in the light of presented results, it seems that to overcome tribological problems of Al alloys it is necessary to apply Functional Gradient

Coatings (FGC) below the temperature which could cause destruction of "tailored" structure on the substrate. In our opinion the point was left without due consideration.

The aim of this work was to improve the lightweight alloys properties on the way of application the low pressure processes for surface modification of aluminum lithium alloy. The improvement of properties of treated Al-Li substrates was proved by series of studied including nanohardness, SEM and AFM investigations.

## 2. Experimental

The material used in this work was Al 2wt.%Li alloy. The surface of the samples was modified using Radio Frequency Chemical Vapour Deposition technique (13.56 MHz, 300 W) with application of  $N_2$  and  $SiH_4$  as nitrogen and silicon precursors.

The prenitriding and  $Si_xN_y$  coating deposition were carried out in RFCVD equipment. Table 1 presents designations of an unmodified sample (Process 1) with  $Si_xN_y$  coating (Process 2) and after nitriding pre-treatment and  $Si_xN_y$  coating deposition (Process 3). To remove oxygen from the surface, each deposition process was started with argon-plasma etching. The sample I was pre-treated and then nitrogenated with nitrogen plasma. The sample II was subjected to the following sequence of stages. Firstly, it was pre-treated and nitrogenated (in the same way as the sample I). Then, it was once more subjected to Ar-plasma etching and finally, a- $SiN_x$ : H layer was deposited with application of  $SiH_4/N_2/Ar$  gas mixture. The sample III was covered with a- $SiN_x$ : H layer deposited directly onto pre-treated alloy surface. Various  $SiH_4/N_2$  ratios were applied for the samples II and III. Table 1 presents designations of an unmodified. The processing parameters: flow of gas-mixture components, substrate temperature –  $T_s$ , gas pressure in the chamber –  $p$ , plasma RF generator power –  $P_{RF}$  and time of deposition –  $t$ , were precisely controlled (Table 1).

Table 1.  
Technological parameters of RF CVD applied in the Al-Li alloy surface modification

| Sample | Process                           | Gas flow [cm <sup>3</sup> /min] |       |                | $T_s$ [K] | $p$ [Pa] | $P_{RF}$ [W] | $t$ [s] |
|--------|-----------------------------------|---------------------------------|-------|----------------|-----------|----------|--------------|---------|
|        |                                   | Ar                              | $N_2$ | $SiH_4/N_2/Ar$ |           |          |              |         |
| I      | 1. Ar-plasma etching              | 200                             | -     | -              | 320       | 53.3     | 40           | 1200    |
|        | 2. Nitrogenation                  | -                               | 80    | -              | 465       | 93.3     | 100          | 7200    |
| II     | 1. Ar-plasma etching              | 200                             | -     | -              | 500       | 53.3     | 8            | 600     |
|        | 2. a- $SiN_x$ :H layer deposition | -                               | -     | 8/24/80        | 500       | 53.3     | 50           | 480     |
| III    | 1. Ar-plasma etching              | 200                             | -     | -              | 320       | 53.3     | 40           | 1200    |
|        | 2. Nitrogenation                  | -                               | 80    | -              | 465       | 93.3     | 100          | 720     |
|        | 3. Ar-plasma etching              | 200                             | -     | -              | 500       | 53.3     | 8            | 600     |
|        | 4. a- $SiN_x$ :H layer deposition | -                               | -     | 8/16/80        | 500       | 53.3     | 50           | 480     |

### 3. Results and discussion

Figures 1a, b show SEM images of Al-Li metallographic cross-sections of samples with  $\text{Si}_x\text{N}_y$  coating without and with prenitriding treatment. It is visible that the 500 nm thick coating has a uniform and dense structure. Nanoindentation test revealed that prenitriding treatment of Al – Li alloy caused increase nanohardness after  $\text{Si}_x\text{N}_y$  coating deposition to about 10.8 GPa comparing with sample with  $\text{Si}_x\text{N}_y$  coating only – 8.0 GPa (Figure 2). From an average grains height analysis, it results that during coating deposition after prenitriding, on the sample smaller (about two times in diameter) grains are formed in comparison with the sample without nitriding pre-treatment (Figure 3). Our experiments point out that when using both: the fine crystalline structure of the coating and prenitriding treatment enhance the hardness of the coating (Process 3). During prenitriding treatment, the surface Al – Li alloy is strongly activated and more preferable sites for crystallization of  $\text{Si}_x\text{N}_y$  grains are available.

