DOI: 10.2478/v10077-008-0019-0

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MICROSTRUCTURE AND CORROSION PROPERTIES OF THE (Mn-N-O-P) TYPE LAYERS CREATED ON ALUMINIUM ALLOYS

ABSTRACT

The microstructure, chemical and phase composition as well as corrosion investigations of the (Mn-N-O-P) type surface layers in comparison to uncoated an aluminium alloy have been performed. An elaborated multiplex surface treatment of aluminium alloys enables forming of phase composition in the several zones of the (Mn-N-O-P) type layers. The zone microstructure with phases consisted of nitrogen, oxygen and phosphorus has fundamental influence on the hardnes and corrosion resistance of aluminium alloys.

Key words: *aluminium alloys, (Mn-N-O-P) type layer, microstructure, microhardness, corrosion resistance*

INTRODUCTION

Reduction in the weight of engines is a key factor in improving the fuel efficiency. The use of lightweight materials has become more prevalent as car manufactures strive to reduce vehicle weight in order to improve lower fuel and oil consumption and to reduce emissions. Most manufacturers have replaced cast iron engine blocks with lightweight and low-cost aluminium-silicon crankcases. However, inadequate wear resistance and low seizure loads have prevented their direct usage in the cylinder bores. The cylinder bores of these aluminium alloy blocks are usually made of cast iron liners because of their good operating characteristics such as wear resistance. These liners need to have a specific wall thickness, which results in a relatively larger web width between the individual cylinder-bores, and increases the dimensions and weight of the engine. Moreover, mechanical friction is another concern that needs to be addressed. Piston system is a major contributor to engine friction. The cylinder bore/piston and piston ring friction constitute nearly all the piston's system friction losses. A major portion of oil consumption arises from bore distortion and poor piston ring sealing resulting from ring and bore wear. Aluminium exhibits a transition from mild to severe wear when the nominal contact stress exceeds a threshold value [1]. Thus, to continue using aluminium alloy engine blocks and to improve wear resistance of the engine bore surface several techniques have been explored. Reduction of about 110 kg in a typical automobile of weight 1100 kg will improve fuel economy by 7% [2]. The employing i. e. electroplating – Al_2O_3 coatings [3], high velocity oxy-fuel (HVOF) – $NiCr/Cr_3C_2$ or NiCrMo/ Cr_3C_2 coatings [4], atmosphere plasma sprayed (APS) – stainless steel and nickel encapsulated hexagonal boronnitride (BN) and the one with iron and its oxide (Fe-FeO) coatings [5], laser-clad - Ni-Cr-Al coatings [6], laser remelting [7] as well as multiplex technology – (Mn-N) [8], (Mn-N-S) [9], (Mn-N-O) [10] surface layers, can significantly improve the wear resistance of aluminium alloys.

The paper presents microstructure morphology, hardness and corrosion resistance of the newly (Mn-N-O-P) type surface layers, produced by multiplex technology on the AlSi10Cu2Mg1Ni1 alloy, used in automotive and aircraft industries.

EXPERIMENTAL

In experiment, for fabrication of the (Mn-N-O-P) surface layers on an aluminium alloys, the specimens 15x15x8 mm (as the base material) were cut from the piston's heads made of the AlSi10Cu2Mg1Ni1 alloy. Then the specimens were grinded, polished, cleaned, etched and next coated by manganese electroplating. Main conditions and parameters of the manganese electroplating process were described in [9]. After the manganese electroplating, the surface of the specimens were treated by phosphorus ion implantation (P^+), forming the (Mn-P) layers. Ion implantation process was made at room temperature, with phosphorus portion $1x10^{16}$ [P^+/cm^2], 25 keV energy and current range 2.0 μA. Finally, an aluminium specimens with the (Mn-P) coating were treated by the oxynitriding process under glow discharge conditions in an atmosphere consisted of (N_2 + H_2 in ratio 1:1) and 15% vol. of air. The oxynitriding process was conducted at the pressure range 3.0 hPa and temperature 460 ºC for 5h. As a result of here described multiplex technology the (Mn-N-O-P) surface layers diffusion bonded with an aluminium base were created.The microstructure morphology of the as-produced the (Mn-N-O-P) surface layers was examined with SEM and AFM microscopy as well as the EDS analyse. The phase composition of the formed layers was identified on the basis of recorded X-ray diffraction lines. The hardness of the layers was determined by microhardness measurements made under a load of 0.196 N. Polarization tests were performed in aerated 0.01 M H_2SO_4 solution at 20°C. Quasistationary data were obtained by applying linear potential rate at 2 $mV\cdot min^{-1}$. 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 .

