Method for phase boundary structure control of laminated materials; destruction process investigations of nanostructured coatings with predetermined phase boundary texture

You may also be interested in:

The influence of ALN-Al gradient material gradient index on ballistic performance
Youcong Wang, Qiwen Liu, Yao Li et al.

Self-amplified Cherenkov radiation from a relativistic electron in a waveguide partially filled with a laminated material
L Sh Grigoryan, A R Mkrtchyan, H F Khachatryan et al.

Optimization of laminates for transient heat conduction
T Yamanaka

A portable lamination detector for steel sheet
B O Smith, A P H Jennings and A G Grimshaw

Active vibration control of composite laminated cylindrical shells via surface-bondedmagnetostrictive layers
Wu Qian, G R Liu, Lu Chun et al.

Predicting the deformation characteristics of rectangular unsymmetrically laminated piezoelectric materials
M W Hyer and A Jilani

Laminated materials with plastic interfaces: modeling and calculation
Gilberto Sandino Aquino de los Ríos, Rubén Castañeda Balderas, Van Anh Duong et al.

Recent developments in electrical insulating materials
L Hartshorn

Method for phase boundary structure control of laminated materials; destruction process investigations of nanostructured coatings with predetermined phase boundary texture

T A Konstantinova[*]**, A I Mamaev, A K Chubenko and V A Mamaeva**
Tomsk State University, 36 Lenina ave., Tomsk, 634050, Russia

E-mail: konstantinova.ta9@gmail.com

Abstract. New surface texturing method by means of microplasma coating deposition with the following etching of the coating was shown and described. The method of step by step microplasma texturing was proposed to control the phase boundary of laminated materials. Micrographs of nanostructured inorganic non-metallic coating surface were obtained and analyzed before and after mechanical deformation. The nature of cracks formation and growth was investigated.

1. Introduction

The problem of new functional laminated materials creation and development and their application methods is relevant topic nowadays. The relevance of laminated materials design is directly related to durability issues of these materials under external impacts including temperature and mechanical loads.

Laminated materials are widely used in industries such as electronics (multilayered boards), protecting coatings for aviation and aerospace.

The method of coating formation (nanostructured inorganic non-metallic NIN coatings) by means of high-energy flows localization at the phase boundary with emergence of microplasma processes in solutions allows creating composites of different structures and functions [1] including multilayered materials. Currently known papers in this area are dedicated to single-layered coatings formation [2, 3].

The formation of predetermined phase boundary texture provides increased durability of the coating under external impacts. Microplasma method allows forming of laminated materials with predetermined phase boundary texture. Thus phase boundary texturing results in maximum adhesion of the laminated coating to the metal surface.

The texturing is defined as a set of technological operations resulting in surface structure changes and thus reaching the required surface profile parameters including roughness.

The following coating formation provides the material with predetermined metal – coating phase boundary texture. This approach results in maximum adhesion of the ceramic coating to the metal surface and durability of the coating in terms of exfoliation and destruction under different external impacts.

In this paper we offer texturing by microplasma deposition with the following etching of the coating as a new method to obtain a given metal surface texture. The method contains ceramic coating

formation on processed valve metal by microplasma oxidation in solution. Texturing of the metal-ceramic coating phase boundary takes place due to multiple microplasma discharges and related processes during the coating formation.

It is evident that one can adjust the texture parameters by adjusting the parameters of electric impact during the coating formation. The following ceramic layer etching provides a metal surface with predetermined texture. The process can be carried out repeatedly achieving the required texture parameters. Thus, the number of formation – etching operations can also be an operation factor of the processed material texture.

Investigations of NIN coatings destruction process under mechanical loads provides conclusions about the nature of cracks formation and their growth on the coating surface and the way these processes are affected by phase boundary texturing.

2. Materials and methods
Flat square samples made of MA 2-1 magnesium alloy were investigated. Each side of the square was 3 cm.

2.1 Sample preparations
All samples were preliminarily subjected to polishing up to 10 roughness class in order to remove scratches and the oxide film. Then organic contaminants were removed from the surface. The cleaning operation consisted of rinsing the samples with 1 M Na_3PO_4 solution at a temperature not lower than 60 °C for 10 minutes. Then samples were rinsed with distilled water, alcohol and distilled water again. Samples were dried in desiccator for 30 minutes at 60 °C.

