Research of structure and properties of boride hardening coatings

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Abstract. High strength aluminum alloys are particularly suitable as lightweight materials in vehicle and aircraft engineering. The wear resistance of materials can be improved by surface and coating technology. Strengthening of parts and units of machines, increased reliability and longer service life is an important task of modern industry. The aim of research was to apply boride coatings on surface of steel parts. Timeliness is subject to necessity to harden surface of steel used in high-load conditions. Samples of coatings on 65 G grade steel, applied by HFC-heating, were obtained. Research of samples with different coatings by means of metallurgical microscope was carried out. Data on samples with different coatings research by means of an eddy current measuring system was obtained and conclusion on electrical conductivity distribution along the sample surface depending on flux quantitative content during boriding was made.

1 Introduction

High strength aluminum alloys are particularly suitable as lightweight materials in vehicle and aircraft engineering. Because of their high specific strength, accelerated masses can be reduced, which enables savings of energy costs and the reduction of CO2 emissions. A further improvement of material properties can be achieved by the creation of aluminum matrix composites (AMCs). An enhancement of strength, hardness, E modulus and creep resistance can be achieved by ceramic particle reinforcement of aluminum alloys as small particles (below 1 μm) contribute to dispersion hardening and grain refinement during material processing. The resistance of materials against abrasion and adhesive wear generally increases with increasing hardness. Thus, AMCs exhibit superior wear resistance compared with aluminum alloys and cast iron under sliding wear conditions. This enables the implementation of AMCs in automotive applications such as brake discs, drum brakes, calipers and cylinder liners [1] and weight reduction due to the substitution of iron base materials. However, as reviewed by Deuis et al. [2], AMCs consisting of high-strength aluminum alloys and micron or submicron scale particles are susceptible to fatigue wear at higher normal loads. Crack initiation takes place at pores, which arise close to particles due

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to plastic deformation of the matrix alloy at the critical depth beneath the surface. Finally, plate-shaped material volumes are delaminated from the surface.

The wear resistance of materials can be improved by surface and coating technology. Especially ceramic coatings provide efficient wear protection due to high abrasion resistance and low adhesion against metallic counter bodies. Compact oxide ceramic coatings can be generated by plasma electrolytic oxidation (PEO) on aluminum alloys. The conversion coatings exhibit excellent adhesion to the substrate and a maximum thickness of more than 100 μm.

Creation of promising disposable and reusable hypersonic airborne devices in aerospace industry requires complex solutions of a range of problems, one of which is research and development of high-temperature heat-protective coatings.

Relevance of this research is based on the fact that space airborne vehicles, when in a long-duration flight in the atmosphere, are exposed to considerable aerodynamic heating under impact air pressure. Materials of space vehicles have to maintain high durability, temperature resistance, minimal linear shrinkage.

Rise of efficiency effectiveness of heat-protective materials is assured with use of coatings that raise temperature resistance and mechanical durability of materials. In virtue of theoretical and experimental research, basic requirements for a hardening coating composition were created: working temperature – 1650, 20-30% raise of compressive strength of gradient fibrous material with no more than 3% change of its thermophysical properties [3, 4].

Process of "classic" diffusion boriding is a rather common method of steel and steel parts case-hardening. During boriding, two-phase saturable surface is most often obtained, it consists of mixed borides FeB, Fe_2B and transition zone — solid boron solution, as well as other elements of steel in α-Fe.

Boron atoms have relatively small size and high mobility; therefore, they can easily diffuse into ferrous alloys, forming FeB and Fe_2B intermetallic [5]. According to the boron–iron phase diagram, maximum amount of boron that can form a single-phase Fe_2B is 33.5 at.% [6].

Boron is one of the elements that can generate unique properties in the steel surface. The use of hard layer (such as boride) to improve surface properties is a method for protecting substrate from environmental effects. The boride layers have high hardness, low porosity, high corrosion resistance, and adhesive wear resistance [7].

