5. Danilenko T.P. *Optimizatsiya rezhimov termicheskoy obrabotki na osnove razrabotki novogo metoda opredeleniya parametrov prostranstvennoy zerennoy struktury*. [Optimization of the modes of heat treatment on the basis of development of new method of determination of parameters of spatial grain structure. Doctoral dissertation of PhD in Technical Sciences]. DMetI. Dnipropetrovsk, 1988. 227 p.
6. A. c. 1397832 USSR. The method for determining the distribution of the grain sizes of flat sections of metallographic samples. E.Ya. Lezinskaya, T.P. Danilenko. *Byulleten' izobreteniy*. 1988. No19.
7. Danilenko T. New method for stereological reconstruction of nontransparent materials space structures. Proc. 1-st Int. Conf. "*Development, Testing and Application of Materials*". Croatia, 1996, p.p. 89 – 95.
8. The patent for invention No 97453 Ukraine. Method for determining the basic parameters of the bulk structure of metallic materials. T.P. Danilenko, E.I. Danilenko. *Promyslova vlasnist'*. 2012. No3.

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Peculiarities of protective coating of constructional details with powder obtained from industrial wastes

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Abstract
The main processes of combined application of a protective coating on the details are described in the article. The characterization of progressive coating process, which includes electric metallization followed by synthesis was given. Microstructure and performance of protective coatings for structural parts made of powder obtained from industrial wastes was stadied.

Keywords: PROTECTIVE COATINGS, INDUSTRIAL WASTES, METALLIZATION, OXIDE CERAMIC COATING, WEAR RESISTANCE

Actuality of problem

Lately new powder materials cause great interest to the technology of plasma coatings that are characterized by high productivity, versatility, ease of automation, unlimited size of surfaces that are covered. Special attention is paid to applicaton of composite ceramic, metal, bio metal and other synthetic compositions [1-3].

Earlier the development of protective coating was based on creating of high-performance equipment and improvement of technological processes, now it is especially important to create new powder materials that provide a set of protective coatings during operation of parts and components, machines and mechanisms.

On the other hand, methods and technological processes of powder metallurgy allow to use widely industrial wastes: chip scrap, scrap metal, off-cuts that after melt may be sprayed into powder with specified physical-chemical and technological properties. Obtained powders may be used for the manufacture of composite materials of structural and tribotechnical destination. Utilization of grinding wastes of bearing production allows to get powders of high-alloy bearing steel BBS15.

Theoretical and experimental researches to improve the physical-mechanical and technological characteristics of powdered steel BBS15 obtained as a result of utilization of grinding sludge are being conducted in Lutsk National Technical University for many years.

Special attention should be given to application of protective coatings on various details that will significantly increase their durability.

One of the basic directions of coating improvement is the use for their spraying of powder-like compositions, where characteristics of different by nature components - metals, oxides, borides, carbides etc are combined.

At present, an effective way to protect parts is the application of hot-gas composition coatings with complex of improved physical and mechanical properties. In order to create special purpose coatings (wear-resistant, heat resistant and corrosion-resisting), methods of protection, which include micro- and nanostructured films and phases are widely used.

Problem statement

At present the questions related to the process of interaction of surfaces in contact during their mutual movement. Creation and selection of tribotechnical materials are based on the solution of interrelated tasks on the basis of study of mechanics of friction and physical and chemical phenomena that take place on the surface.

Interaction contact of solid bodies is observed only in specific areas, the size and density of the placement of which depends on the applied load, as well as the stress-strain state of contacts. These contacts depend on the microscopic geometrical shape and mechanical properties of the surface layer.

Application of electrometallic coating with further oxidizing will give the possibility to protect details from wear and increase their lifetime infinitely. Oxide ceramic coatings are characterized by very high microhardness. With the introduction of this technology of details protection from wear in the most responsible nodes and mechanisms of machines, it is possible to extend significantly the operating time of equipment before repair or refusal. This method of protection next to wearproofness will considerably increase corrosive firmness of details that work in the conditions of aggressive environment.

The purpose of the work

The aim of this paper is to analyze the main methods for protecting of details surfaces of constructional purpose obtained from powders of industrial wastes and to investigate the application of the coating process that meets modern requirements.