2.2 Microplasma texturing
Microplasma texturing of magnesium alloy was performed using the following fluoride phosphate solution: $NaF – 5$ g/l, $Na_2B_4O_7 \cdot 10H_2O – 7$ g/l, $HBO_3 – 10$ g/l, $Na_2HPO_4 – 18$ g/l.

This electrolyte composition provided porous coatings forming on magnesium mainly consisting of magnesium oxide and phosphate:

$$Mg – 2e \rightarrow Mg^{2+},$$
$$Mg^{2+} + PO_4^{3-} \rightarrow Mg_3(PO_4)_2,$$
$$Mg^{2+} + O^{2-} \rightarrow MgO.$$
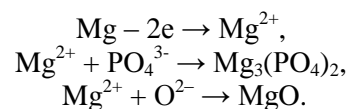
Such coatings could be easily removed afterwards by chemical methods, for example, by processing in phosphoric acid solution or concentrated alkali solution.

Samples were immersed in 1 M H_3PO_4 solution directly before the coating formation for 10-20 seconds in order to remove natural oxide layer from the surface.

The processed sample of magnesium alloy served as anode, a tub made of stainless steel with water cooling was cathode.

The temperature in the tub did not exceed 40 °C. Electroinfluence was implemented in the form of voltage impulses with 400 V amplitude and 200 microseconds duration. Entire duration of the process was 20 minutes. The obtained coatings had almost white uniform colour (Figure 1) and were quite dense and fitting well to the substrate. Thickness of the coatings determined by eddy currents method was (20±5) micrometers.

Figure 1. Coating formed on MA 2-1 magnesium alloy by microarc oxidation method.

The coating was etched by 1 M H_3PO_4 solution for 5 minutes. Reaction products were removed from the surface of the metal sample by momentary immersion in 30 % nitric acid solution after rinsing the samples with distilled water. The process was carried out repeatedly in order to determine how the formation – etching operations number influenced on metal texture. The M0 sample was etched without preliminary coating formation to reveal the separate effect of chemical etching on the surface texture. This approach was determined by high magnesium activity in chemical reactions with acids. Designations of samples and the number of cycles are shown in Table 1.

Table 1. Designations of samples and processing stages.

Sample	M0	M1	M2	M3	M4	M5
Number of coating formation operations	0	1	2	3	4	5
Number of coating etching operations	1	1	2	3	4	5

Roughness and profiles after texturing were studied by means of three-dimensional contactless profilometer (Micro Measure 3D Station) by STIL.

Results were processed by Mountains Map Universal software (Version 2.0.13). The software ensured formation of surface profile projections and determination of roughness parameters according to ISO 25178 and ISO 4287.

3. Investigations of samples under mechanical tensile loads

All samples were made of MA2-1 magnesium alloy in the form of flat trowels. Preparation of samples was carried out according to GOST 1497-84 (ISO 6892-84).

Metal with a special texture could be re-coated owing to the features of NIN coatings formation by microplasma deposition, and two-layered material with defined texture of the metal - ceramic coating phase boundary would be formed taking into account the additional stage of microplasma impact.

Treatment of the samples was carried out as described above.

Preparation of the samples and NIN coatings formation in microplasma mode with predetermined phase boundary texture also were carried out as described above.

Designations of samples and the number of deposition – etching stages during the formation of two-layered NIN coating on magnesium with predetermined phase boundary texture are shown in Table 2.

Table 2. Designations of samples and processing stages.

Sample	M1	M2	M3	M4	M5
Number of coating formation operations	1	2	3	4	5
Number of coating etching operations	0	1	2	3	4

3.1 Tensile tests

Tensile tests were carried out in accordance with ISO 21180-201 by means of INSTRON 5948 testing machine together with Bluehill software. The software and its application for metal testing provided simple user interface and full control over all testing parameters in accordance with requirements of ISO 6892-1.

Edges of the sample were fixed in clamps of INSTRON 5948 testing machine so that the sample was straight without application of force and was not slipping in clamps during the test.