The thermo-chemical boriding process of steel allows FeB and Fe_2B phases to be obtained. Generation of these layers can improve the surface hardness and wear resistance of equipments and components for tribological applications. By controlling the boron potential in the steel surface, both single-layer (only the Fe_2B phase) or multilayers (FeB–Fe_2B phases) can be produced [8]. The presence of the FeB phase in the layers leads to the brittleness of layers and high stress intensity at FeB–Fe_2B interface [9].

After the "classic" boriding, the coating microstructure, most often, is coalescent at the bottom of boride needles, that form a coating layer. Resulting internal tensile stresses in the borated coating significantly reduce their plasticity, therefore peeling and chipping of such a hardening coating occur, until its complete destruction, at relatively small bending, shock or compressive stresses and especially reversed loads and vibrations.

All of the aforesaid restrains application of isothermal boriding process for wide use when hardening parts surfaces made of steel in agricultural machinery industry.

Boriding, is a thermochemical surface treatment, in which boron is diffused into, and combines with the substrate material forming a single or double-phase metal boride layer at the surface. Unlike many other surface treatments, hard boride layers can be developed on most alloys and metals by boron diffusion. The boriding of ferrous materials causes the formation of either a single layer (Fe_2B) or double-layer (FeB/Fe_2B) with definite composition. The thickness of the layer formed (which is known as the case depth), has an effect on the mechanical and chemical behaviours of the borided steels, that depends on the boriding temperature, the treatment time and the boron potential that surrounds the sample surface [10]. When the treatment time, and temperature are increased, the FeB regions become much deeper, and they grow from compact and oriented Fe_2B crystals. The phases grow preferentially in the (002) plane, increasing the mechanical stress over the FeB/Fe_2B interface because of the significant differences between the expansion coefficients of both phases in the range of 473 to 873 K [11].

The surface hardness of the boride layers is usually measured by traditional techniques such as the Knoop and Vickers microhardness. However, as a result of its wide acceptance for exploring the mechanical behavior of elastic–plastic materials, such as ceramics, the nanoindentation technique has also been used to measure different mechanical properties under monotonic loading and unloading, in which the data are usually processed by the manner proposed by Oliver and Pharr [12]. Some devices also enable continuous stiffness measurement (so-called CSM mode), where a small harmonic signal (amplitude of several nmor a fraction of amN) is added to the monotonously increasing basic load. The harmonic contact stiffness is measured continuously, and makes possible the determination of properties during loading from “zero” to the maximum force. However, the CSM mode is especially suitable for materials with time-dependent response, such as plastics or biomaterials [13].

In recent years, Culha et al. [14] employed ultra-microhardness tests to estimate the mechanical properties of FeB layers, such as the dynamic hardness and the Young's modulus in AISI 1020 and 1040 borided steels.

The steels were exposed to different experimental conditions during the boriding process. The load-dependant elastic modulus and the dynamic hardness values of the FeB layer were within the range of 125–397 GPa and 775–1381 HV, respectively. The validity of the Young's modulus values proposed in [15] was verified taking into account that the indentation depth should not exceed 10–25% of the boride layer thickness, avoiding the effect of the steel properties in the elastic values of the FeB layer. In addition, finite element modelling was applied to simulate the yield strength of the FeB layer on a low-alloy steel substrate; the resultant values ranged from 5 to 7 GPa [15].

The mechanical properties such as fracture toughness, compressive residual stresses, and the indentation size effect (ISE) were also evaluated in the tips of the needles of the Fe_2B layer using the Berkovich nanoindentation technique [16]; the results showed an apparent hardness of approximately 14 GPa with a fracture toughness between 2.4 and 2.7 MPa, and the compressive residual stresses were between 351 and 471 MP

In case of boriding by HFC-heating, the speed of coating formation increases hugely more due to increase of heating rate, if special fluxes are used there is no need to create a protective atmosphere, since the boriding time does not exceed several minutes. Besides HFC-heating allows to reduce time of high temperatures effect on the base material, as well as to combine easily the boriding process with subsequent heat treatment. In the future, little time for boriding carried out by HFC-heating, may promote the use of this boriding method in flow production lines, in mass production, and production of large quantities of hardened parts per shift.