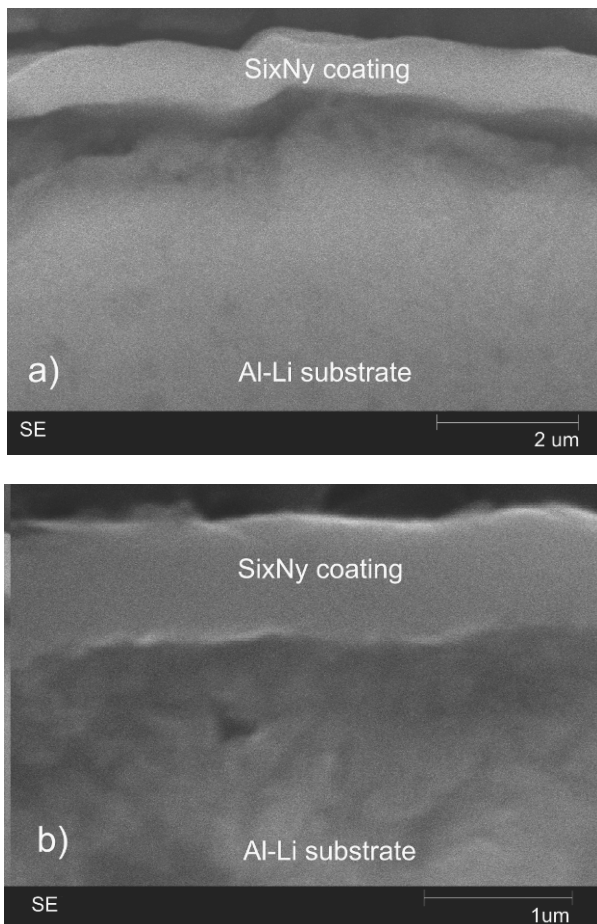


Fig. 1. SEM images of Al-Li metallographic cross-sections with  $\text{Si}_x\text{N}_y$  coating (sample 2) (a) without and (b) with prenitriding treatment (sample 3), respectively

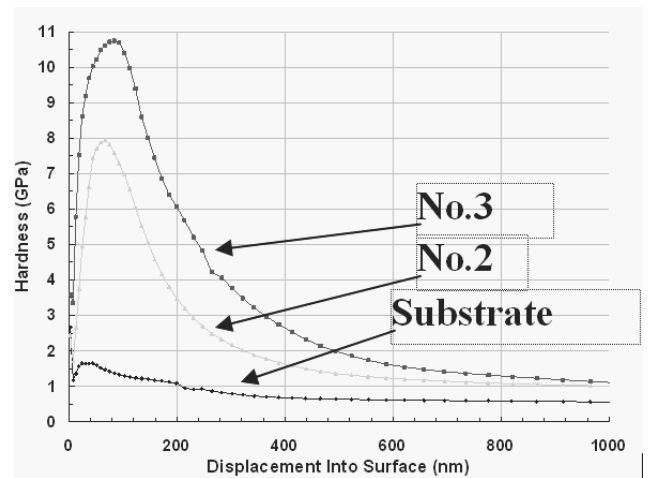


Fig. 2. Microhardness profiles of Al-Li substrate; blue line - bare substrate; yellow line - after  $\text{Si}_x\text{N}_y$  coating deposition (sample 2); pink line - after prenitriding treatment and  $\text{Si}_x\text{N}_y$  coating deposition (sample 3), respectively

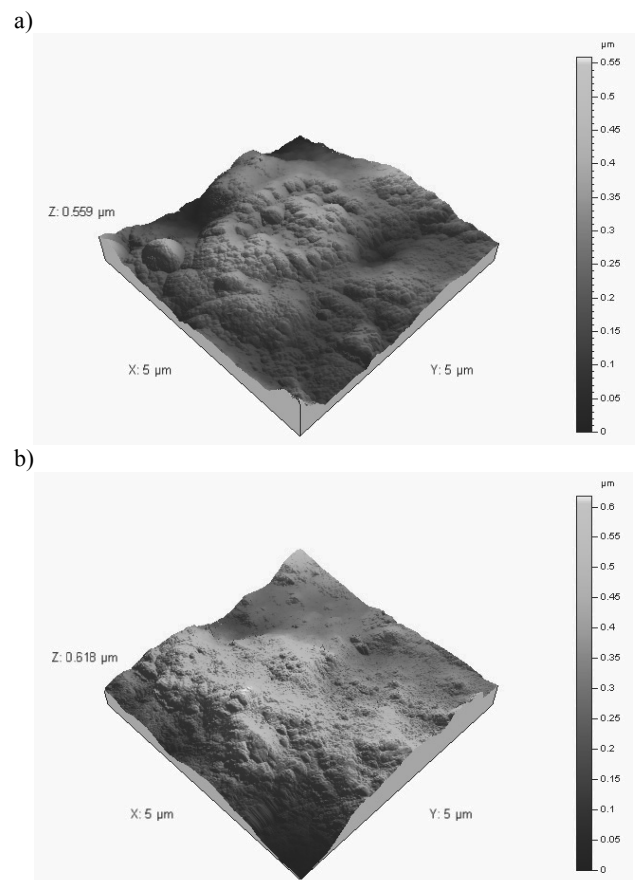


Fig. 3. AFM images of Al-Li substrate (a) after  $\text{Si}_x\text{N}_y$  coating deposition – (sample 2); (b) after prenitriding treatment and  $\text{Si}_x\text{N}_y$  coating deposition - (sample 3), respectively

## 4. Conclusions

The present results show that RFCVD method allows to produce homogeneous thin  $\text{Si}_x\text{N}_y$  coating. Applying prenitriding option causes decrease in grains size and increase in hardness of  $\text{Si}_x\text{N}_y$  coating comparing to the sample without prenitriding, what can influence on increase of wear resistance [19]. It is a promising method to enhance mechanical properties of aluminium alloy surface without destruction of “tailored” structure of the substrate because temperature of deposition is below 200°C. However, more experiments need to be done to optimise mechanical properties and clarify prenitriding influence.