Constant tensile load was applied to the sample at a rate of 5 mm/min.

Coating surface analysis was carried out after deformation by means of raster scanning electron microscope SEM 515 without preliminary preparation of the sample.

4. Results and discussion

Figures 2 - 7 show profilograms of magnesium samples after microplasma texturing.
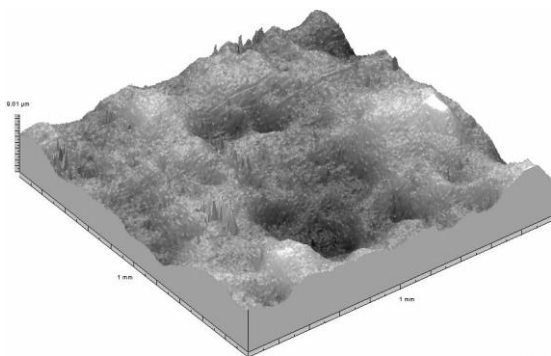
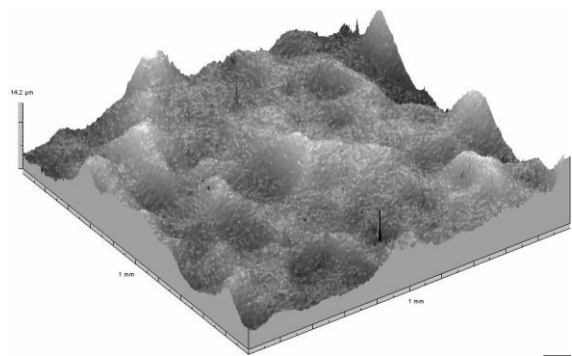**Figure 2.** Profilogram of M0 magnesium sample.
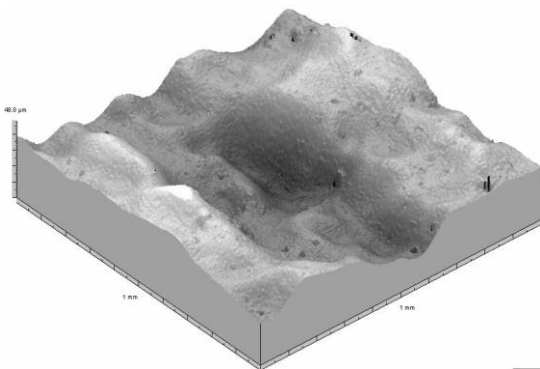

Figure 3. Profilogram of M1 magnesium sample.

Figure 4. Profilogram of M2 magnesium sample.
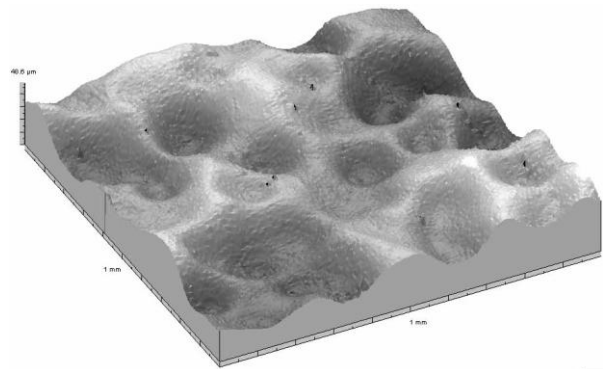

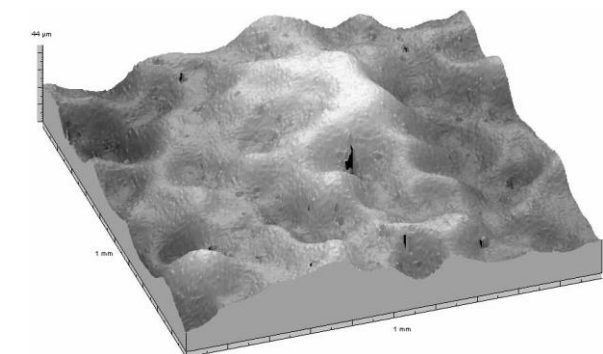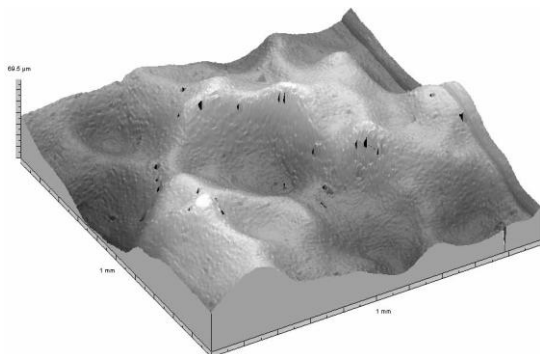**Figure 5.** Profilogram of M3 magnesium sample.