Preliminary experiments carried out by us showed the principal possibility of boride coatings formation on steel parts surface during HFC-heating. During preliminary experiments, it was ascertained and confirmed that when the heating rate was increased, the rate of reaction and consequently the formation of coating increased hugely more in comparison with an isothermal case-hardening in furnace, and it was ascertained that it was necessary to use borate fluxes, for example P-0.66 flux, to obtain high-quality, indistinguishable coatings.

2 Materials and methods

As an promising materials for protective-strengthening coatings, offered matrix composites based on the ternary system Fe-B-Fe_nB, formed directly on the surface of the reinforcing parts, when it boriding in conditions of induction heating of the charge of the original composition and the various functional fillers.

Coating the ternary system Fe-B-Fe_nB formed by induction heating on the surface of the reinforcing parts when passing exothermic topochemical reaction between iron steel and boron the charge, the reaction captures the surface layer of the base-material and the reaction products form with it a single whole and characterized by smoothly changing the chemical composition of the transition at the interface base-coat which determines their high adhesion strength and durability, special properties [17, 18].

Coating samples were obtained for 65 G grade steel made of compositions of boron carbide and amorphous boron under conditions of high-frequency heating to research boriding processes performed together with HFC-heating of surface of structural and alloy steels of main grades used in an agricultural machinery industry, and the effect of carbon and alloying elements in steel, physical, physical and mechanical properties and wear resistance of boride coatings.

Boride coatings of 65 G steel during simultaneous SHS process and HFC-heating were obtained from a modified mixture of 2Al + B2O3 composition containing 20 and 30% of P-0.66 flux. Temperature of boriding process in all cases was 950 - 1250°C, saturation time was 40 - 180 sec.

The higher composition of Al in FeB-Al coating results thicker coating. Interdiffusion layer, which is composed of intermetallic phases, is formed in FeB-50 at.% Al coating after heat treatment [19].

The compositions were applied to prepared (cleaned) surface of 50*100*5 mm 65 G steel plates as daubing, and after drying they were subject to HFC-heating according to the same mode: first, before the initiation of the SHS process, and then, at reduced generator power by 25% within 60-80 sec.

Templates and samples for metallographic examination were prepared from the obtained samples. To prepare microsections, a manual cutting machine, a sharpening machine and a manual grinding-and-polishing machine were used.

To determine samples structure, the surface of prepared microsections was treated with 4% nitric acid solution in ethyl alcohol within 5-7 seconds. The main objects of study in the work were selected steel 65G, wear-resistant boride coatings, which were investigated by electron microscopy (Philips SEM - 515) and eddy-current measurement system [20-23].

3 Experimental results

Photos of samples were taken by means of OLYMPUS GX51 inverted metallographic microscope after etching of microsections, and response value of VDDS-5 eddy-current gage system was obtained as it moved above the sample surface.

Research results for the structure of coating obtained by SHS process during HFC-heating of modified mixtures containing 20 and 30% P-0.66 flux for 65 G steel are shown in Figures 1-8.