RESULTS AND DISCUSSION

Fig. 1(a, b) shows the surface and cross-section microstructure of the (Mn-N-O-P) surface layers created on the AlSi10Cu2Mg1Ni1 alloy. The surface layers produced by multiplex technology on aluminium alloys demonstrates smooth (Ra = 217.11 nm) and porous surface (Fig. 2), that can be an oil accumulator during sliding friction of piston and the cylinder bearing surface in the motor-car engines. Microstructure of these surface layers consists of some zones (Fig. 1b), in which the contents of Mn, Al, N, O and P depend on the distance from the surface (Fig. 3). Nitrogen is mainly concentrated in the outer zone (p. 1, Fig. 3), and oxygen and phosphorus are localized in the centre (p. 3 and 4, Fig. 3) and in diffusion-bond zone (p. 5, Fig. 3) of the (Mn-N-O-P) surface layers. The X-ray diffraction analyse shows that the formed layers consist of the following phases: Mnα, Mn(x), MnO and Mn_4N. The lattice partameters of these phases are shown in Table 1, and identified as the Mn(x) phase is most probable composed of the manganese and phosphorus. The utilization of the multiplex technology enables manufacturing the diffusion-bonded with an aluminium substrate the (Mn-N-O-P) type surface layers. The thickness and hardness tested on the surface and in the centre zone of the layers are shown in Table 2.

The results of the corrosion investigations in 0.01 M H_2SO_4 solution of the formed layers are shown in Figs. 4, 5 and Table 3. Corrosion potentials (E_c) are similar in case of the AlSi10Cu2Mg1Ni1 alloy (as substrate) and the (Mn-N-O-P) type surface layers. It means that mentioned materials have also similar susceptibility to pitting corrosion in 0.01 M H_2SO_4 solution. However, the corrosion current density (J_c) for the (Mn-N-O-P) type surface layers is about 12 times lower than that measured for the substrate material. This improvement is certainly related to the formation of Mn_4N or, most probably $Mn_4(O,N)$ phases in outer zone of the (Mn-N-O-P) type surface layers (Fig. 3). The SEM surface images of the (Mn-N-O-P) type surface layers before and after corrosion test are shown in Fig. 6. The (Mn-N-O-P) type surface layers can establish the protective coatings for the AlSi10Cu2Mg1Ni1 alloy in 0.01 M H_2SO_4 solution.