Application and description of the methodology

The following basic requirements are put forward to the protective coaitngs: they must be solid, impermeable, have high adhesion strength with basic metal, high hardness, wear resistance and should be distributed uniformly across the surface they applied.

According to the development trends of modern technology concerning creation of high-quality composite materials and coatings with complex of high physical and mechanical characteristics, devepolment of new topical powders, which are formed from such compositions, are currently important.

There are various technologies for producing composite powder including gilding metal jacket [4, 5]. Such methods of cladding of powders have their advantages and disadvantages.

For example, superficial electrodeposition of metals (Fig.1) prevents protection of nonconducting powders, as their pre-metallization in other ways is required. The possibility of cladding of powders by carbides, nitrides and other hard compounds is also excluded. Electrolytic and chemical coatings are used for the restoration and strengthening of parts (chroming, ironing, nickelage), corrosion protection and attribution of good appearance of details (nickelage, chroming, zincing, cadmiuming and others.).

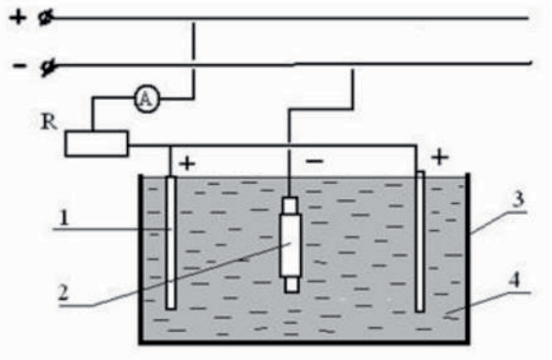


Figure 1. Installation scheme for the electrolytic precipitation of metals: 1 - coating material (anode); 2 – product(cathode) 3 - bath; 4 - electrolyte

Chemical metallization of powders allows to create single and multilayers of different powder materials (Fig. 2). Disadvantage of thie method is the need for washing and drying of powders.

Method of ion-plasma sputtering of metals (Figure 3) takes a special place among the common vacuum technology of condensing of metal films in the conditions of arc discharge [6-10]. This perspective method of cladding of powders thanks to its physical and technological capabilities allows to spread the metal shell with high rates of deposition and the metal part of condensate up to 25%. Thus it is possible to form complex compositions of ceramics with different connections, including the ones, occuring during banded precipitation of different metals. High temperature on the surface in certain cases can become a negative factor in the process of cladding; as a result the particles of powder stick together forming conglomerates.

Variant of reactive (chemical) ion-plasma coating offers the same opportunities for oxides, nitrides and other compounds as reactive cathodic sputtering.

In addition, the vacuum-arc cladding can move and mix the powder with the help of vibrating devices.

In this regard, researches on improving and optimizing the processes of vacuum condensation deposition of films on the powder mixtures are relevant and focused on the creation of qualitative clad powder material for further its use, including thermal spraying coatings.

There are a lot of general points in the methods and technological peculiarities of vacuum condensation spraying. In this regard, it is appropriate to consider a generalized process diagram (Figure 4).

The main advantages of considered method is its simplicity and the possibility to obtain exceptionally pure films (at a high vacuum). However, it has serious disadvantages: difficulty of spraying of refractory materials and the inability to reproduce chemical composition on the backup of evaporant. The last is explained by the fact that at high temperature chemical compounds dissociate and their components condense on the backup separately. Natural is the probability that new combination of atoms on the lining

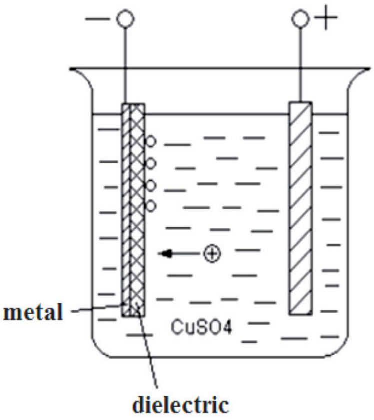


Figure 2. Scheme of chemical metallization

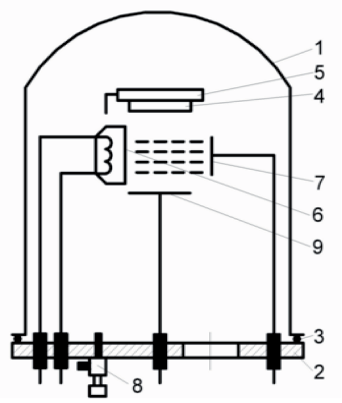


Figure 3. Scheme of installation of ion-plasma spraying: 1 - cover 2 - base plate, 3 - gasket, 4 - lining, 5 - holder, 6 - incandescent cathode 6,7,9 - electrodes, 8 - socket