Figure 6. Profilogram of M4 magnesium sample.   **Figure 7.** Profilogram of M5 magnesium sample.

Table 3 shows Ra and Rz averaged over 3 definitions.

Table 3. Roughness of magnesium samples textured by microplasma method.

Sample	M0	M1	M2	M3	M4	M5
Ra av., μm	0.818	1.123	4.180	5.523	3.977	2.883
Rz av., μm	3.75	5.88	19.83	20.53	23.57	13.50

The obtained data showed that the value of Ra roughness increased after every stage of microplasma texturing from stage 1 to stage 3. Then the surface smoothened, and the value of Ra roughness decreased. Thus, it was advisable to carry out three consecutive stages in the described mode of microplasma texturing that provided Ra values up to 5.5 μm.

The value of Rz roughness increased until the fourth stage of microplasma texturing and then decreased. Profilograms analysis showed that during the microplasma texturing of magnesium submicrotexturing took place aside from microtexturing. Submicrotexturing is rather difficult to quantify now but it will be useful in order to increase the adhesion with subsequent coating layers.

Mechanical characteristics obtained by tensile tests of the samples are presented in Table 4.

Table 4. Mechanical characteristics of coated MA2-1 magnesium alloy samples with different phase boundary texturing stages under mechanical loads.

Sample	M1	M2	M3	M4	M5
Maximum load, N	1230.00	900.00	900.00	700.00	490.00
Tension, MPa	224.59	190.57	165.01	130.91	104.79
Deformation (elongation), %	21.40	20.76	20.16	14.88452	10.91
Deformation (elongation) in total creep, %	7.13	1.87	5.77	0.83	0.69
Elongation, mm	3.27	1.62	2.47	0.69	0.37
Elongation in total creep, mm	1.14	0.29	0.92	0.13	0.11
Modulus of elasticity, MPa	2 612.87	4 061.91	3 976.41	5 195.19	4 526.07

The obtained data showed that maximum tensile load decreased, modulus of elasticity increased and the value of creep decreased with increasing of texturing stage number. This fact was connected to the thinning of the sample as a result of NIN coatings formation features in microplasma mode with the following etching. Plasticity reduction was proportional to the thickness reduction of the sample.

Thicknesses of samples are presented in Table 5.

Table 5. Thicknesses of samples.