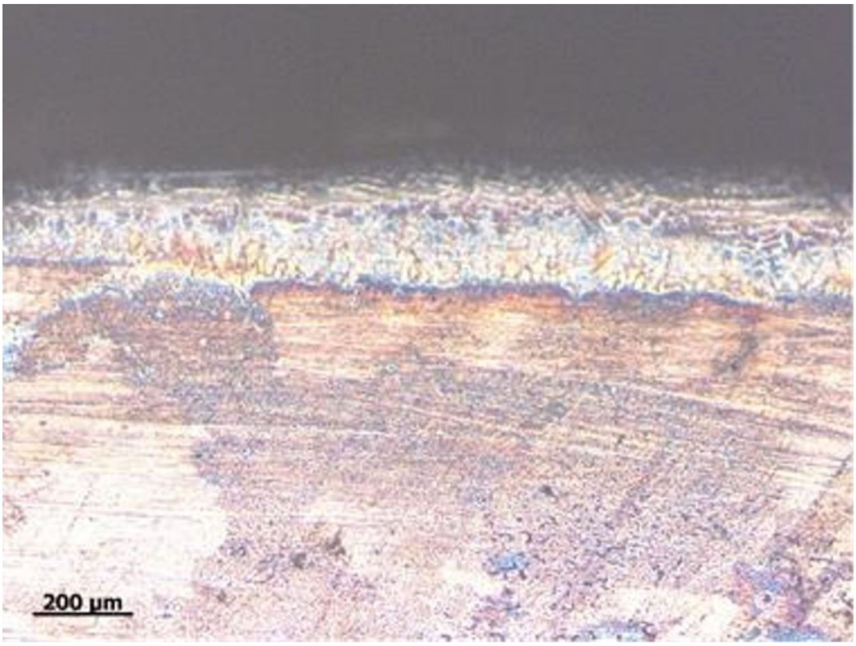

Fig. 1. Microstructure of coating received from modified mixture with 20% of P-0.66 flux (enlargement ×100)

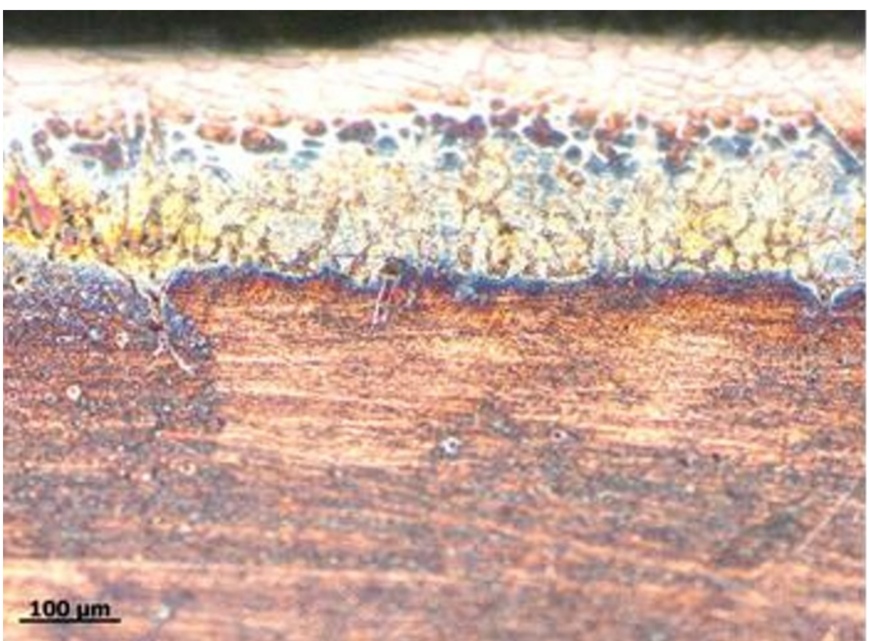

Fig. 2. Microstructure of coating received from modified mixture with 20% of P-0.66 flux (enlargement ×200)