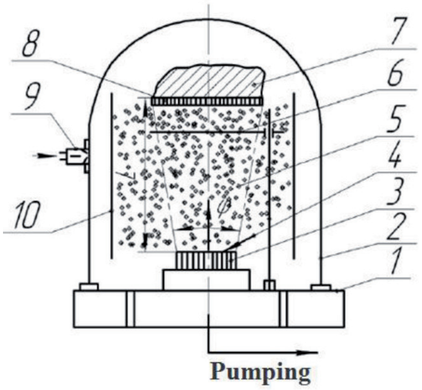


Figure 4. The generalized scheme of vacuum condensation spraying 1 - base plate; 2 - camera; 3 - material is sprayed; 4 - a supply power for spray material; 5 - a stream of particles; 6 - flap; 7 - spraying product; 8 - coverage; 9 - working gas filler; 10 - screen

will not correspond to the structure of initial molecule [11].

Electric arc spraying is one of the ways of application of metallic coatings on metallic and non-metallic surfaces. Electric arc spraying is used for a long time, mainly to produce zinc and aluminum corrosion-resistance coatings and application of wear resistant coatings and recovery coatings.

The protective coating was obtained by spraying of continuous wire by means of electric metallizer with the modified spray system (Fig. 5), where electric arc burns in the spray head channel that allows to obtain finely dispersed coverages. [12]

To power metallizer with direct current there used welding rectifier of VDU – 505 type.

To clean the compressed air from the solid parts, water and mineral oil there applied filter separators 23–25–4–4HL4.

The process of coating of the sample includes the following operations: sample degreasing; shot peening processing; spraying of samples; quality control of spraying; grinding of samples.

As source material there used grinding steel sludge of BBS15 steel, formed after mechanical processing of rings and rollers of bearings in terms of PJSC "SKF Ukraine." Grinding steel sludge of BBS15 steel contains a significant amount of iron oxides and chromium, products of abrasion grinding of grinding-wheels, and various oils, synthetic fluids, water, which are the coponets of coolant.

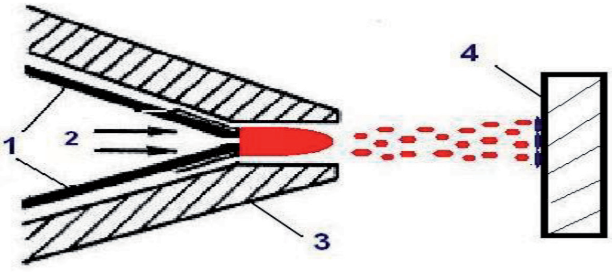


Figure 5. The process electric arc spraying:
1 - wires; 2 - air stream; 3 - body spray head; 4 - lining

To obtain high-quality powder BBS15 there was applied a new patented technology, where the main difference from existing processing of sludge industrial wastes is that after the fine grinding of formed sintered material, there fulfilled additional grinding-pelletizing on the ball mill to give the powder particles smaller and regular spherical form [13, 14]. Obtained by this technology metal powder is a high-quality powder with particles of regular shape and size, with high technological properties.

For applying corrosion protective coating on the details of construction designation, method of plasma electrolytic oxidation (PEO) is widely used. It is one of the most modern and advanced methods to obtain protective layers on the surface of metals and alloys that have a set of important characteristics. The properties of the coatings are determined by composition of electrolyte and process modes of PEO. To make a directed synthesis of surface layers of a given composition on metals and alloys in the mode of plasma electrolytic oxidation when choosing the electrolyte composition and modes of oxidation, one should be guided by a number of provisions, taking into account the possibility of changing the form of anionic complexes in solution depending on the pH value both in the capacity of electrolyte and in the local area of electrode space [15].

