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New sulphiding method for steel and cast iron parts

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Abstract. A new method for sulphiding steel and cast iron part surfaces by electroerosion alloying (EEA) with the use of a special electrode is proposed, which method is characterized in that while manufacturing the electrode, on its surface, in any known manner (punching, threading, pulling, etc.), there is formed at least a recess to be filled with sulfur as a consistent material, and then there is produced EEA by the obtained electrode without waiting for the consistent material to become dried.

1. Introduction

Improving reliability and durability of machine parts is inseparable from a surface layer quality. Manufacturing the parts entirely made of wear-resistant materials is impractical due to the difficulty and high cost of processing such materials. Therefore, to improve operational performance and increase the service life of the machine parts, there are used wear-resistant coatings, which have found wide application in manufacture of various products, a lot of various methods for surface hardening, and also other ways to prevent seizing and galling friction surfaces, which are particularly important for the parts working under conditions of dry friction.

2. Analysis of the main achievements and publications

Improvements of protective and tribology properties of the machine part surfaces can be achieved both through creating a special topography of the surface layer [1, 2], and applying special coatings [3, 4] thereto. The coatings, which are applied to the friction surfaces, can significantly improve reliability of machines and devices. On applying the coatings, there could be provided running-in ability of the friction surfaces, prevention of scuffing; lubrication at the initial time before oil supply to the friction surfaces, minimal wear of the friction surfaces, the lowest coefficient of friction and minimal changes of the same during operation, increasing contact friction fatigue of friction unit materials, and others [5].

At present in industry, there is an acute problem of creating multifunctional wear-resistant coatings for heavy duty friction pairs operating at high line speeds and applied pressure with insufficient lubrication or complete lack thereof [6].

Recently, there have been conducted works on producing products, which could be used without external lubrication. These products are specified as "self-lubricating" ones because they use no external lubrication in the course of operation, and there are mainly used composite materials having molybdenum disulphide (MoS2) in their composition. Formation and research of coatings based on molybdenum disulfide is one of the most promising directions in the field of creating solid lubricating coatings [7].

The ability to demonstrate a "self-lubricating" effect, i.e. provide for operability of a sliding friction assembly unit without introducing external lubrication, is the main feature of the most amount of polymers used in friction units. The nature of the "self-lubricating" effect of those polymers lies in the features of a so-called "third body" that is formed on the polymer and metal surfaces. In this case, the structure and composition of this "third body" is a kind of a "lubricating" layer, which provides an opportunity of redeformation without any abrasive wear and galling [8].

There is known **a sulphiding method** that prevents seizing, and provides creating a film of sulfides on a part surface [9]. The sulfides increase the surface activity of metals and alloys, as well as the process of wetting the surfaces with active agents, and they also increase seizing resistance. An iron sulfide (FeS) film increases wearing resistance of friction surfaces and improves running-in ability thereof. A ferro - sulfide coating has relatively high porosity and it absorbs a large amount of grease providing the material with the self-lubricating property.

Traditionally, a **sulphiding method** is a process of saturating a metal surface layer (of steel, cast iron, titanium alloys, etc.) with sulfur in appropriate salt baths. A depth of a sulphided layer is up to 50 microns. Besides increasing a surface roughness and dimensions of a part being processed, the disadvantages of the conventional sulphiding method includes the necessity to heat the entire part, and accordingly, the structural changes of metal, distortions and warpage, large processing time, high consumption of electricity, negative impact on the environment, and others. [10].

There is known a method wherein sulfur is introduced into the part surface by electric spark alloying (ESA), the same as electroerosion alloying (EEA). To introduce sulfur, it is deposited on a part surface as a powdered sulfur layer, and then there is carried out the process of alloying the part surface through the above said layer by the materials of the part or a coating. In the course of processing, applying of the sulfur powder is repeated 2-3 times [11].

It should be noted that this method does not result in a desired result.

The special features of forming properties and surface structure are provided by EEA entity that is as follows. Having been thrown out of the anode, the material in the liquid-drop and vapor states as an expanding beam enters the inter-electrode space heated by the passed electrical pulse to a temperature, at which the substance can exist in ionized state. The particles of the material collide with the cathode surface (a part) also locally heated by electric pulse, interact with it to form alloys, solid solutions or mechanical mixture. The micro-bath materials formed on the cathode and the anode incoming particles interact with each other and with the elements surrounding the electrodes.

