Selective transfer phenomenon in lubricated sliding surfaces with copper and its alloy coatings made by electro-pulse spraying

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Abstract

The decrease of the coefficient of friction and wear are characteristics of the selective transfer phenomenon caused by the self-formation of a non-oxidising metal film in the friction zone. In this paper, the possibility of providing the selective transfer phenomenon by electro-pulse spraying (EPS) will be discussed. The analysed copper and brass coatings were manufactured by an electric pulse at 5 kV and an energy density of about 4.7–5 MJ/kg. EPS manufactured coatings have a fine-grained, multi-layer structure with a small share of voids and non-metal inclusions. The analysis (tribological test, microscopy) of such conditioned friction pairings has shown that a protecting metal film will be formed by itself, even at marginal lubricated test conditions. As a consequence, a low coefficient of friction ($f = 0.003–0.004$) occurs in the contact zone, which is similar to those, which indicate viscous friction.

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1. Introduction

Up to 85 till 90% of observed machine breakdowns are caused by mechanical wear of their moved parts, 80% of the machines lose their efficiency when the friction surface wears out up to 0.2 mm [1]. Therefore, the reduction of frictional losses and wear intensity between moving machine parts has become a key problem, which needs to be solved.

One attempt to achieve this goal has been made by the application of structural improvements of the involved parts and the use of new combinations of friction partners with lower coefficients of friction. Due to the use of high-quality materials the mass of machine parts and modules could be decreased, but the smaller dimensions of these parts have affected higher partial loads. That’s why a higher quality of the manufacturing processes, chemical composition compatibility, etc. is required.

During the manufacturing processes of the friction surfaces different types of coating methods are used in addition to surface strengthening technologies. The reduction of surface wear by increasing its hardness is efficient up to a certain level but does not minimise the frictional losses between two moving surfaces (coefficient of friction).

This research paper deals with soft copper and brass coatings, formed by the use of electro-pulse spraying (EPS).

2. Background of investigations

The selective transfer phenomenon (STP) is scientific discovery registered at State Register of former Soviet Union at 13.09.1966. The authors of discovery are Prof. D. Garkunov and Prof. I. Krageskij [1].

The selective transfer phenomenon is a type of friction, induced by the self-formation of a non-oxidising metal film in the contact zone, which has a low resistance against shear strain and does not accumulate dislocations during its deformation. In dependence on the used chemical components the metal film consists of copper or different metals and is up to 1–2 μm thick [1,2]. Such film is called servovitic film (Latin...
servo-vite, rescue the life). Important feature of STP is that servovitic film forms in friction pair only during operation, friction is creative factor of it. Properties of servovitic film differ basically from usual metal (copper, brass, etc.). Servovitic friction is creative factor of it. Properties of servovitic film differ basically from usual metal (copper, brass, etc.). Servovitic film is porous [1]. Conditions for STP could be created during design and production of friction pairs, but STP itself is realised only during friction process. It protects the surfaces in the contact zone against wear and is regenerating by itself constantly. In comparison to analogue load conditions combined with conventional lubrication conditions this applied film reduces the frictional losses considerably and increases the wear resistance of friction surfaces [1,3,4].

Servovitic film has low quantity of dislocations, but high quantity (>10% of volume) of vacancies \( \text{C} \). Servovitic film is in metastable state and deforming easily because of loads. Contrariwise diffusive flows of vacancies arise spontaneously in the material, which are blocked by dislocations and vacancies come to the surface and vacancies coagulate to the discs because of STP [1,2,4]. Servovitic film is in metastable state and deforming easily because of low quantity of dislocations and high quantity of vacancies. It makes low friction coefficient during STP which is close to the coefficient of viscous lubrication [1,4].