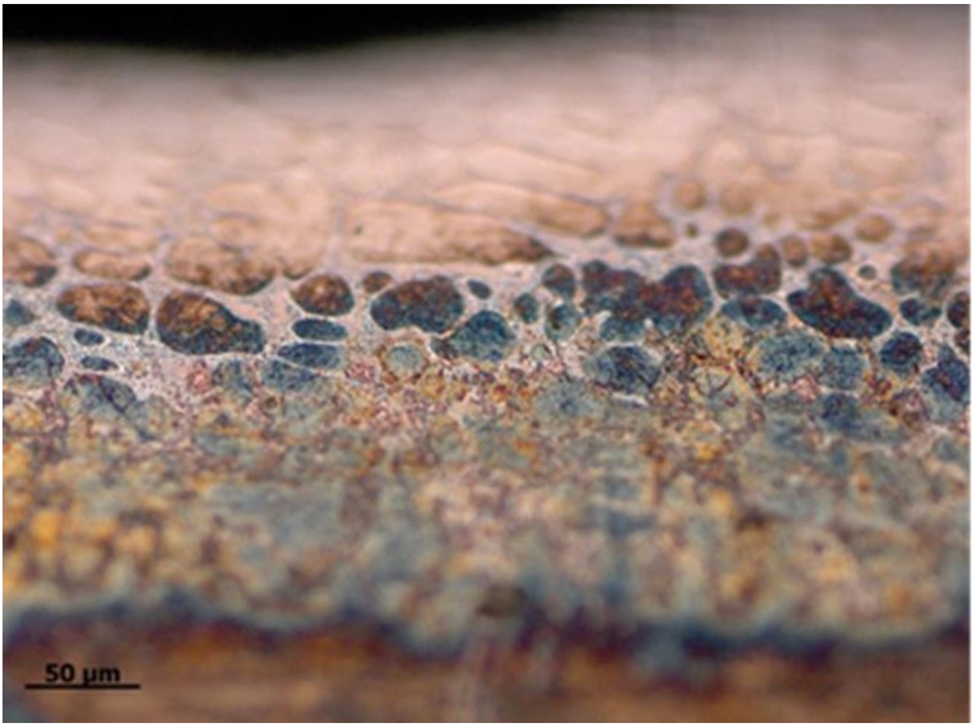

Fig. 3. Microstructure of a coating received from modified mixture with 20% of P-0.66 flux (enlargement ×500)

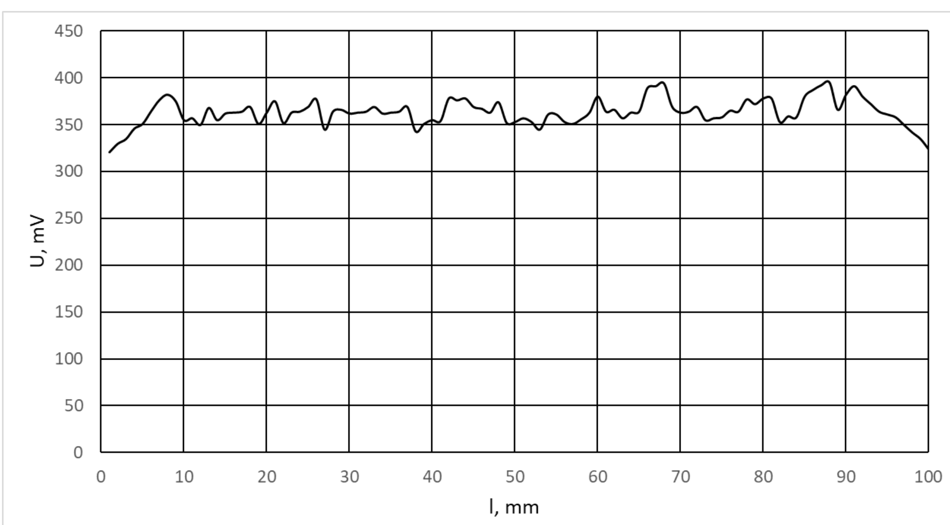

Fig. 4. Signal of eddy-current transducer VS location of sensor above the object that is under research

As it can be seen at Figures 1-3, the structure of coating formed is one of the typical ones found earlier in boride coatings obtained from mixtures based on amorphous boron, the thickness of the resulting coating is 230-250 μm. Signal amplitude of eddy current transducer (Figure 4) when scanning along the surface of sample under research varies significantly (RMS deviation - 12.6 mV), this allows to conclude that the obtained coating is unevenly conductive.