Sulfur is a non-electrically conductive powder and to be used in the EEL process, that is to provide the alloying electrode contact with the surface being alloyed, the sulfur should be pushed aside by the alloying electrode. In this case, entering of the sulfur into the liquid phase zone of the electrode materials and forming of chemical compounds becomes significantly difficult, and if it occurs, it only happens at some isolated places. Continuity of the sulphide film surface is very low.

There is known an ESA method performed by iron sulfide electrode for processing steels 45, H12F, gray and pearlitic malleable cast iron, which method made it possible to form a 40-50 microns thick layer enriched with sulfur on the surface being treated. As a result, there has been significantly reduced the gray cast iron tendency to scuffing at dry friction, its wear has 8-10 times decreased, drawing dies durability has also 3.5 times increased [12]. The electrodes made of iron sulfide have been being produced according to Author's Certificate No. 139 336 published in Bulletin of Inventions of the Former Soviet Union, Number 13, 1961.

To manufacture the electrodes, the iron powder of AM mark previously deoxidized in a hydrogen atmosphere at 1100-1150^{0}C has been mixing with technical sulfur (iron powder/sulfur in a ratio percent of 61/ 39 weight/weight) in a ball mill for an hour. After discharging, the mixture will be heated until the reaction of iron sulfide formation has been completed. The obtained iron sulfide is crushed and then melted in a selit or gas furnace. The electrodes are made of the molten iron sulfide.

The casting process is performed at 1100-1150^{0}C into carefully dried earthen form having a proper permeability. The electrodes are ready for operation after cooling and removing metal burnt-on [13].

Despite the positive results reported above, the use of iron sulfide as EEL electrodes for sulphiding process has several drawbacks: the limited use of steel (iron) electrodes made of unalloyed steels at EEL processing. The electrodes made of unalloyed steels are heated, oxidized, and destroyed in the course of EEL processes, which negatively affects the quality of a coating being formed (high roughness, low continuity, burnt-on, welding separate smaller particles of a damaged anode). The above said electrode manufacturing method is expensive, time consuming and environmentally harmful.

Thus, the further research aimed at eliminating the above mentioned disadvantages of sulphiding process of steel and cast iron parts by the EEL method should be considered relevant and timely.

The purpose of the paper is to develop a new low energy-consuming and ecologically clean method for producing and applying electrodes for sulphiding steel and cast iron parts by the EEL method.

3. Research Technique

To study the sulphiding process by EEL method, there were prepared samples (15 x 15 x 8 mm) made of steel 20 and ductile iron VCH60 which served as the cathodes. The EEL process of the samples was carried out on various conditions of the EEL device of Elitron-22A model. The electrode-tool, namely, the electrode made of 12H18N10T stainless steel wire ∅ 3mm served as an anode. On the surface of the wire, there were provided special recesses performed by thread M3 cutting (Figure 1 (a)).

(a) (b) (c)

Figure 1. The electrodes are made of 12H18N10T stainless steel ∅ 3mm intended for sulphiding the parts by EEL method.

It should be noted that to manufacture a special electrode-tool, there may be used such a material as a corrosion-resistant metal, i.e. chromium, nickel, molybdenum, stainless steel 12H18N10T, 07H16N6, 30H13, nickel alloys HN58MBYUD, HN60VT, HN50VMTYUB etc., and grooves on their surface, besides threading, can be formed by any known method, e.g. punching, pulling through a die, and others.

Sulfur in the form of a consistent material was deposited into the grooves of the threaded surface. In this case, there was applied a sulfuric ointment wherein sulfur content was 33.3% (Figure 1 (b)). An amount of sulfur can be increased by adding the same, for example in the form of colloidal sulfur (Figure 1 (c)). Then, there was produced a process of sulphiding the samples by EEL method without waiting for drying the consistent material on the surface of the electrode-tool.

The qualitative analysis and quantitative composition of the coatings on the surfaces of the samples were carried out using the REMMA-102 scanning electron microscope of the Sumy "SELMI" production, which was equipped with X-ray spectrometer produced on the basis of lithium-silicon semiconductor detector.