The conditions for realisation of STP in friction pairs could be can be provided by one of the following methods:

- the use of a lubricant with special additives. Such additives are metal plating materials like Cu, Zn, Sn and chlorides, bromides and iodides of other metals [1,3]. These materials can be also used for regenerating friction pairings without disassembling them [5,6];
- selective transfer phenomenon is formed during friction inside the contact zone, if one friction surface has been conditioned by non-abrasive anti-friction finish processing (NAFT). This method has been analysed several times in earlier tests, with the task, to reduce the mechanical wear of Radial Lip Seal Shaft Systems [5,7];
- in composite materials obtained by powder metallurgy [1,8,9].

Up to now there is no information about the formation of STP by coating with electro-pulse spraying [1,3,4,8,9]. The EPS is a method of providing coatings of conductive materials by the use of “electric explosions of wire”: when a high-voltage [5–30 kV] and powerful \([\text{density } 10^{11}–10^{13} \text{A/m}^2, \text{impulse } \text{duration } 10^{-6}–10^{-7} \text{s}]\) flows through a conductor 5, the material boils up, gets overheated and evaporates partly while the rest of the conductor turns into micrometer-sized droplets 4 (Fig. 1).

Due to the very short duration of this process and the inertia of the conductor material a thermal blow-out occurs. This blow-out affects a high increase of pressure, which accelerates the droplets to a velocity up to 500-600 m/s [10]. The obtained aerosol, a mixture of vapour and droplets, reaches the surface (6, Fig. 1), which should be coated and the vapour condenses, while the droplets cohere with the surface and a metal coating is formed [10].

Due to the high dynamics of the explained process the droplets will be heated up to several ten thousands degrees Kelvin. This extreme heating can be obtained neither by plasma or other material coating methods nor by processing with concentrated energy.

After the burst of the conductor the accelerated droplets impact on the cold target surface and cool down. The rate of cooling amounts up to \(2 \times 10^{-7} \text{C/s}\) and the formed metal layer are up to 0.005-0.02 mm thick [10].

The investigations of coatings from Pd–Si, Fe–Cr–B and Co–Fe–Si–B alloys made by wire explosion spraying method were performed [11]. The microscopic structure of such coatings was examined by EPMA line analysis, X-ray diffraction patterns, deformation and indentation patterns with a diamond indenter. The amorphous phase was dominant in the produced coatings according to the investigations. Due to the high rate of cooling and the impact velocity of the droplets the metal layer crystallises with a very fine-grained structure and a minimum porosity. That’s why the layer is relatively insensitive to heat influences and mechanical wear [12].

The application properties of EPS made coatings of steel and steel alloys (and additional metals, respectively, metal alloys) have been analysed [10,12]. The analysis shows that coatings of copper and aluminium alloys have a fine-grained structure. The average grain size amounts \(10^{-7} \text{m}\), while adhesion of thin copper coatings amounts up to 90–130 MPa [13].

Carboniferous steel and refractory metal EPS coatings are exceptionally wear resistant. The reason is very fine-grained structure 0.1–1.0 \(\mu\text{m}\) [14].

The most applied materials, which provide the STP, are:

- brass L63 (Cu 62.7%, Zn 37.1%) and
- copper M1 (Cu 99.9%).
The application of brass affects an essential problem. While the process temperature of EPS does not influence mono-component coating materials, the handling of alloys is difficult because they consist of diverse components with different boiling temperatures (brass: Cu 2590 °C, Zn 907 °C [15]). Japanese scientists have figured out, that the entire zinc fraction of a brass conductor can be evaporated completely, if the energy density of the generated electric impulse is too high 37 J/mm³ [16]. Optimal spraying energy of brass C-2800 (Cu 60%, Zn 40%) is 33 J/mm³ [16]. Test results show that the zinc concentration in a brass based coating is approximately 19% lower than in the appropriated brass conductor (primary chemical composition of sprayed wire: Cu 62.3%, Zn 37.5%; chemical composition of coat Cu 79.43%, Zn 18.45%) [17].

3. Subject of investigation

The task of this paper is the determination of application possibilities of STP formations of copper, respectively, copper alloy coatings, which are formed by EPS.