Development of oxide-ceramic coating was conducted in Karpenko Physico-Mechanical Institute of the National Academy of Sciences of Ukraine. The task was to create on the details combined coating from D16 alloy using elektrometalization followed by oxidation. For realization of PEO process a detail-hob was fastened in the device, surfaces that is not covered by D16 alloy were protected from a contact with an electrolyte, as oxidizing of iron is impermissible (this is connected with the fact that for formation of oxide-ceramic coating only valve metals are suitable) and will result in worsening of the process of formation of oxide-ceramic coating.

The main electrical parameters of the process are anode voltage U_a, cathode voltage U_c, density of cathode and anode current I_c, I_a, pulse duration and their frequency, duration of the process τ, min. [16].

General view of installation of plasma electrolytic oxidation depicted in Figure 6.

For application of oxide ceramic coating (OCC), the modes should be set. They include current density

Figure 6. General view of installation for PEO

on the anode and cathode and their voltage. The area of surface is defined the first. It is subjected to oxidizing and depending on the required thickness the time of process duration is determined. In this case, the oxide ceramic coating was applied on parts with different thickness and modes of PEO process. PEO coating of different thickness according to thickness ratio of voltages I_c/I_a=1 and I_c/I_a=1.5 was applied on detailsl.

PEO process took place in the electrolyte of the following composition: 3 g/l KOH + 2 g/l of sodium silicate, the remaining - water. Current density was adopted as i= 20 A/dm^2 for three samples and i = 7,5 A/dm^2 for one sample.

Presentation of material

The authors of the research carried out the experiments using four samples - hubs, which are made of industrial wastes (powder steel BBS15). Microsections were previously made and pickled. Pickling of samples was carried out by pickler - 0.5 ... 3% alcoholic solution of hydrofluoric acid HF.

Let us present first a general view of the sample No1 after applying of combined coverage (Fig.7). Samples No2 and No3 have a similar appearance, but applied coatings are of different thicknesses and modes of PEO, so only one photo is available.

When studing of the microstructure of samples, pressed and sintered of powder from steel BBS15, there revealed significant amount of graphite and copper particles and ferrite (Figure 5).

In Figure 8 in the upper limit one may see the base metal (position 1), and below with a dark gray there represented electro metal cover (position 2) and plasma electrolytic oxidized coating (position 3). The boundary between base metal and electric arc coating is clearly defined, but not uniform. To see and compare how the microstructure of the sample changes before and after pickling, let us consider microstructure of sample before pickling (Fig.9).

Fig. 9 shows the area of sample, which was not pickled. Comparing microstructure of unpickled and pickled areas of electric arc sprayed coating, one may see not only the difference in color (in Fig. 9 electric arc coating has a bright color, and in Fig. 8 it is darker) and also in the pickled area one may see the structure and grains of coating. The microstructure of pickled areas at magnification × 250 and × 400 is shown in Figure 10.

Figure 10 shows that the area between base metal and coating is small, consequently electric arc coating has a very high adhesion towards the base metal. Fig. 8 and Fig. 9 revealed that the inclusion of graphite are observed in the structure of base metal and are arranged randomly.

The microstructure of plasma electrolytic oxidized coatings is characterized by a homogeneous structure and peculiar porosity. After pickling there observed clearer line of distribution of electro metallic coating and coating, which is formed by plasma electrolytic oxidation. This is typical for all samples.

Figure 11, a represents non-pickled area of the sample, and Figure 11, b - the pickled one. Herein it