The micrographs of the surface areas of the examined samples were obtained at various zoom levels under a mode of an image forming by secondary electron current at the microscope electron gun accelerating voltage of 20 kilovolts and the probe (beam) current of 200 pico amps. At the same time, on the surface of the coating, there were chosen three characteristic points (the smooth coating, the rough coating and the pore), and at each one of these points, there was determined an elementwise composition of the applied layer. In addition, the elementwise composition was determined along the depth of the layer with varying a scanning pitch.

As being under condition of X-ray microanalysis operation, the accelerating voltage was 20 kilovolt, and the beam current was one (1) nanoampere. Having been excited by electron beam, the characteristic X-rays were detected by a semiconductor detector.

The calculation of weight (mass) percent concentration was carried out by comparison of the examined samples with the standards. At the same time, there were taken into account the physical corrections for atomic number, fluorescence and absorption of radiation (three corrections method).

At all the research stages, the surface roughness of a sample was measured by the Profilograph-Profilometer (model 201) of the "Caliber" plant production. The device was modernized in such a way that the results of measurements were transferred to a computer through a special device.

4. Results of Researches

Figure 2 shows the topography of the surface portion of the coating formed by EEL method on a part made of steel 20 with the help of an electrode produced of stainless steel 12H18N10T at discharge energy Wp = 0.55 J, wherein there were selected three characteristic areas (1 - the smooth surface, 2 – the rough surface, 3 – the pore).

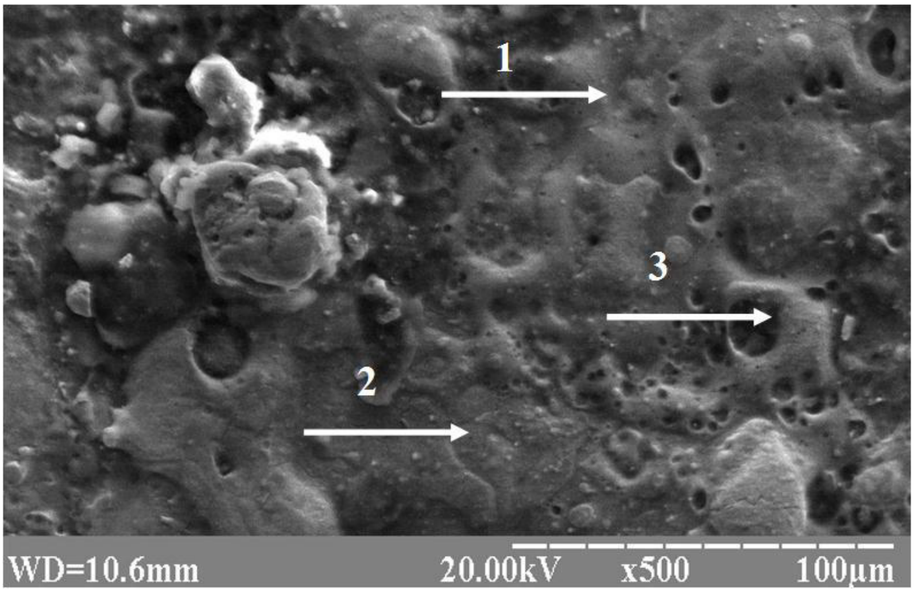
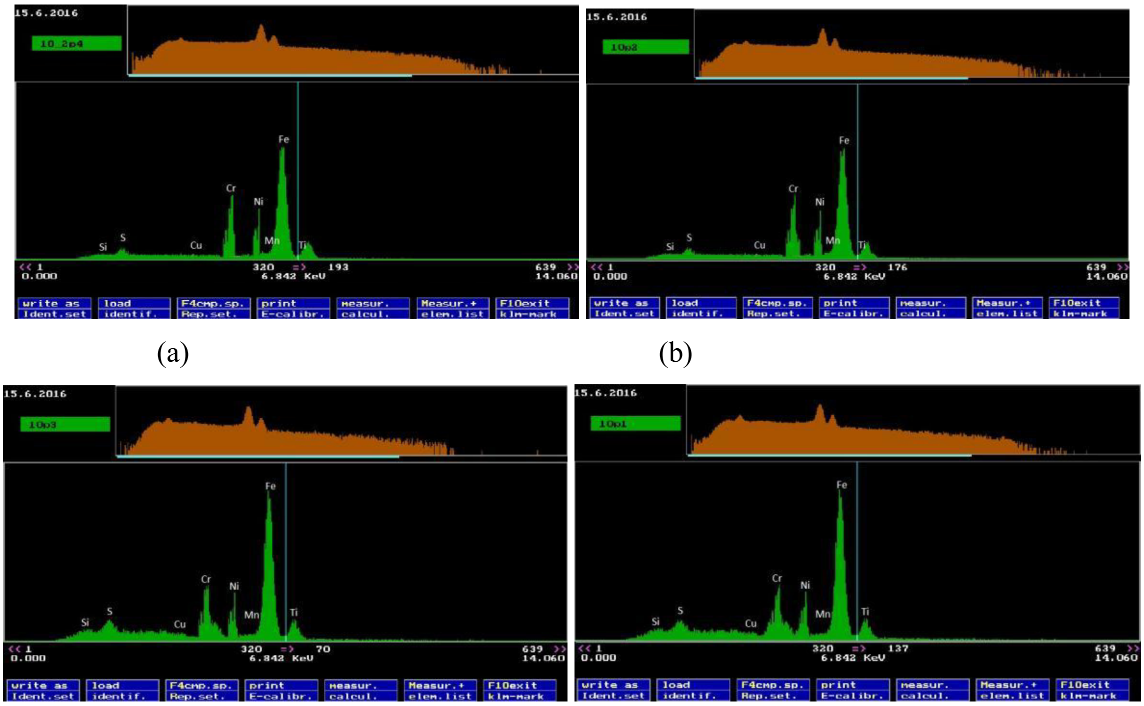


