

## **THE WEAR RESISTANCE AND THERMAL STABILITY OF THE MANGANESE-NITROGEN-OXYGEN LAYERS CREATED ON Al-Si ALLOY**

### **ABSTRACT**

The demands made on products of the automotive and machine-building industry are becoming increasingly stringent. These requirements can only be fulfilled with high quality materials and modern processing methods in design manufacturing.

The possibility of fabrication of the manganese- nitrogen-oxygen Mn-N-O layers on the Al-Si alloy substrate is presented. Hardness, microstructure and phase composition of the formed Mn-N-O layers have been examined. Results of the wear and thermal stability testing of the above layers on Al-Si alloy substrate are presented. The beneficial effect of the Mn-N-O layers on the surface hardness and wear resistance of the Al-Si alloy is observed.

### **INTRODUCTION**

The aluminium alloys are increasingly applied for fabrication of bush-free cylinder blocks of the fuel engines and compressors. However, severe operating conditions such as high specific pressures, high temperatures, corrosive environment or abrasive wear often limit the possibility of direct use of aluminium alloys [1]. The intensive research has been carried out to improve the properties of these alloys, and one of the trends in metallurgical development is surface strengthening [2].

In the case of aluminium alloys the surface strengthening can be achieved by burnishing, cladding, padding, metal spraying, electroplating, electroplating with co-depositing or CVD and PVD methods [3].

The co-depositing method is chemical or electrochemical co-depositing of metallic, non-metallic compounds or polymers fine particles simultaneously with the base metal of the layers to improve material properties, such as wear resistance [4, 5, 6], lubrication [7] or corrosion resistance [8].

The most of the research concerning anodic oxidation, chromium electroplating, or nickel and iron electroplating of aluminium alloys has been carried out to increase their resistance to wear. However, electroplated layers are characterized by lower adhesion than diffusion layers. The attempts to form a diffusion bond between electroplated coatings and the aluminium base by means of diffusion annealing in vacuum or nitriding have not been entirely successful because of scaling and chipping of these coatings from the base metal. This is mainly caused by difference in thermal expansion between the chromium, nickel or iron coatings and aluminium substrate. Manganese is a metal which coefficient of thermal expansion is similar to aluminium and its alloys.

The present paper describes fabrication technique of the Mn-N-O layers on the Al-Si alloy substrate. Experimentally, the following possibilities were confirmed:

- formation of the electroplated manganese coating on the Al-Si alloy substrate,
- generation of the Mn-N-O layer by selective nitriding process (short oxidizing and next nitriding) of the manganese electroplated coating. As a result, diffusion of oxygen and nitrogen to the manganese coating and diffusion bonding between the electroplated coating and the Al-Si alloy substrate, occur.

The hardness, microstructure, phase composition, wear resistance and thermal stability of the Mn-N-O layers created on the AlSi10Cu2Mg1Ni1 alloy substrate were investigated.

## EXPERIMENTAL

The manganese coatings were electroplated onto specimens of dimensions  $15 \times 15 \times 5$  mm, made of the AlSi10Cu2Mg1Ni1 alloy. The electrolyte composition, process parameters and other conditions of electroplating have been described in detail elsewhere [9, 10, 11].

The experiments to achieve oxygen and nitrogen diffusion and structural bonding of the electroplated manganese coating with the aluminium substrate (formation of Mn-N-O layer) were carried out during short-duration gas selective nitriding – consisting of oxidizing and next nitriding process. The results of the gas selective nitriding depend on temperature, time as well as chemical composition of the oxidizing and nitrogen hardening atmosphere. The gas selective nitriding of the manganese electroplated coating on the aluminium substrate consisted of short oxidizing process in steam atmosphere at temperature  $500^\circ\text{C}/30$  min and the next (in the same chamber) nitriding process at temperature  $480^\circ\text{C}/120$  min, where the ammonia ( $\text{NH}_3$ ) was used as the reactive environment.

The surface and cross section microstructure of the Mn-N-O layers was examined by a scanning electron microscope (SEM) at 1000 and 3000x magnification. The phase composition of the layers was determined by an X-ray diffraction analysis. The microhardness of the coatings was measured by the PMT-3 microhardness tester, using a load of 0.098 N.

The study of the wear of the Mn-N-O layers and the substrate (AlSi10Cu2Mg1Ni1 alloy) were made by means of the PT-3 tribometer [12]. In order to measure the wear by slide friction were used:

- samples (size  $15 \times 15 \times 5$  mm),
- anti-sample (bush  $\varnothing 11 / \varnothing 8$  mm),
- nominal pressure 27 MPa and sliding speed 0.1 m/s.