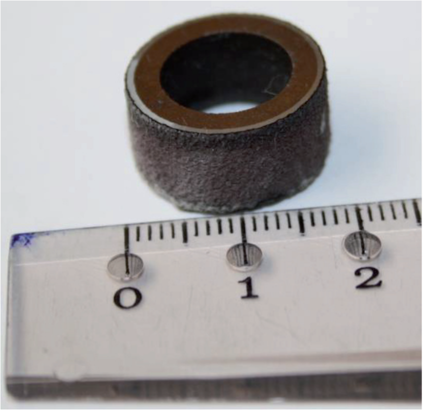


Figure 7. General view of the hubs after applying the combined coating

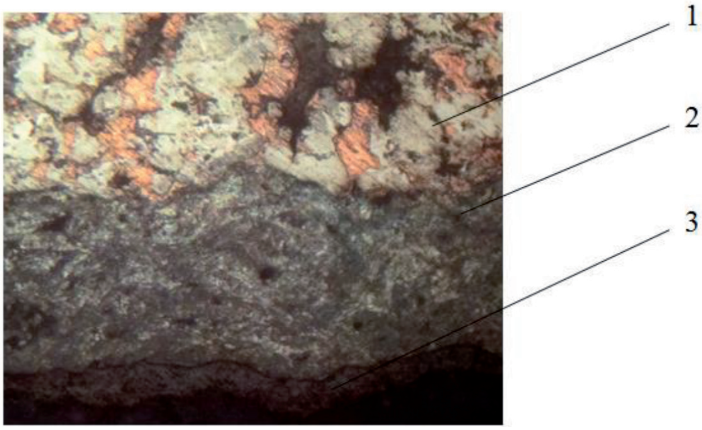
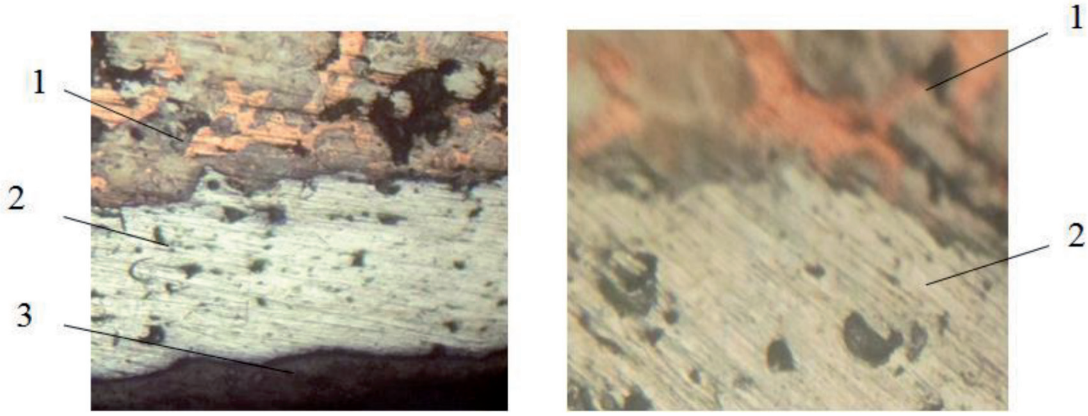


Figure 8. The microstructure of samples-hubs (× 100)

a) b)

Figure 9. Microstructure non-pickled areas of the sample at magnification: a) × 100; b) × 250
1 - base metal; 2 - electro metalic coating; 3 - plasma electrolytic oxidized coating



a) b)

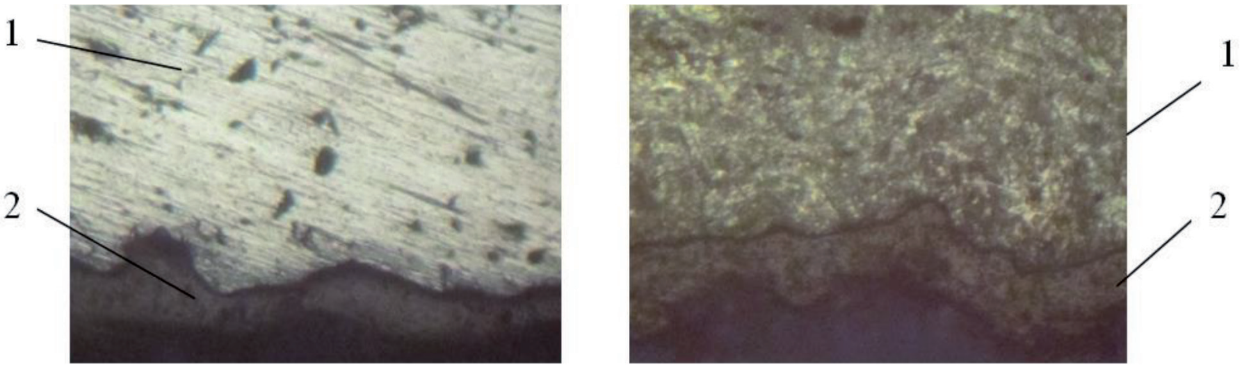
Figure 10. The microstructure of pickled area of the sample at magnification: a) × 250; b) × 400
1 - base metal; 2 - electro metalic coating; 3 - plasma electrolytic oxidized coating

is noticable that the PEO coating is characterized by layer unevenness (dimples and knobs).