Sample	M1	M2	M3	M4	M5
Thickness, mm	1.10	1.00	0.95	0.85	0.75

Figures 8 – 12 show micrographs (magnification 500 and 1000) of coatings before and after application of mechanical load. Micrographs under magnification 500 appeared to be more informative for most samples.
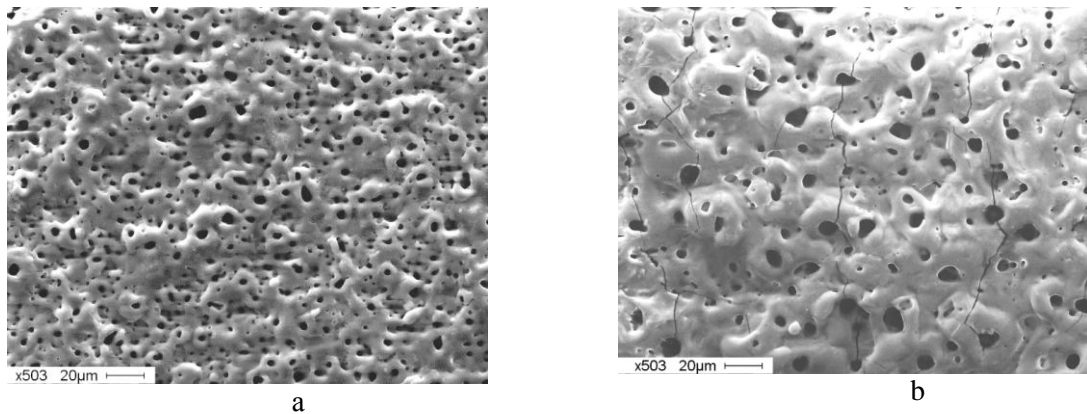
Figure 8. Surface micrographs of coatings formed on magnesium alloy with predetermined phase boundary textures – one texturing stage, before (a) and after (b) application of mechanical load.
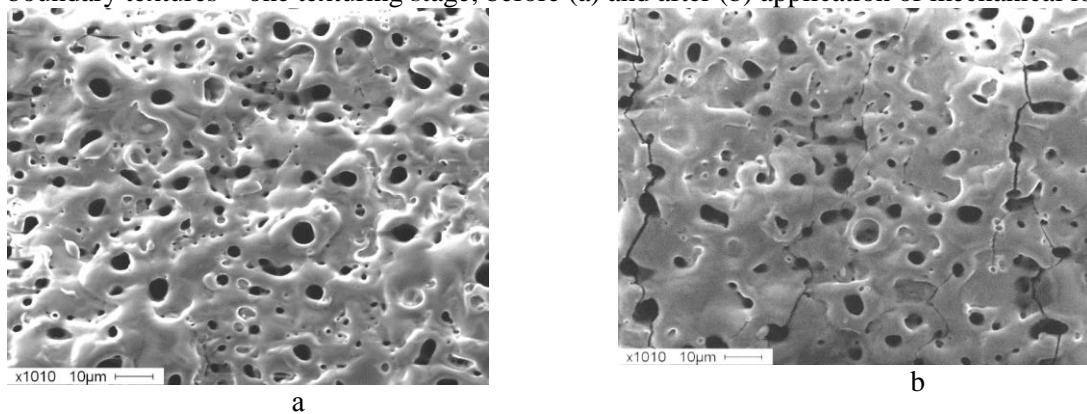

Figure 9. Surface micrographs of coatings formed on magnesium alloy with predetermined phase boundary textures – two texturing stage, before (a) and after (b) application of mechanical load.
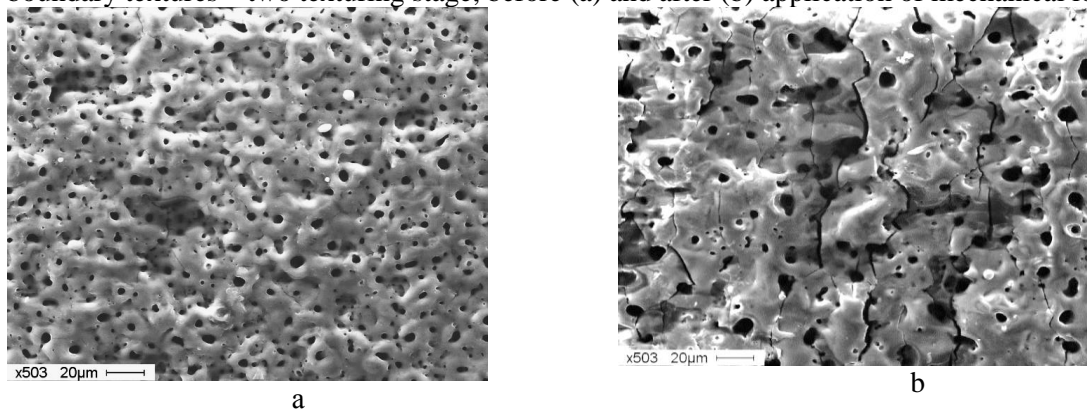