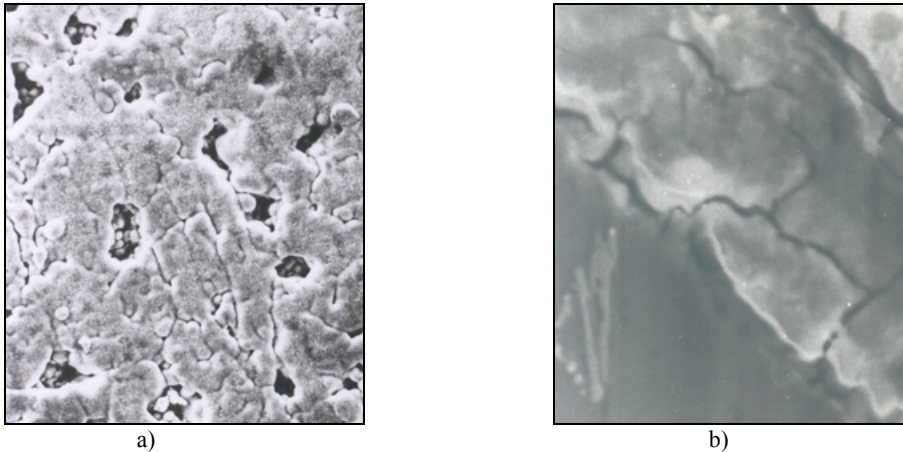
The sliding elements were inserted in oil SAE 15/40 at temperature  $80^\circ\text{C}$ .

The anti-sample was made of perlite grey cast-iron (hardness 197 HB). The linear wear of the samples was determined by the profile measurement gauge after 2, 5, 8, 11 and 14 hours of exploitation. The value of the moment of friction was measured to find out the friction factor.

The thermal stability (oxidation kinetics) of the Mn-N-O layers formed on Al-Si alloy substrate was determined by means of a thermo-gravimetric method at temperature 500, 450, 400 and  $350^\circ\text{C}$  in air of 40 to 50% of humidity, 1013 hPa of pressure, during 17.5 hours.

## RESULTS AND DISCUSSION

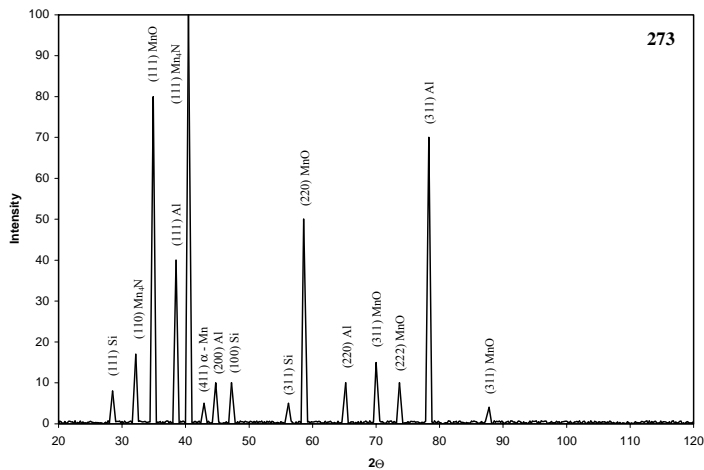
Fig. 1a shows the SEM image of the surface microstructure of the Mn-N-O layers obtained on AISi10Cu2Mg1Ni1 alloy substrate. The appearance of the pores in the Mn-N-O layers can result from presence of the silicon crystals in microstructure of the Al-Si alloy substrate and influence of silicon on the formation of the manganese coating during of the electroplating process. The study [13] showed that the size of such pores in manganese coatings decreased as the result of the selective nitriding treatment.



**Fig. 1.** SEM of Mn-N-O layer on AISi10Cu2Mg1Ni1 alloy: a) surface (1000x), b) cross section (3000x)

An X-ray radiographic analysis of the phase composition of the gas selective nitrided manganese coatings – Mn-N-O layers demonstrated presence of the  $\alpha$ -Mn, MnO and  $Mn_4N$  phases (Fig. 2).

The occurrence of MnO in the studied layers is observed as the surface zone in the created multicomponent layer (Fig. 1b). The  $Mn_4N$  phase is dispersed in the  $\alpha$ -Mn matrix saturated with nitrogen. The previously mentioned oxide (MnO) can also appear in the matrix of the layer in the form of high dispersion particles.