After pickling there is a clear distribution limit of elektrometalic and oxide-ceramic coating. The grains on oxide ceramic surface are not deposited.

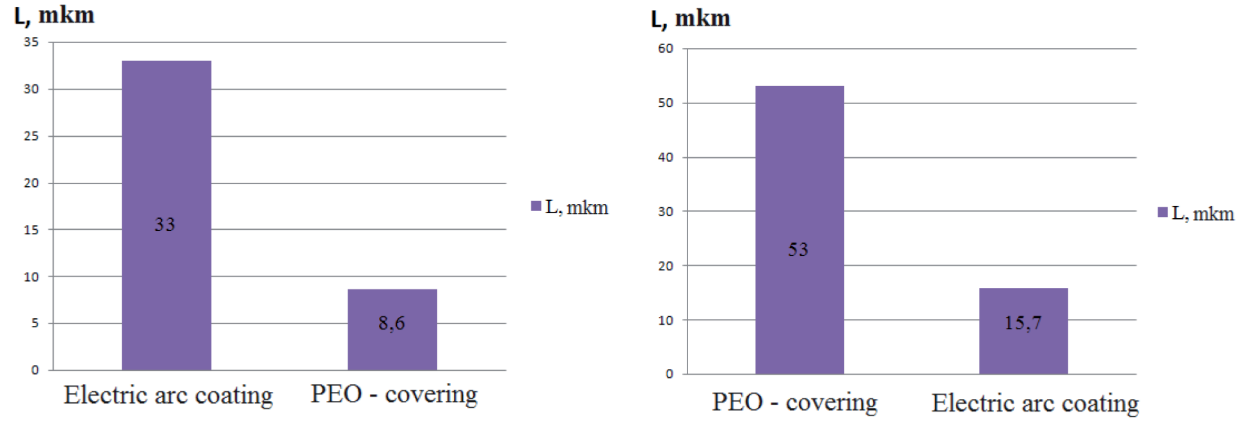
Combined protective coating is formed by deposited electo-metallic layer and plasma electrolyte oxide ceramic layer. The thickness of each coating was determined by measurements in three places and determination of the average value of thickness for each coating. By adding averages of thickness of electric arc and PEO coatings, there was found an average thickness of the combined protective coating.

Dependence diagrams of coating thickness on the method of application for four samples-hubs are presented in Fig. 12 and 13.



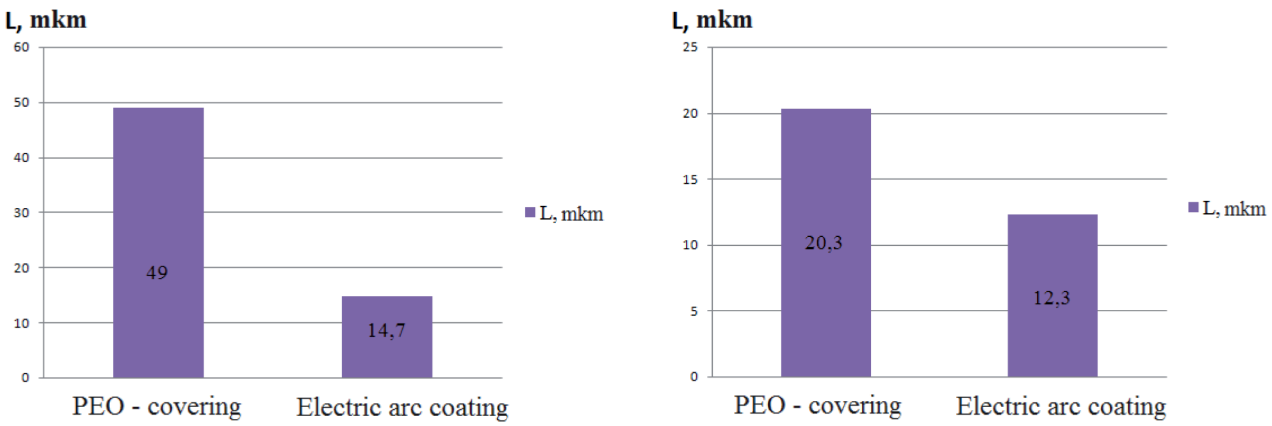
a) b)