Figure 2. The topography of the surface portion of steel 20 after sulphiding by EEL method.

The spectrum of the surface and the elementwise composition both at the characteristic points, and on all the examined surface are, accordingly, shown in Figure 3 and Table 1.



(a) (b)

(c) (d)

Figure 3. The spectra of the surface at the characteristic points (a – the smooth surface, b - the rough surface, c - pore), and on the entire surface (d).

Table 1. The elementwise coating composition at the characteristic points and on the entire examined surface.

The examined point and the surface area	Elements, %							
	S	Cu	Si	Mn	Cr	Ni	Ti	Fe
1	0.56	0.20	0.24	0.60	16.20	9.30	0.71	72.16
2	0.60	0.21	0.22	0.58	17.21	8.89	0.69	71.60
3	0.53	0.23	0.18	0.62	15.23	9.19	0.83	73.9
Σ	0.55	0.87	0.21	0.60	16.87	9.07	0.89	70.94

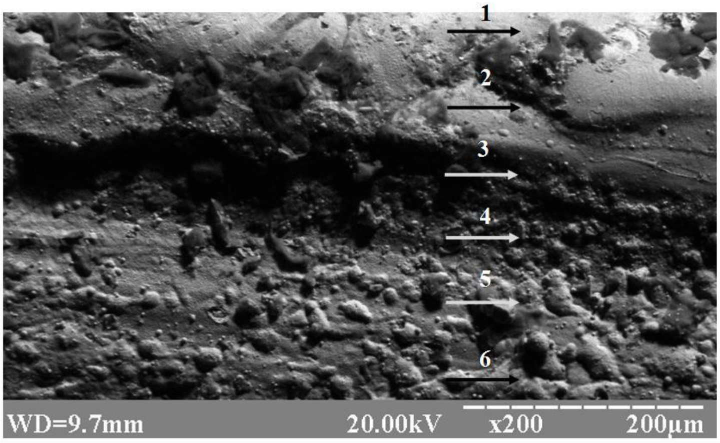


Figure 4. The points of scanning the coating along the layer depth.

Table 2. The elementwise coating composition with deepening from the surface.

The examined point of the surface	Elements, %							
	S	Cu	Si	Mn	Cr	Ni	Ti	Fe
1	0.41	0.23	0.24	0.58	9.21	5.21	0.61	83.51
2	0.31	0.19	0.22	0.51	5.23	3.19	0.34	90.01
3	0.12	0.20	0.21	0.62	3.19	2.23	0.21	93.22
4	0.09	0.21	0.23	0.57	1.16	1.21	0.17	96.36
5	0.06	0.16	0.16	0.54	0.53	0.76	-	97.79
6	0.03	0.24	0.17	0.53	0.21	0.25	-	98.57

In Table 3, there are represented the results of sulphiding the samples made of steel 20 and ductile cast iron VCH60 by a special electrode-tool made of steel 12H18N10T at various discharge energies.