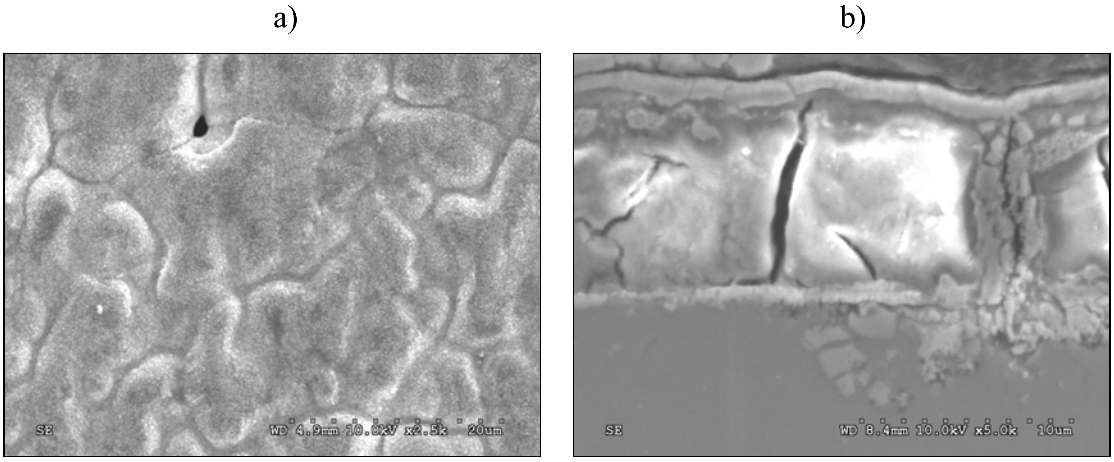


Fig. 1. SEM view of the (Mn-N-O-P) surface layer formed on the AlSi10Cu2Mg1Ni1 alloy: a – surface, b – cross-section

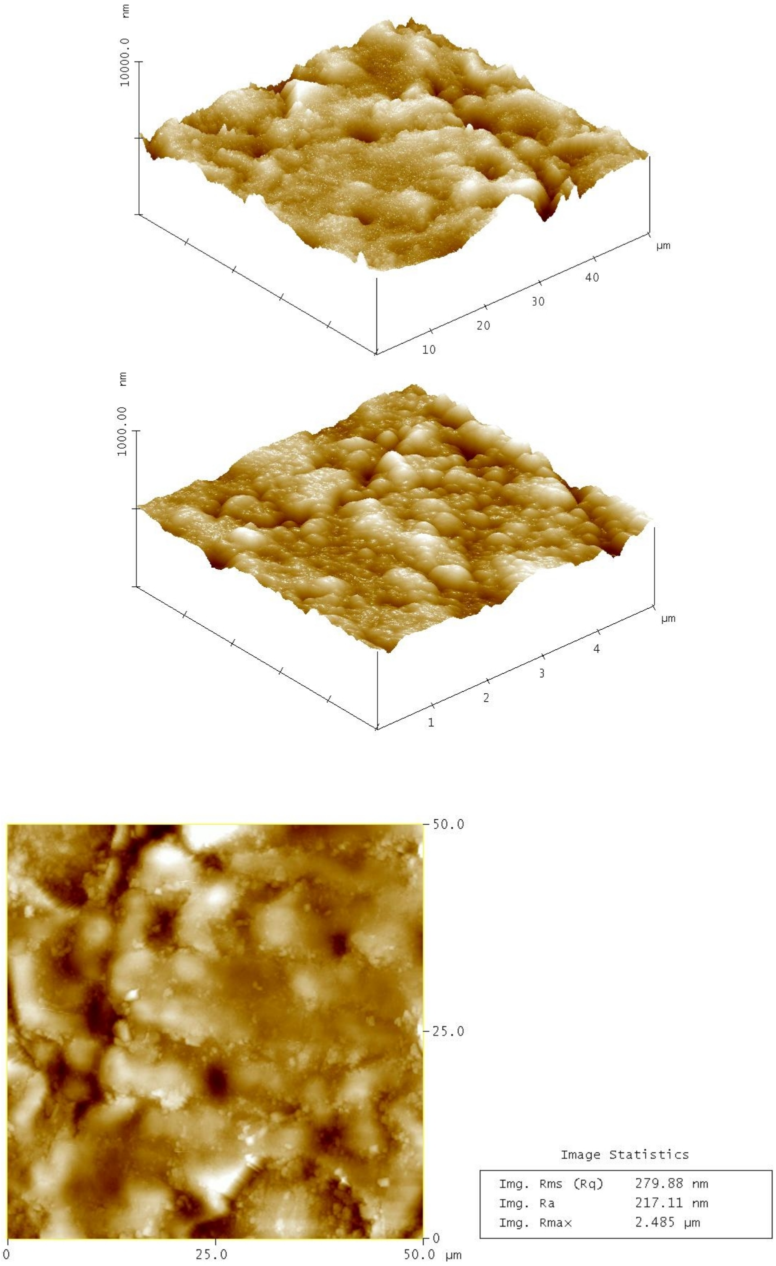
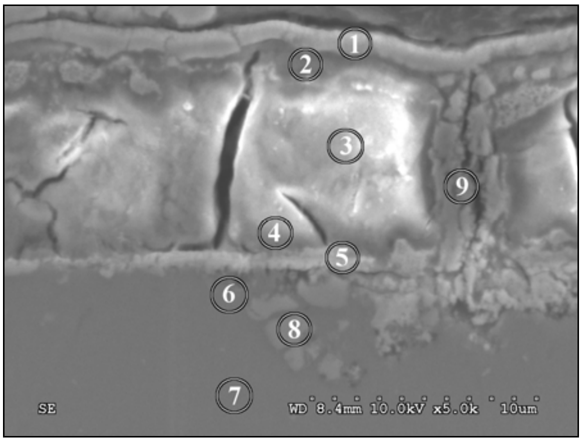


