Creation and properties of the (Mn-N-O) layers on aluminium

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Manufacturing and processing

ABSTRACT

Purpose: Many methods are well-known for surface consolidation of aluminium alloys. Fabrication of the new surface layers on aluminium alloys with high hardness and good tribological properties are presented in this paper.
Design/methodology/approach: In that aspect, the conception of creating the surface layers containing manganese, nitrogen and oxygen (Mn-N-O) on AlSi13Mg1CuNi alloy used in production of the internal-combustion engine pistons was considered and described.
Findings: The (Mn-N-O) layers are structurally connected by diffusion with aluminium base, demonstrates a zonal microstructure with the surface hardness about 358 HV0.01. The (Mn-N-O) layers increase significant the wear resistance of AlSi13Mg1CuNi alloys in frictional association with grey cast iron (hardness 197 HB) and simultaneously decreases the corrosion resistance in 0.01 M solution H_2SO_4.
Research limitations/implications: In the future tribological researches should be applied also another materials as anti-specimens, for example spheroidal cast iron with chromium or molybdenum coatings.
Practical implications: The (Mn-N-O) surface layers can be recommended as the tribological layers limiting the abrasive wear of the machine parts made from aluminium alloys.
Originality/value: In the article performed the fabrication method of the new (Mn-N-O) surface layers and its beneficial structural and tribological properties for increase the wear resistance of the aluminium alloys.
Keywords: Surface treatment; Mn-N-O layers; Tribology; Corrosion

1. Introduction

Aluminium alloys are the materials of choice when high-strength-to-weight ratios are required in structural components, and are used widely in the automotive and aerospace industries [1-4]. As an example, the use of aluminium components in the automobile industry has greatly increased due to weight savings and resultant fuel economy improvements. However, strong unit pressure, high temperature, corroding medium or wear and friction, limit the use of the aluminium alloys. Thus, new methods of both total and surface consolidation of the construction elements made from aluminium alloys are sought. The consolidation is usually done by burnishing, cladding, padding, spraying, sputtering or electroplating [5-8].

Among the above-mentioned methods, electroplating is the most commonly used one. However, electrolytic coatings on aluminium are less adhesive than the layers made by the hybrid method. One of such methods is the multicomponent layer containing manganese, nitrogen and oxygen [9].

To do this, theoretical and experimental confirmation of the following possibilities was required [10]:

- formation of an electroplated manganese coating on aluminium alloy base,
- creation of the Mn-N-O composite layer by gas oxynitriding treatment of manganese electroplated coating, resulting in the simultaneous diffusion of nitrogen and oxygen to manganese and diffusion bonding between the electroplated coating and the aluminium base.

The aim of this paper is to present the technology of creating, the microstructure, phase composition, microhardness, wear

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resistance and corrosion characteristics of the (Mn-N-O) layers fabricated on the AlSi13Mg1CuNi alloy.

2. Description of the experiments

Manganese coatings were electroplated onto specimens made of the AlSil3Mg1CuNi alloy. The electrolyte composition, process parameters, and other conditions of electroplating are described in detail in the literature [11-13].

The experiments to achieve simultaneous nitrogen diffusion and structural bonding of the electroplated manganese coating with the aluminium base (formation of the Mn-N-O composite coating) were carried out during short-duration gas oxynitriding process. The phase composition of the formed layers was identified on the basis of recorded X-ray diffraction lines. The structure of the layers was examined by both optical and scanning electron microscopy. The hardness of the layers was determined by microhardness measurement made under a load of 0.098 N.

The wear resistance of the electroplated and the oxynitrided manganese coatings (Mn-N-O) and of their metal bases were compared using the PT-3 tribometer [14]. The conditions applied to determine quantitatively the wear, due to sliding friction were as follows:

- samples size 15 mm x 15 mm x 5 mm,
- load on the specimen 27 MPa,
- sliding velocity speed 0,1 m/s,
- specimen temperature 80°C,
- lubrication by means of SAE 10 W/ 40 oil.