Figure 11. The microstructure the sample-hub: a) × 100 non-pickled area; b) × 100 pickled area
1 - electric arc coating; 2 - PEO coating



a) b)

Figure 12. Dependence diagram of coating thickness on the method of application:
a) sample No1; b) sample No2



a) b)

Figure 13. Dependence diagram of coating thickness on the method of application:
a) sample No3; b) sample No4

Microhardness tester PMT-3 was used to determine the microhardness. Microhardness of base metal, electrical arc and plasma electrolytic oxidized coatings by applying three spikes in each area (two spikes were made on the edges and one in the middle of coating or base metal) were determined. After the spikes there were imprints of indentor (diamond pyramid). Diagonal of print was measured and applied to the formula. Microhardness each of sample was found.

The formula for determining of microhardness is as follows:

$$H_{\mu} = \frac{1{,}854 \cdot P(\text{kg})}{(N_{л} \cdot 0{,}0003)^2} = \left[\frac{\text{kg}}{mm^2}\right] \quad (1)$$

where P - the weight of the load, kg; $N_{л}$ – he number of limb divisions.

Let us also present the generalized graphics of microhardness changes starting from the base metal and coatings. Numerical data of microhardness values for base metal, elektrometalic and PEO-coating is shown in Table 1.

Table 1. The average value of microhardness of samples produced of industrial wastes

Sample	Covering		
	Base metal	Electric arc coating	PEO - coating
No1	592.8	327	3876.5
No2	653.3	295.6	8305
No3	736.3	613.6	4616
No4	991.6	1526.6	7157

From Fig.14 the change of microhardness depending on the coating method is seen. Microhardness first decreases at electic arc coating, then begins to grow rapidly, moving to PEO coverage.

Conclusions

Based on the analysis of scientific literature and previous studies, one may conclude that the methods

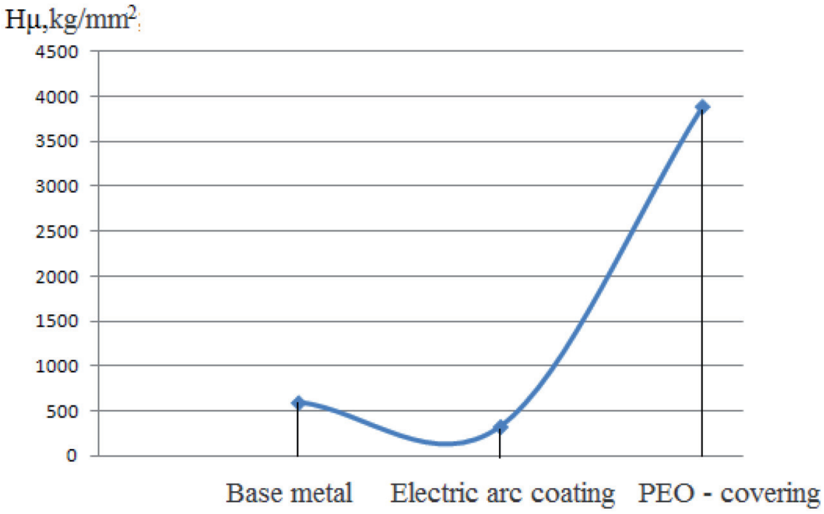


Figure 14. The generalized dependence of microhardness change on the coating application for hubs, which are made of industrial wastes

of powder metallurgy enable the creation of anti-friction composite materials from industrial wastes with different constituents of various structural components that are included into the material (especially steel powder BBS15).

Promising direction is the development of composite materials based on structural steel powders obtained from industrial wastes.

The authors applied the combined protective coating on the details of construction purposes - hubs, operating under conditions of reverse-translational friction. Protective coating was applied with the help of electic arc metallization and plasma electrolythic oxidation.