Fig. 2. AFM view of the (Mn-N-O-P) surface layer formed on AlSi10Cu2Mg1Ni1 alloy



Test number	N	O	Mg	Al	Si	P	Mn
Surface	2,38	13,50	–	0,31	0,17	–	61,13
1	2,14	15,42	–	0,38	0,21	–	68,79
2	–	13,53	–	0,15	0,37	0,59	76,57
3	–	25,78	–	0,28	0,31	1,31	55,21
4	–	31,35	–	0,21	0,15	1,28	57,27
5	1,53	18,63	0,66	2,61	0,20	1,32	69,22
6	–	1,09	0,06	86,76	0,48	–	1,28
7	–	0,23	0,13	88,09	0,32	–	0,53
8	–	0,27	–	3,53	88,15	–	–
9	1,71	15,06	–	0,33	–	–	79,01

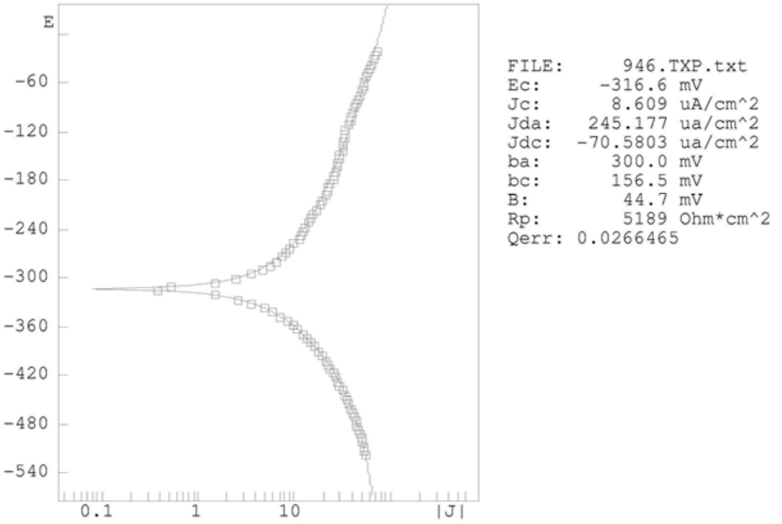
Fig. 3. Distribution of the elements (% wt.) in the cross-section of the (Mn-N-O-P) surface layer formed on the AlSi10Cu2Mg1Ni1 alloy