Table 3. The results of sulphiding the samples made of steel 20 and ductile cast iron VCH60.

Sample material	Discharge energy, Wp, J	Sulphided layer depth, microns	Sulfur content, %	Surface roughness, Ra, microns
Steel 20	0.02	10	0.05*-0.85**	0.7
	0.05	25	0.05-0.80	1.7
	0.11	35	0.05-0.70	2.9
	0.36	50	0.05-0.65	5.2
	0.55	75	0.06-0.60	6.2
Ductile cast iron VCH60	0.02	10	0.05-0.85	0.8
	0.05	30	0.04-0.70	1.9
	0.11	40	0.05-0.65	3.1
	0.36	50	0.05-0.60	5.8
	0.55	75	0.05-0.50	6.7

* - The sulfur content in the lower portion of the sulfided layer;
** - The sulfur content on the surface portion of the sulfided layer.

The result of research aimed at improving the sulphiding process for the steel and iron cast substrates by the EEL method, presented in conclusions.

5. Conclusions

1. In the course of the sulfur saturation (sulphiding) process of the surfaces of steel 20 and ductile cast iron by EEL method with the use of a special electrode-tool made of stainless steel 12H18N10T at the device of "Elitron -22A" model, with increasing discharge energy from 0.02 to 0.55 J, the sulphided layer depth increases from 10 to 75 microns, and the surface roughness Ra increases from 0.7-0.8 to 6.2-6.7 microns.

2. With deepening, the sulfur concentration is gradually reduced from 0.60 - 0.85 and 0.50 - 0.85% on the surface, respectively, for steel 20 and ductile cast iron, and also respectively, from about 0.05-0.06 and 0.04- 0.05% at the depth of 75 microns.

3. An amount of alloying elements of the electrode-tool made of steel 12X18H10T, i.e. chromium, nickel and titanium, gradually decreases with deepening the coating for steel 20, respectively, from 16, 9; 9; and 0.9% on the surface to 1.2 and 0.2% at the depth of 60 microns.

References

[1] Antoszewski, B. 2014 Influence of laser surface texturing on scuffing resistance of sliding pairs. *In Advanced Materials Research* (Trans Tech Publications) **874** pp 51-55

[2] Błasiak S, Kundera C 2012 A numerical analysis of the grooved surface effects on the thermal behavior of a non-contacting face seal *Procedia Engineering* **39** pp 315-326

[3] Martsynkovskyy V, Yurko V 2014 Solutions for Increasing the Bearing Capacity of Thrust Bearings *In Applied Mechanics and Materials* (Trans Tech Publications) **630** pp 208-219

[4] Yurko V, Martsynkovskyy V 2014 Influence of Changing the End Floating Seal Dynamic Characteristics on the Centrifugal Compressor Vibration State *In Applied Mechanics and Materials* (Trans Tech Publications) **630** pp 356-364

[5] Hinber A M, Ivanova A F 1982 Wear-Resistant and Anti-Friction Coatings (Moscow: Mechanical engineering) p 43

[6] Shipway P H, McCartney D G, Sudaprasert T 2005 Sliding wear behaviour of conventional and nanostructured HVOF sprayed WC–Co coatings *Wear* **259** (7) pp 820-827

[7] Andreev M A, Markova L V, Moyseychik A N, Kaleda V V. 2011 Proc. Int. Conf. on Polymer Composites and Tribology (Gomel: Belarus) pp 32-33

[8] Krasnov A P et al 2011 Proc. Int. Conf. on Polymer Composites and Tribology (Gomel: Belarus) pp 11-12

[9] Zozulya V D et al 1990 Reference Dictionary. Friction, Wear and Lubrication of Machine Parts ed I M Fedorchenko (Kiev: Naukova Dumka) p 203

[10] Denisov N E et al 2006 *Tribological Materials Science and Tribotehnology* (Penza: Publ. Penza State University) p 246.

[11] N I Lazarenko N I 1976 *Electric Spark Alloying of Metal Surfaces* (Moscow: Mechanical engineering) p 46

[12] Hitlevich A E et al 1985 *Electric Spark Alloying of Metal Surfaces* (Chisinau: Shtintsa) p196

[13] Scherbinsky A G 1961 Method for Sulfur Saturation of Metal Surfaces *AS139336 Reports the USSR Inventions* (Moscow: Science) **13** pp 2-3