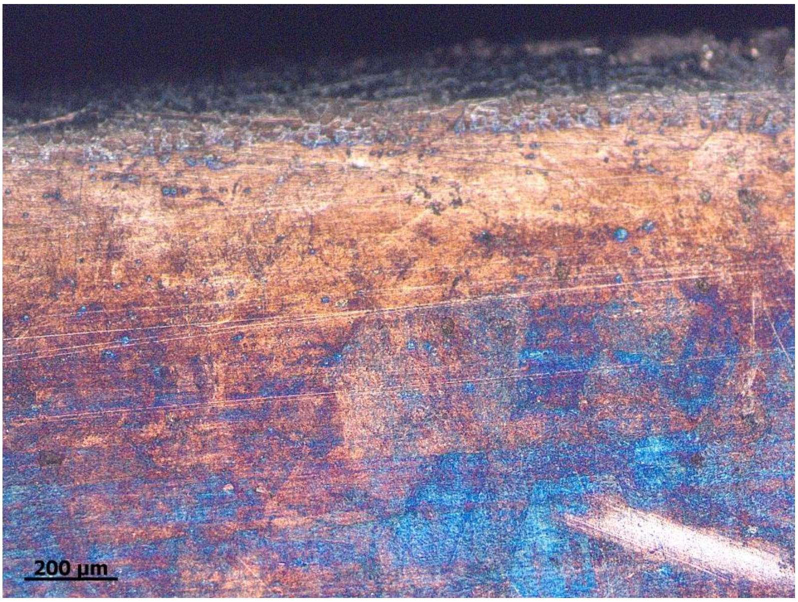

Fig. 5. Microstructure of coating received from modified mixture with 30% of P-0.66 flux (enlargement ×100)

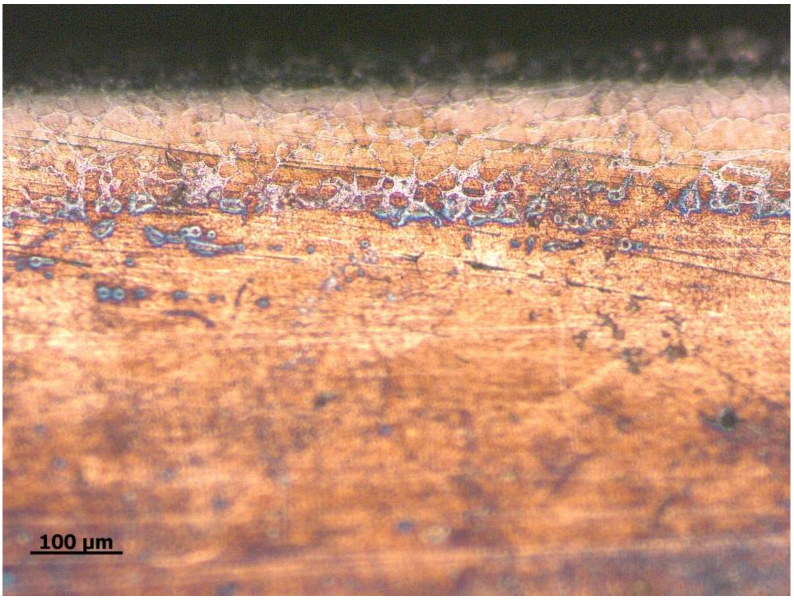

Fig. 6. Microstructure of coating received from modified mixture with 30% of P-0.66 flux (enlargement ×200)