Figure 10. Surface micrographs of coatings formed on magnesium alloy with predetermined phase boundary textures – three texturing stage, before (a) and after (b) application of mechanical load.
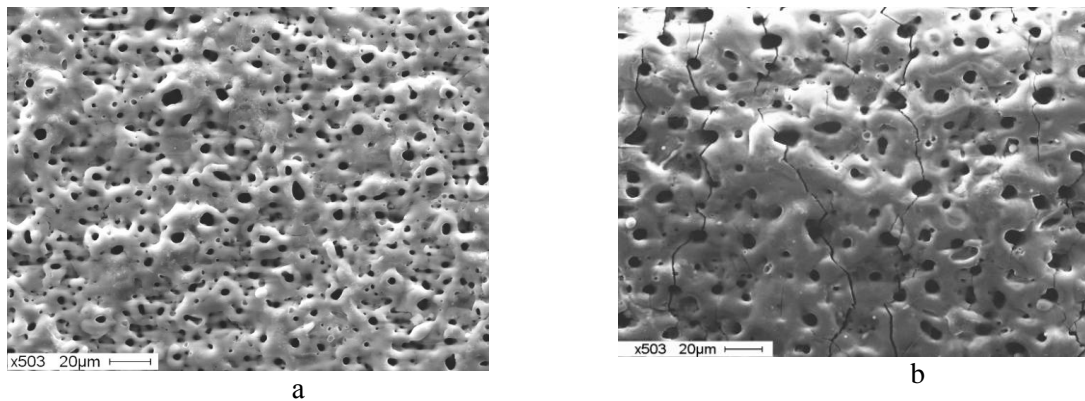
Figure 11. Surface micrographs of coatings formed on magnesium alloy with predetermined phase boundary textures – four texturing stage, before (a) and after (b) application of mechanical load.
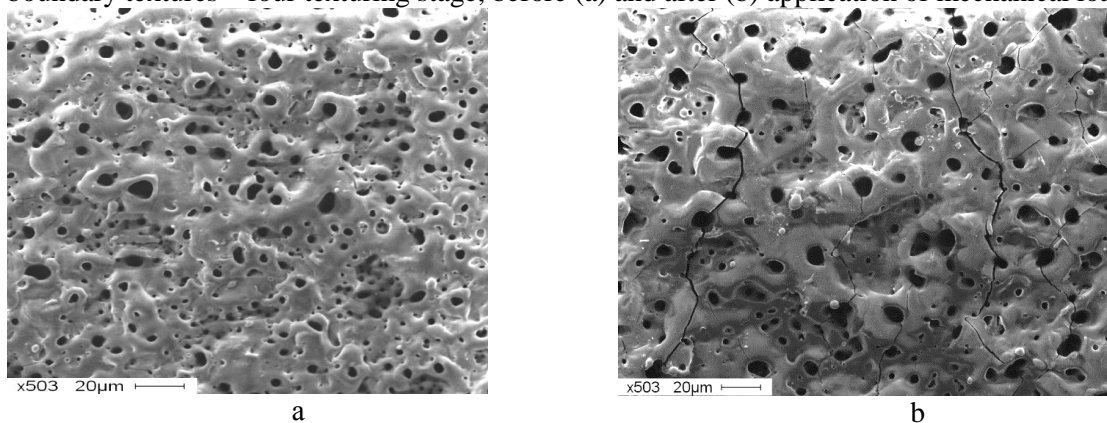

Figure 12. Surface micrographs of coatings formed on magnesium alloy with predetermined phase boundary textures – one texturing stage, before (a) and after (b) application of mechanical load.

Micrographs showed that the coating was porous with pore size 1 - 5 μm, nanoscale pores were also observed. Visible cracks directed normal (parallel) to the loading line were apparent on the coating surface after mechanical load application. Cracks were wavy and characteristically curving around pores.

Cracks distribution character did not change for each cycle of texturing unlike the average distance between cracks. Thus, the average distance between cracks for samples after one texturing stage was 40 - 50 μm that corresponded to average texturing step at that stage (Figure 3), two texturing stages – 35 - 40 μm (Figure 4), three texturing stages – 25 - 35 μm (Figure 5), four texturing stages – 30 - 35 μm (Figure 6), five texturing stages – 35 - 45 μm (Figure 7).

Analysis of micrographs obtained after tensile tests for MA 2-1 magnesium alloy sample with NIN coating – one texturing stage under maximum load 1287 N (Figure 13) with deformation value 26.61 % – showed that there was a partial removal of upper coating layer. This fact indicated that the load was concentrated inside the coating. Since the coating was inelastic, the net of microcracks relaxing at the pores appeared.