The anti-sample (bush $\varnothing 11/ \varnothing 8$ mm) was made from 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 friction resistance was measured to find out the friction factor (μ).

Polarization tests were performed in aerated 0.01 M sulphuric acid solution at 20°C. Quasistationary data were obtained by applying linear potential rate at 2 mV·min^{-1}. Polarization was started at cathodic potential after the corrosion potential was observed, constant and increased towards anodic potentials. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum wire. To obtain flat and well-defined surface, in contact with the electrolyte, the sides of the specimens were coated with M-COAT-D (Vishay-Micromesures).

The surface microstructure observations before and after the corrosion test of the AlSi13Mg1CuNi alloy and (Mn-N-O) layers were provided by Scanning Electron Microscope (SEM).

3. Description of achieved results

Table 1 shows the microhardness of the manganese-nitrogen-oxygen (Mn-N-O) layers created on AlSi13Mg1CuNi alloy.

The microhardness of the electroplated manganese coating was 1508 HV0.01. After oxynitriding the manganese coatings based on the AlSi13Mg1CuNi exhibited on the surface a hardness of 358 HV0.01, while in the area adjacent to the base the value was 467 HV0,01.

Table 1.
Hardness of the (Mn-N-O) layers on AlSi13Mg1CuNi alloy

Aluminium alloy	AlSi13Mg1CuNi
Kind of the layer	Mn-N-O
Thickness of the layer (μ)	20-25
Hardness (HV0.01), surface	358
Hardness (HV0.01), transition zone (diffusion)	467

Figure 1a illustrates the microstructure of the cast AlSi13Mg1CuNi alloy used as the base material of samples with the (Mn-N-O) layers. Considerable number of pores in the microstructure of the (Mn-N-O) layers created on the AlSi13Mg1CuNi alloy were observed (Fig.1b).
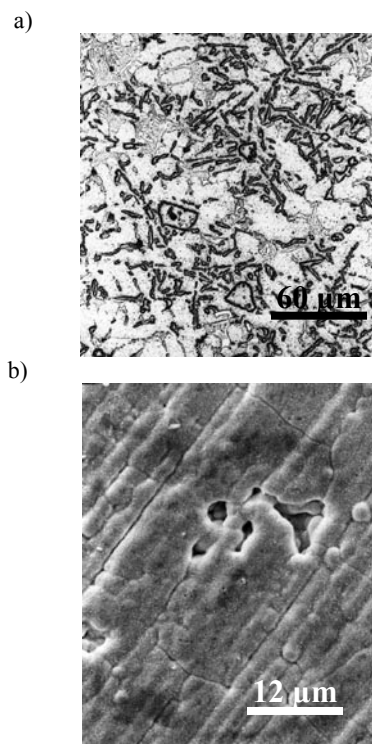

Fig. 1. SEM micrographs: a) structure of the AlSi13Mg1CuNi alloy, b) surface of (Mn-N-O) layer

The existence of the pores in the (Mn-N-O) layer created on AlSi13Mg1CuNi alloy can be accounted for by the presence of silicon (next to aluminium it is the main phase ingredient of the base microstructure – Fig. 1a) and its influence on the formation process of the manganese electrolytical layer. The amount of the pores in electrolytic coat decreases during oxygen and nitrogen diffusion, at the thermo-chemical treatment (gas oxynitriding process).

An X- ray analysis of the phase composition of the (Mn-N-O) layers created on the AlSi13Mg1CuNi alloy proved the presence of Al, α-Mn, MnO and Mn$_4$N phases [15].

The arrangement of MnO in the studied layers can be seen mainly in the surface zone (Fig. 2).