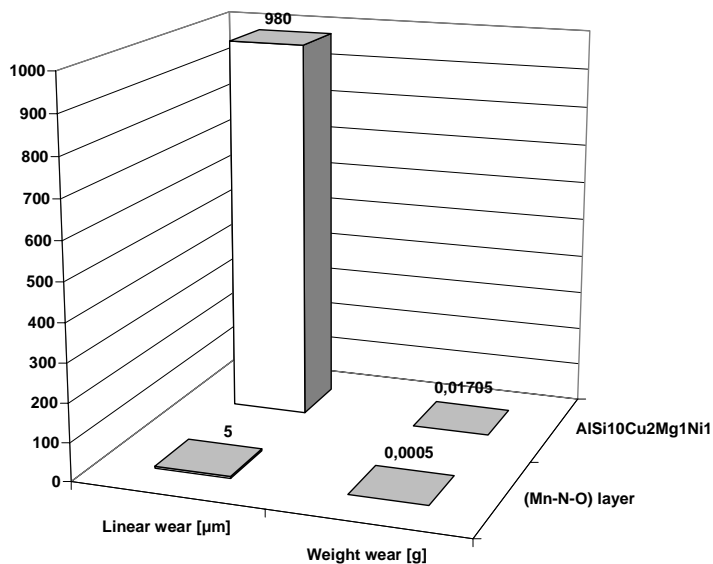
**Fig. 2.** XRD patterns recorded for Mn-N-O layer created on AISi10Cu2Mg1Ni1 alloy substrate

The study of the microstructure shows the zonal structure of the Mn-N-O layers on AlSi10Cu2Mg1Ni1 alloy substrate (Fig. 1b). There are substantial differences in the microhardness on the surface of the layers and the base-adjointing zone. The results of the measurement of the microhardness in the respective zones of the Mn-N-O layer are shown in Table 1.

**Table 1.** Microhardness HV0.01 of the Mn-N-O layer

Surface	Base-adjointing zone
359 HV0.01	583 HV0.01

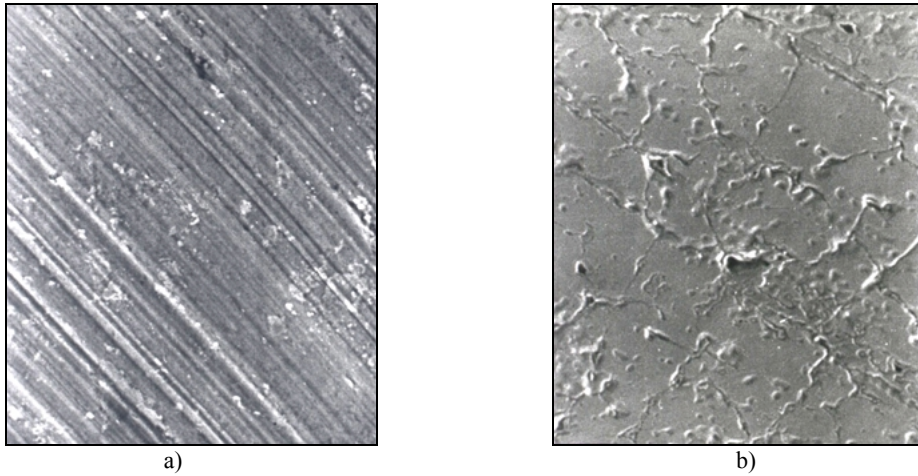
There are no reference data, to which obtained here results on the wear resistance of the Mn-N-O layers might be compared. The following tribological features are the most important in case of mixed friction: the friction factor ( $\mu$  factor), the quantity of wear and the microstructural change of the friction surface of the elements forming the sliding pair. The values of linear and mass wear are presented in Fig. 3.



**Fig. 3.** The value of linear and mass wear of the AlSi10Cu2Mg1Ni1 alloy with and without Mn-N-O layer

The values of the friction factor ( $\mu$ ) of the AlSi10Cu2Mg1Ni1 uncoated and coated alloy with the Mn-N-O layers in co-operation with the perlitic cast iron anti-sample were: 0.087 (test was interrupted after 2 hours) and 0.082 (after 14 hours).