In the process of experimental studies there were defined the following main characteristics of coatings: the largest thickness of combined protective coating of hubs is equal to 63.7 microns; the largest microhardness of electric arc coating of hubs is H_μ=1526,6 kg/mm^2, and the greatest microhardness of plasma electrolytic oxidized coating of hubs was H_μ=1526,6 kg/mm^2

References

1. Rudenskaya N.A. (2004). New plasma multipurpose coating and their self-organization. *Protection of Metals.* No 2, p.p. 173-177.
2. Lima R.S., Marple B.R. (2007). Thermal Spray Coatings Engineered from Nanostructured Ceramic Agglomerated Powders for Structural, Thermal Barrier and Biomedical Applications: A Review. *J. Thermal Spray Technol.*, No 16(1), p.p. 40–63
3. Cai J. P., Li B. (2000) Thermal Spraying Ceramic Coatings. *Mater. Mech. Eng.* Vol 24 (No. 1), p.p. 5-7.
4. Vishenkov S.A. *Khimicheskie i elektrokhimicheskie sposoby osazhdeniya metallopokrytiy.* [Chemical and electrochemical methods of depositing of metal coatings]. Moscow, Mechanical engineering, 1975, 312 p.
5. Vashchenko V.V, Golubev O.N., Svetuhina S.P., Tsidulko A.G. Plakirovanie poroshkov tugoplavkikh soedineniy metodom khimicheskogo. Temperaturoustoychivye funktsional'nye pokrytiya [Cladding of powders of refractory compounds by chemical. Temperature resistant functional coatings]. Tula, Science, 1985, p.p. 131-134.
6. Horoshux V.M. (2003). A stationary vacuum arc in technological systems for surface treatment. *Physical Surface Engineering.* No 1, p.p.19-26.
7. Denbnovetsky S.V., Barchenko V.T., Shmyreva L.N. *Fizicheskie osnovy generatsii plazmy v ionno-plazmennykh ustroystvakh tekhnologicheskogo naznacheniya* [Physical fundamentals of plasma generation in ion-plasma devices of technological purpose]. Study guide. Kyiv, UMK VO, 1989, 152 p.
8. Pustotina S.R., Novikov N.N., Glukhov P.K. Study of the properties of metallized powders of refractory compounds and plasma coatings on their basis. Temperature resistant coating. Works of XI All-Union Conference on heat-resistant coatings, Tula, Leningrad, Science 1985, p. p.157-161.
9. Novikov N.N. Features of behavior of particulate materials when they are in a vacuum metallization . Head of NIINTP Ukraine from 09.12.87, 20 p.

10. Sharonov E.A. Vannovsky V.V., Alekseev S.V. Vacuum arc deposition of copper on ceramic powder SiO2-FeOn. Works of the 6th International Conference “Films and Coatings - 2001”. SPb .: SPbGTU, 2001, p.p. 146-149.
11. Lipin Yu.V., Rogachev A.V., Sidorsky S.S, Kharitonov V.V. Technology of vacuum metallization of polymeric materials. Gomel. Gomel Department of Belarusia Ingineering tehnological Academy, 1994, 206 p.
12. Pohmursky V.I., Student M.M. Dovgunik V.M. Pohmurska G.V. Sidorak I.Y. *Elektrodugovi vidnovni ta zakhisni pokrittya* [Electro- arc restoration and protective coatings]. Lviv. National academy of sciences of Ukraine, Karpenko G.V.Physical-mehanical institut, 2005, 192 p.
13. Patent of Ukraine No 63558 A МПК 7 B22F9/04. A method of producing of metal powder from sludge wastes / V.D.Rud, T.N.Halchuk, O.Yu.Povstyanoy. Presented 06.05.03; Published 15.01.04. Bulletin No1, 2004.
14. Povstyanoy O. Yu. Improving of technology of manufacturing of porous powder materials using industrial wastes: Ph.D. thesis in Engineering Science. Lutsk, 2007, 169 p.
15. Imbirovych N. Yu. Development of oxide ceramic coatings on zirconium and titanium alloys by plasma electrolytic processing: Ph.D. thesis in Engineering Science. Lutsk state Technical University. Lutsk, 2006. 125 p.
16. Belozerov V.V., Mahatylova A.I., Rebrov E.M. (2005). Influence of chemical composition of aluminium alloys on the structure and properties of MAO-coatings. Bulletin of National Technical University “Kharkiv Polytechnic Institute”. Technologies in engineering science. Kharkiv, No23, p.p. 25-30.