It is assumed that the Mn$_4$N and MnO phases are precipitated at the form of high dispersion particles in the α-Mn matrix

saturated by nitrogen. The study of the microstructure shows of the zonal structure of the (Mn-N-O) layers created on the AlSi13Mg1CuNi alloy (Fig. 2).
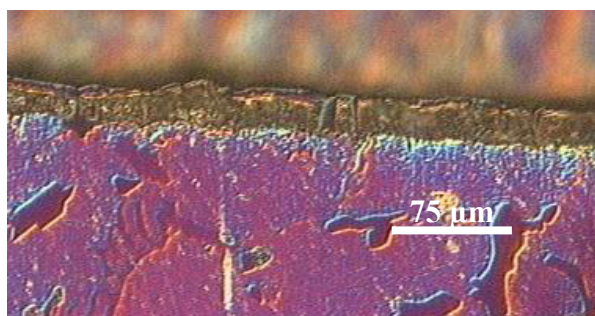

Fig. 2. SEM of cross section of (Mn-N-O) layer created on the AlSi13Mg1CuNi alloy

There are marked differences between the surface and the base-adjoining zone microhardness of these layers. The measured microhardness of the (Mn-N-O) layer exhibited 358 HV0.01 on the surface and 467 HV0.01 in the base-adjoining zone.

In work [9] were determined the tribological characteristics of the (Mn-N-O) layers created on the AlSi13Mg1CuNi alloy (Fig. 3).
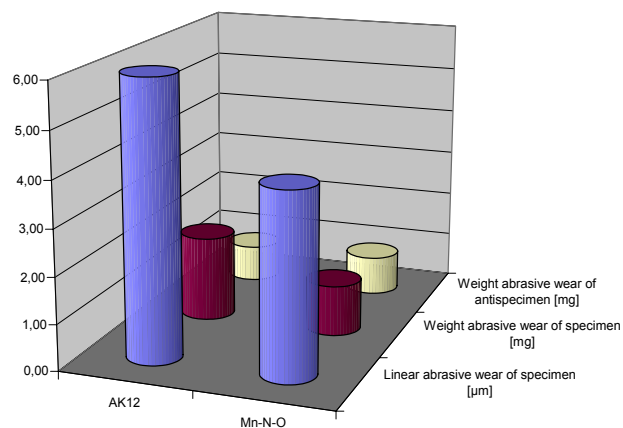

Fig. 3. The value of linear and mass wear of the AlSi13Mg1CuNi (AK12) alloy with and without (Mn-N-O) layer

The values of the friction factor (μ) of the AlSi13Mg1CuNi uncoated and coated alloy with the (Mn-N-O) layers in co-operation with the pearlitic cast iron anti-samples were 0.102 and 0.082 (after 14 hours). This confirms that the main factors in determining the wear resistance are the material microstructure, its elastic-plastic nature and the presence of the internal stresses. The hardness of the material isn't the primary index of the wear resistance. In studies of the friction surface path of the AlSi13Mg1CuNi alloy (Fig. 4a) has been observed increase of surface roughness from Ra = 0.262 μm to Ra = 0.509 μm. For the AlSi13Mg1CuNi alloy coated with the (Mn-N-O) layers the surface roughness decreases from Ra = 0.870 μm to Ra = 0.167 μm (Fig. 4b).

The polarisation characteristics in 0.01 M H_2SO_4 for AlSi13Mg1CuNi coated with (Mn-N-O) layer (Fig. 5) were obtained by potentiostatic measurements.
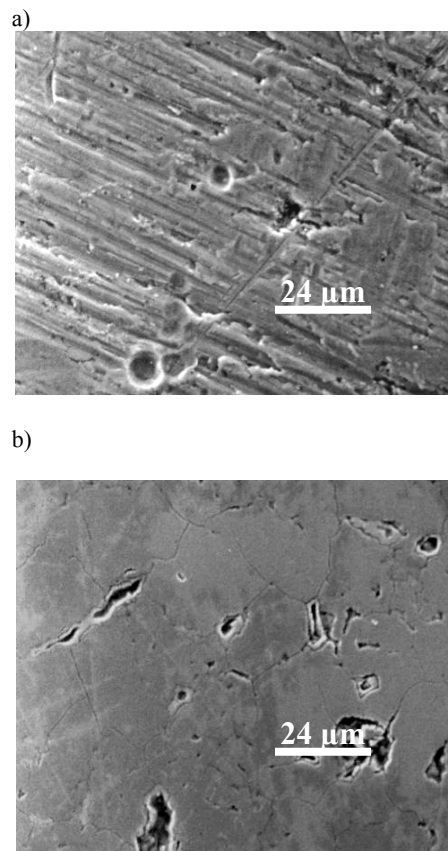
a)

b)