This confirms that the main factors in determining the wear resistance are the material structure, its elastic-plastic nature, and the presence of the internal stresses. The hardness of the material is not the primary index of the wear resistance. In studies of the friction surface path of the AlSi10Cu2Mg1Ni1 alloy (Fig. 4a) has been observed increase of surface roughness from  $R_a = 0.189 - 0.235$  to  $R_a = 0.282 - 324$ . For the AlSi10Cu2Mg1Ni1 alloy coated with the Mn-N-O 1 ayers the surface roughness decreases from  $R_a = 0.683 - 0.798$  to  $R_a = 0.320 - 0.523$  (Fig. 4b).



**Fig. 4.** SEM of the friction path (500x): a) AlSi10Cu2Mg1Ni1 alloy substrate, b) Mn-N-O layer

The results presented in Fig. 5 demonstrate the relative mass change as a function of oxidation time of specimens at temperature 500, 450, 400 and 350°C.

Each curve in Fig. 5 describes the oxidation kinetics as an average of 5 tests [14]. The kinetics of oxidation process of tested layers may be described by logarithmical function according to the following equation:

$$y = a (1 - e^{-bx}) \quad (1)$$

where:

$y = \Delta m/S$  – mass change, [g/m<sup>2</sup>]

$x$  – oxidation time, [h]

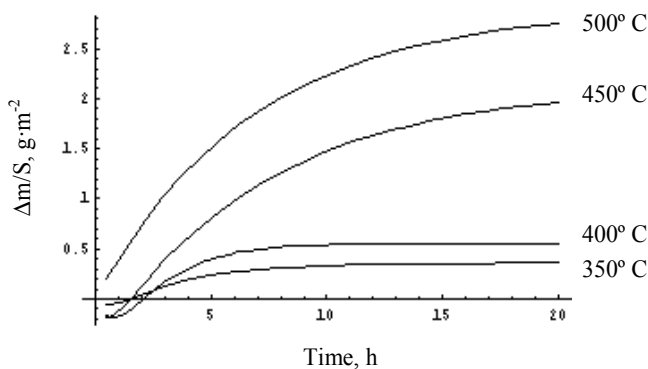
$a = 2.9085 \cdot 10^0$

$b = 1.4597 \cdot 10^{-1}$ .

At lower temperatures the oxidation kinetics may be described by following exponential function:

$$y = a (1 - e^{-bx}) - c (1 - e^{-dx}) \quad (2)$$

where  $a$ ,  $b$ ,  $c$ ,  $d$  - temperature dependent coefficients, given in Table 2.



**Fig. 5.** Oxidation kinetics of the Mn-N-O layers, created on AlSi10Cu2Mg1Ni1 alloy substrate

**Table 2.** Values of *a*, *b*, *c*, *d* coefficients in equation (2), dependent on oxidation temperature of the Mn-N-O layers

Oxidation temperature [°C]	Coefficient values			
	a	b	c	d
450	$2.6600 \cdot 10^0$	$1.3851 \cdot 10^{-1}$	$5.2306 \cdot 10^{-1}$	$2.3517 \cdot 10^0$
400	$1.9986 \cdot 10^0$	$5.0486 \cdot 10^{-1}$	$1.4451 \cdot 10^0$	$1.1028 \cdot 10^0$
350	$6.0688 \cdot 10^{-1}$	$3.1523 \cdot 10^{-1}$	$2.4723 \cdot 10^{-1}$	$1.6927 \cdot 10^0$

The Mn-N-O layers show some porosity due to galvanic process. These pores increase the real surface of specimens but precise measurement of this surface is impossible. That is why it can be assumed that relative oxidation rate of the Mn-N-O layers is – as a matter of fact – smaller than that given in Fig. 5.

The change in oxidation kinetics from exponential law at temperature 450, 400, and 350°C to logarithmic law at temperature 500°C is accompanied by the increase of chemical reaction rate and of oxygen rate diffusion in the Mn-N-O layers. At temperature 500°C the growth gradient is many times greater than that at temperature 450, 400, and 350°C. It can be assumed that at temperature 500°C an intensification of oxidation process in the Mn-N-O layers created on AlSi10Cu2Mg1Ni1 alloy substrate may occur.

The mass decrement at initial stage of oxidation at temperature 450, 400, and 350°C is likely caused by partial de-diffusion of nitrogen from the layer to environment and further increase of the relative mass of the specimen is connected with the oxidation reaction of manganese. The de-diffusion phenomenon of nitrogen at temperature 500° C proceeds very quickly and, as demonstrated by mass growth, apparently takes place after the soaking period of 0.5 h. Therefore, two simultaneous phenomena occur in the oxidation process of the Mn-N-O layers created on AlSi10Cu2Mg1Ni1 alloy substrate:

- the partial de-diffusion of nitrogen from the layer which caused the decrease of specimen mass,
- the oxidation of layer matrix (mainly Mn) which caused the increase of mass.