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## References

- [1] W.S. Miller, L. Zhuang, J. Bottema, A.J. Wittebrood, P. De Smet, A. Haszler, A. Vieregge, Recent development in aluminium alloys for automotive industry, *Metal Science and Engineering A280* (2000) 37-49.
- [2] A. Heinz, A. Haszler, C. Keidel, S. Moldenhauer, R. Benedictus, W.S. Miller, Recent development in aluminium alloys for aerospace applications, *Metal Science and Engineering A280* (2000) 102-107.
- [3] P. Mrva, D. Kottfer, Evaluation of Thickness Influence of Coating onto Thermal Expansion of Titanium Alloy, *Výrobné Inžinierstvo* 4 (2007) 21-22 (in Slovak).
- [4] P. Mrva, D. Kottfer, Research of Mechanical Pre-treatment of Titanium Alloys VT-18 Surfaces Based on Shot Peening in Aviation Engineering, *Výrobné Inžinierstvo* 3 (2007) 69-72 (in Slovak).
- [5] S. Michna, I. Lukac, P. Louda, V. Ocenasek, H. Schneider, J. Drapala, R. Koreny, A. Miskufova, *Aluminium material and Technologies from A to Z*, Presom, 2007, Czech Republic.
- [6] A.M. Merlo, The contribution of surface engineering to the product performance in the automotive industry, *Surface and Coatings Technology* 174-175 (2003) 21-26.
- [7] S. Gredelj, S. Kumar, A.R. Gerson, P. Cavallaro, Radio frequency plasma nitriding of aluminium at higher power levels, *Thin Solid Films* 515 (2006) 1480-1485.
- [8] D. Manowa, S. Mandl, B. Rauschenbach, Evolution of surface morphology during ion nitriding of aluminium, *Surface and Coatings Technology* 180-181 (2004) 118-121.
- [9] A.L. Thomann, E. Sicard, C. Boulmer-Leborgne, C. Vivien, J. Hermann, C. Andreazza-Vignolle, P. Andreazza, C. Meneau, Surface nitriding of titanium and aluminium by laser-induced plasma, *Surface and Coatings Technology* 97 (1997) 448-452.
- [10] E. Sicard, C. Boulmer-Leborgne, T. Sauvage, Excimer laser induced surface nitriding of aluminium alloy, *Applied Surface Science* 127-129 (1998) 726-730.
- [11] L. Pawlowski, Thick Laser Coatings, *Journal of Thermal Spray Technology* 8 (1999) 279-295.
- [12] M. Okumiya, Y. Tsunekawa, T. Murayama, Surface modification of aluminium using ion nitriding and fluidized bed, *Surface and Coatings Technology* 142-144 (2001) 235-240.
- [13] M. Wenzelburger, D. Lopez, R. Gadow, Methods and application of residual stress analysis on thermally sprayed coatings and layer composites, *Surface and Coatings Technology* 201 (2001) 1995-2001.
- [14] M. Wenzelburger, M. Escribano, R. Gadow, Modelling of thermally sprayed coatings on light metal substrates: layer growth and residual stress formation, *Surface and Coatings Technology* 180-181 (2004) 429-435.
- [15] T. Telbizova, S. Parascandola, F. Prokert, E. Richter, W. Moller, Ion nitriding of aluminium-experimental investigation of the thermal transport, *Nuclear Instruments and Methods in Physics Research B* 161-163 (2000) 690-693.
- [16] S. Gredelj, A.R. Gerson, S. Kumar, G.P. Cavallaro. Interaction of aluminium with stainless steel during plasma nitriding, *Applied Surface Science* 193 (2002) 189-194.
- [17] N. Renevier, T. Czerwiec, A. Billard, J. Stebut, H. Michel, A way to decrease the nitriding temperature of aluminium: the low-pressure arc-assisted nitriding process, *Surface and Coatings Technology* 116-119 (1999) 380-385.
- [18] M. Quast, P. Mayr, H.R. Stock, Plasma monitoring of plasma-assisted nitriding of aluminium alloys, *Surface and Coatings Technology* 120-121 (1999) 244-249.
- [19] D. Bialo, J. Zhou, J. Duszczuk, The tribological characteristics of the Al-20Si-3Cu-1Mg alloy reinforced with  $\text{Al}_2\text{O}_3$  particles in relation to the hardness of a mating steel, *Journal of Materials Science* 35 (2000) 5497-5501.