Fig. 4. SEM of the friction path: a) the AlSi13Mg1CuNi alloy, b) the (Mn-N-O) layer created on the AlSi13Mg1CuNi alloy
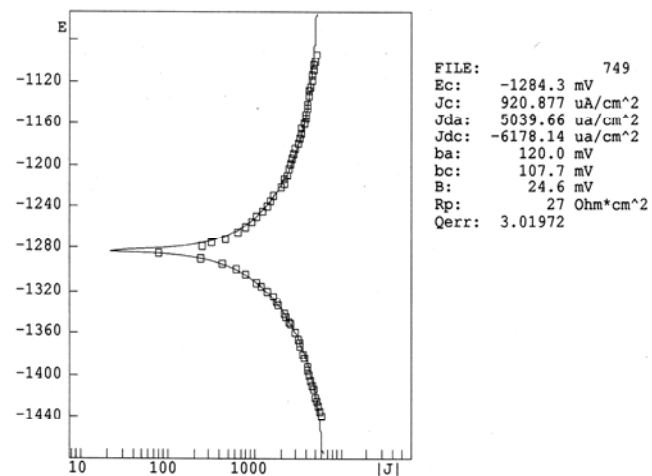

Fig. 5. Corrosion characteristics in 0.01 M H_2SO_4 of the (Mn-N-O) layer created on the AlSi13Mg1CuNi alloy

The corrosion potential (Ec) and corrosion current density (Jc) of the AlSi13Mg1CuNi alloy and (Mn-N-O) layer were as follows:

- the uncoated alloy: Ec = - 449.8 mV, Jc = 10.6 $\mu A/cm^2$,
- the (Mn-N-O) layer: Ec = - 1284.3 mV, Jc = 920.9 $\mu A/cm^2$.

The current density is a measure of corrosion resistance at anodic condition, often used for comparative evaluation of materials in a certain environment.

The lower corrosion potential and corrosion current density of uncoated than coated with the (Mn-N-O) layer of the AlSi13Mg1CuNi alloy in 0.01 M sulphuric acid solution is effected by presence of the corrosion resistant oxide film on the surface of uncoated aluminium alloy. It was found that the susceptibility for pitting corrosion uncoated the AlSi13Mg1CuNi alloy is localised on the boundaries between silicon and aluminium in eutectic mixture (Fig. 1a). The observations suggest that the initiation and propagation of the pitting corrosion in the (Mn-N-O) layer takes mainly place at the pores existed in their surface microstructure (Fig. 1b). The study of the corrosion behaviour of the (Mn-N-O) layers in mentioned solution demonstrates the worsening corrosion resistance of the AlSi13Mg1CuNi alloy.

4. Conclusions

1. It is possible to create the triboresistant layers containing manganese, nitrogen and oxygen on the AlSi13Mg1CuNi alloy using of the hybrid surface treatment.
2. The created the (Mn-N-O) layers are structurally bonded with the aluminium base and have a zonal structure of different hardness (358 HV0.01 – on the surface and 467 HV0.01 – in the base-adjoining zone).
3. The uncoated and coated with the (Mn-N-O) layer the AlSi13Mg1CuNi alloy is susceptible to the pitting corrosion in 0.01 M H_2SO_4 solution.
4. The (Mn-N-O) layers demonstrates lower corrosion resistance of the AlSi13Mg1CuNi alloy in mentioned solution.

Acknowledgements

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