Table 1. *Phase composition of the (Mn-N-O-P) type surface layer*

Type of the surface layer	Substrate	Phase composition	Lattice parameter [nm]			
			Mnα	Mn(x)	MnO	Mn_4N
(Mn-N-O-P)	AlSi10Cu2Mg1Ni1	Mnα, Mn(x), MnO, Mn_4N	0.912	0.8935	0.4445	0.3856

Table 2. *Microhardness HV 0.02 and thickness of the (Mn-N-O-P) type surface layer*

Surface layer	Substrate	Thickness [μm]	Microhardness HV0.02	
			Surface	Centre of layer
(Mn-N-O-P)	AlSi10Cu2Mg1Ni1	11,7	851	552



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Ec:     -316.6 mV
Jc:      8.609 uA/cm^2
Jda:   245.177 ua/cm^2
Jdc:  -70.5803 ua/cm^2
ba:      300.0 mV
bc:      156.5 mV
B:        44.7 mV
Rp:       5189 Ohm*cm^2
Qerr: 0.0266465
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Fig. 4. Potentiostatic curve in 0,01 M H_2SO_4 solution of the AlSi10Cu2Mg1Ni1 alloy (as substrate)

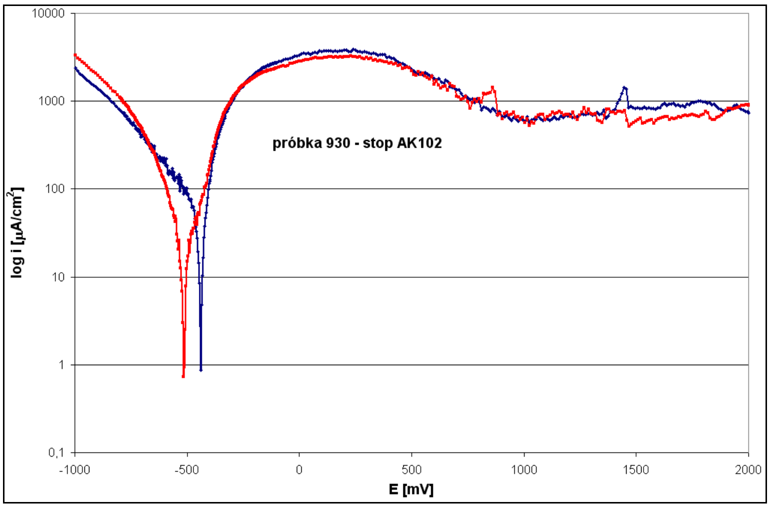

Fig. 5. Potentiostatic curves in 0,01 M H_2SO_4 solution of the (Mn-N-O-P) type surface layer formed on AlSi10Cu2Mg1Ni1 alloy

Table 3. *Potential corrosion (E_C) and corrosion current density (J_c) of the substrate and (Mn-N-O-P) type surface layer*

Surface layer	Substrate	No specimen	Corrosion potential E_c [mV]	Corrosion current density J_c [µA/cm^2]
-	AlSi10Cu2Mg1Ni1	946	- 464,2	8,6843
(Mn-N-O-P)	AlSi10Cu2Mg1Ni1	930	- 516,5	0,7279