Deformation value was 26.61 % that resulted in macrocracks formation. Exfoliation of the coating was not observed.
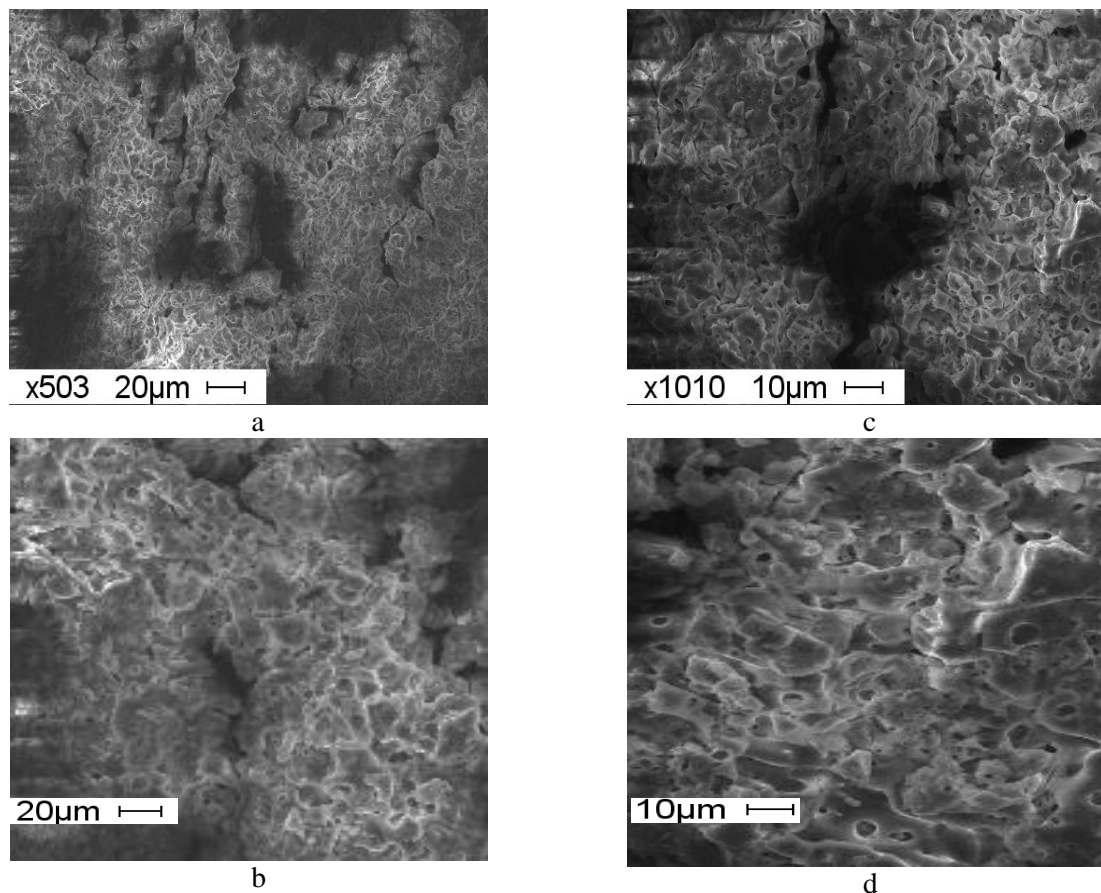
Figure 13. Surface micrographs of coatings formed on magnesium alloy after 26.61% deformation value under different magnifications: a – magnification 500, b – separate section on the photos a, c – magnification 1000, d – separate section on the photos c.