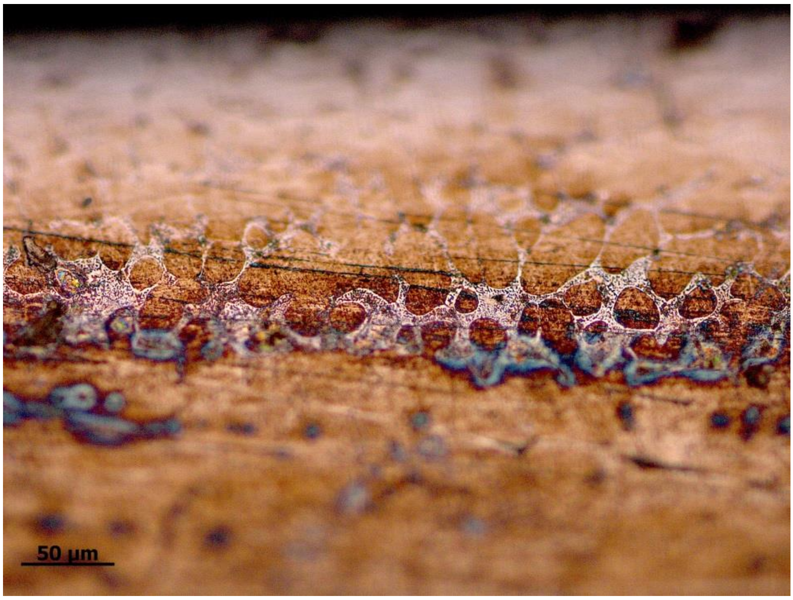

Fig. 7. Microstructure of coating received from modified mixture with 30% of P-0.66 flux (enlargement ×500)

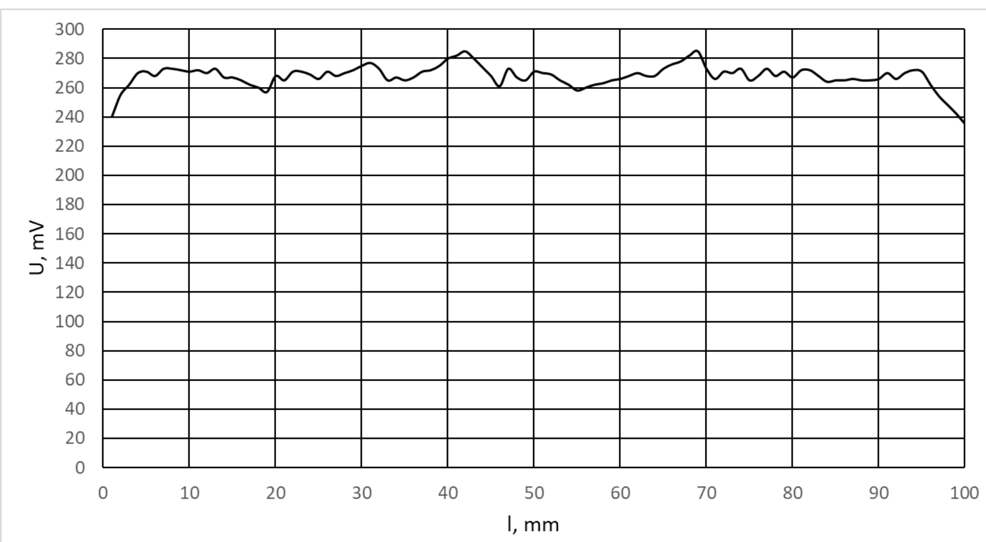

Fig. 8. Signal of eddy-current transducer VS location of sensor above the object that is under research

As it can be seen at Figures 5-7, if content of P-0.66 flux increases, a similar structure of boride coating is formed in modified mixture, with marked boundary with base metal, but its thickness is smaller and amounts to 170 - 190 µm. Signal amplitude of eddy current transducer (Figure 8) when scanning along the surface of sample under research changes significantly less than in the standard mixture (RMS deviation of 4.6 mV), this allows to conclude that there is much less change in electrical conductivity of the obtained coating.

4 Conclusion

We applied the developed measuring system to examine the objects being by nature of conductive and non-conductive coatings, placed on the conductive base, as well as to measure the thickness of the solid conductive objects. We determined that the thickness of the coating influences the eddy-current transducer signal. This allows us to prospectively use the amplitude control method of such object class for exact local measurements of the thickness of conductive and non-conductive coatings as well as of other objects. Owing to the received dependencies of the eddy-current transducer signal on various coatings, it becomes possible to use the developed system in the diagnostic testing of composite hardening coatings.

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