Taking into consideration the effect of environment on the oxidation rate it can be ascertained that increase in humidity of the environmental air promotes the oxidation process. The examination results of the Mn-N-O layers presented in Fig. 5 correspond to relative air humidity in range of 40% – 50%.

X-ray phase analysis of the Mn-N-O layers oxidised at temperature 500, 450, 400 and 350°C showed the presence of  $Mn_3O_4$ ,  $(MnO \cdot Mn_2O_3)$ ,  $\infty$ - $Mn_2O_3$ ,  $\gamma$ - $Mn_2O_3$  as well as  $\alpha$ -Mn, MnO and  $Mn_4N$  phases, constituting the essential components of the layers. The examinations did not determine the morphological structure of the Mn-N-O layers after oxidation and were only limited to qualitative evaluation of phase composition of the formed layers.

In contrast to layers tested at temperature 350°C (Fig. 6b), the tendency to form cracks and chips within of the Mn-N-O layers oxidised at 500°C (Fig. 6a) was observed.

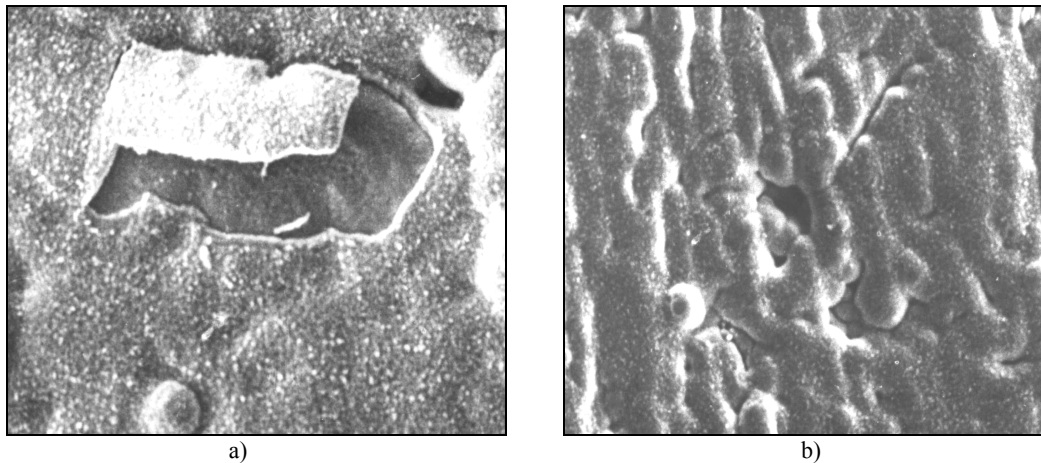


Fig. 6. SEM images of the Mn-N-O layers oxidised at temperature: a) 500°C, b) 350°C

## CONCLUSIONS

1. The electroplated manganese coatings can be deposited on the AlSi10Cu2Mg1Ni1 alloy substrate.
2. The gas selective nitriding process of the manganese electroplated AlSi10Cu2Mg1Ni1 alloys results in creation of the manganese, nitrogen, and oxygen containing surface layers which are structurally bounded to the Al-Si alloy substrate due to mutual diffusion of the manganese and aluminium.
3. The Mn-N-O layers created on the AlSi10Cu2Mg1Ni1 alloy substrate have a zonal structure of the varying hardness.
4. The abrasive wear resistance of the Mn-N-O layers is many times higher than that of the AlSi10Cu2Mg1Ni1 alloy.
5. Oxidation kinetics of the Mn-N-O layers in air at temperature 500°C can be described by the equation (1).
6. The oxidation of tested layers at temperature 450, 400 and 350°C may be described by the exponential function according to the equation (2).
7. During the oxidation process two simultaneously occurring phenomena are observed: partial de-diffusion of nitrogen and oxidation of manganese-based matrix of the layers.
8. The  $Mn_3O_4$  and  $\alpha$ - $Mn_2O_3$  and  $\gamma$ - $Mn_2O_3$  oxides are present in the oxidised the Mn-N-O layers.
9. The cracks and chips on the outer surface of the specimens tested at 500°C were observed. Such cracks and chipping no appeared at lower temperatures of oxidation.

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