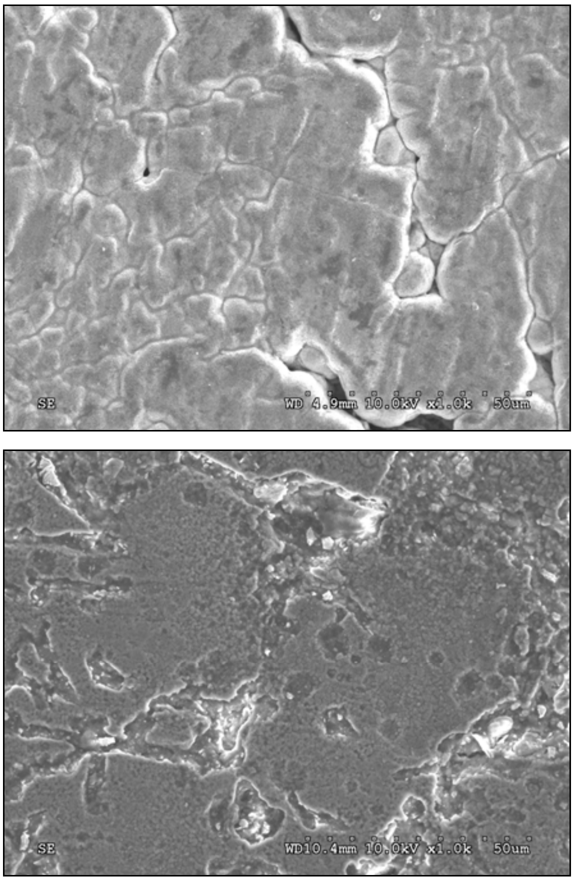

Fig. 6. Surface view (SEM) of the (Mn-N-O-P) type surface layer – specimen no 930: a – before, and b – after corrosion test in 0.01 M 0,01 M H_2SO_4 solution

CONCLUSIONS

1. The (Mn-N-O-P) type surface layers, diffusion bonded to an aluminium substrate, were successfully formed using here described multiplex technology.
2. Microstructure of formed multizone surface layers consists of Mn_4N, MnO, Mn(x) and Mnα phases.
3. The formed layers demonstrate high hardness (851HV0.02) due to the formation of Mn_4N or $Mn_4(O,N)$ phases at the surface.
4. The (Mn-N-O-P) type surface layers produced on aluminium alloys significant decrease corrosion susceptibility in 0.01 M H_2SO_4 solution.

REFERENCES

1. Taylor C.M.: Automobile engine tribology-design considerations for efficiency and durability. Wear 221 (1998), pp. 1-8.

2. Cole G.S., Shreman A.M.: Lightweight Materials for Automotive Applications. Materials Characterisations 35:3-9 (1995), pp. 1-9.
3. Gnedenkov S.V., Khrisanfova O.A., Zavidnaya A.G., Sinebrukhov P.S., Kovryanov A.N., Scorobogatova T.M., Gordienko P.S.: Production of hard and heat-resistant coatings on aluminium using a plasma micro-discharge. Surface and Coatings Technology 123 (2000), pp. 24-28.
4. Wuest G., Barbetaz G., Keller. SAE Paper No 970016 (1997).
5. Dahotre N.B., Nayak S.: Nanocoatings for engine application. Surface and Coatings Technology 194 (2005), pp. 58-67.
6. Liang G.Y., Su J.Y.: The microstructure and tribological characteristics of laser-clad Ni-Cr-Al coatings on aluminium alloy. Materials Science & Engineering A290 (2000), pp. 207-212.
7. Serbiński W., Olive J.M., Frayret J.P., Desjardins D.: Morphology and corrosion characteristics of laser surface remelted Al-Si alloy at cryogenic conditions. Materials and Corrosion 53 (2002), pp. 335-340.
8. Serbiński W.: Tribologiczne warstwy powierzchniowe mangan-azot wytwarzane na stopach aluminium z krzemem. Inżynieria Materiałowa, vol. 27 (2006), pp. 532-535.
9. Serbiński W.: Manganese-nitrogen-sulphur layers produced on aluminium alloys. Proc. 13th International Scientific Conference Achievements in Mechanical and Materials Engineering AMME 2005. Gliwice-Wisła, 16-19.05.2005. Gliwice: Politechnika Śląska (2005), pp. 577-580.
10. Serbiński W., Zieliński A.: Creation and characteristics of the (Mn-N-O) surface layers on aluminium alloy. Proc. 15th IFHTSE : International Federation for Heat Treatment and Surface Enginnering Congress : proceedings, Vienna, 25-29 September 2006 / ed. Reinhold Schneider / Austrian Society for Metallurgy and Materials. - Leoben : ASMET (2006) pp. 495-499.