5. Investigations of NIN coatings destruction under critical tensile load

Figure 10 shows surface micrographs of NIN coating produced by microplasma oxidation after critical tensile load application.
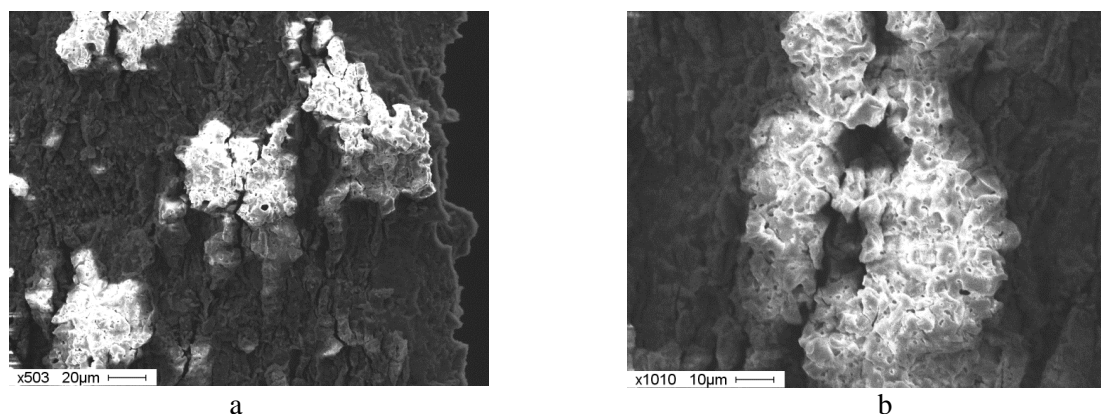

Figure 14. Surface micrographs of the coating formed on magnesium alloy after critical tensile load application: a – magnification 500, b – magnification 1000.

   Micrographs showed that circular microcracks were strongly marked around pores after exfoliation of upper coating layer, and circular cracks formation was also observed.

6. Conclusions

Step by step microplasma texturing method for metal surfaces was proposed and considered.

Special feature of magnesium alloys microplasma texturing was increase of Ra roughness value after every stage of microplasma texturing from stage 1 to stage 3 with the following surface smoothening characterized by decrease of Ra roughness value. Rz roughness value also increased until the fourth stage of microplasma texturing and then decreased.

Thus, the proposed method of step by step microplasma texturing can be considered as one of the best ways of valve metal surface texturing. Hence, microplasma texturing is an operation factor of phase boundary structure in laminated materials.

Destruction and deformation processes in two-layered NIN coatings with predetermined metal-coating phase boundary texture were investigated.

Metal thickness decreased during the coating formation with increase of texturing stage number, and the two-layered material became elastic and resilient wherein plasticity reduction was proportional to the thickness reduction of the sample.

Micrographs showed that the microcracks obtained during deformation processes were parallel to each other and normal to the loading line with wave nature of distribution.

Linear microcracks appeared at the thinnest parts of the coating, namely, on texture tops (Figure 8), and then relaxed at the pores during their extension. Since the load increased in that point, some new microcracks appeared starting from the previous relaxation point. New microcracks grew up to the next pores and so on.

With increase of texturing stage number, i.e. with increase of the surface roughness, the average distance between cracks decreased, in its turn the distance between cracks was inversely proportional to deformation values.

Exfoliation of upper coating layer and circular microcracks around pores were revealed after critical tensile load application, and circular cracks formation was also observed.

Samples with textured coatings were able to withstand substantial elongations up to 26 %.

Thus, investigations showed that insular circular microcracks were formed after moderate tensile loads. These microcracks did not result in coating exfoliation as the load was removed (Figures 8 - 10). Since the microcracks were circular, they relaxed on themselves during their extension. Circular cracks emergence removed the load within the coating and prevented the main crack leading to exfoliation of the coating. The obtained data corresponded to theoretical review from section 3.

References

[1]   Mamaev A I, Mamaeva V A, Beletskaya E Yu, Chubenko A K and Konstantinova T A 2013 A teory of a collective microplasma process for formation of nanostructural inorganic nonmetallic coatings through localization of high-energy flows in the nanolayers of the metal-electrolyte interface. mathematical modeling. Part 1. *Russian physics journal* (Springer New York Consultant Bureau) **56** pp 959–969

[2]   Dey A, Mukhopadhyay A K, Gangadharan S, Sinha M K and Basu D 2009 Development of hydroxyapatite coating by microplasma spraing. *Materials and manufacturing processes.* **24** pp 132 –1330

[3]   Xin S, Jiang Z, Wang F, Wu X and Zhao L 2001 Effect of current density on Al alloy microplasma oxidation *J. Mater. Sci. Technol* **17** pp 657–660