The coatings were formed by the use of an EPS device in an Electro-Pulse Spraying Laboratory of the Lithuanian University of Agriculture. The EPS coats of copper and brass were produced using the copper M1 (Cu 99.9%) and brass L63 (Cu 62.3%, Zn 37.5%) wire of 2.0 mm diameter. Thickness of coat layer 0.3–0.35 mm. The regimes of spraying: voltage 4.0–4.2 kV, capacity of battery 2.4 × 10⁻³ F, energy of discharge 19.2–21.2 kJ.

The microstructure of coatings and coated surfaces were analysed at the Materials Testing Institute of Stuttgart University, Germany. There is an optical metal-graphic microscope provided. This device is equipped with a digital camera and automatic focusing software.

The friction pairs were tested tribologically on the upgraded test rig SMC-2 in Department of Mechanics of Lithuanian University of Agriculture. A friction pairing is simulated by a “roller/block” arrangement. A scheme of the used test rig is given in Fig. 2. The roller 2 (35 mm × 16 mm × 12 mm) is simulating a shaft and is made of steel 45 (C 0.42–0.5%, Si 0.17–0.37%, Mn 0.5–0.8%, Cr <0.25%). Its surface hardness amounts up to 35–40 HRC and the surface roughness up to \( R_z = 0.87 \mu m \).

The tribological tests have been carried out at a relative speed between roller and block of about 0.945 m/s (500 1/min). The test parameters were acquired in real time by a computer system. The load sensor was “Z” shape transducer ZF-500 made by SCAIME firm. Under the maximum load the pressure inside the contact zone can reach up to 37.5 MPa. The friction pairings were lubricated with PEMCO Oil SN 350 ISO 68 L-AN. Investigation performed at marginal lubrication-roller was immersed for 6 mm in the oil tank of tests’ chamber.

4. Test results and their analysis

4.1. Analysis of coating’s structure

According to former analyses [17,18] a specific energy of \( E = 4.7–5.0 \text{ MJ/kg} \) has been chosen. The coat will rip off rather quickly because of high internal stresses, if more than 5.4 MJ/kg would be applied. A specific energy of lower than 4.3 MJ/kg causes a worst quality of the formed coating as well because of unacceptable big droplets. \( E (J) \) is calculated with

\[
E = 0.637 \frac{C(U)^2}{d_l \rho l}
\]

where \( C \) is the capacity of the battery (F), \( U \) the voltage of the battery (V), \( d \) the diameter of the wire (m), \( \rho \) the density of the wire (kg/m³) and \( l \) is the length of the spraying wire segment (m).

The structure of 39% zinc containing brass is a hard α zinc solution in copper (20 °C), therefore it remains in the coating unchanged [15,19]. The grain (matrix) size of rolled brass L63 blocks, used for the comparison, was 50–100 \( \mu m \) and formed coatings (due to immediate cooling) are fine. The analysed polished micro-grounds show a low porosity of the...
coating (Fig. 3) because the sub-layers are filled properly due to very high density and velocity of the overheated particles. Darker inter-layers (oxides) can be seen on the coating as well.

Grain of EPS coating of copper M1 was investigated by AFM (Fig. 4).

Cross-section investigations of polished and etched EPS copper coats show that they are fine-grained (Fig. 4). Software package Scanning Probe Image Processor (SPIP, batch processing, grain analysis) for the statistical evaluation of grain structure parameters of EPS coats was used. Fig. 4a presents the cross-section fragment 2.0 μm × 2.0 μm of EPS copper coat. Outstanding horizontal strips of 0.2–0.3 μm width are seen, there are the droplets of coat forming with the pits in between which are more intensively etched contacts of deformed droplets. Grain distribution histogram of EPS coat is presented in Fig. 4b. Average size of grains is ca. 60–170 nm.

After 20 times analysis of EPS formed brass and copper coats, the following conclusions can be done:

- the structure of coatings is particularly fine-grained 60–170 nm;
- the coatings have a low porosity and a low share of voids and other non-metal inclusions;
- the coatings have a multi-layer structure, the inter-layers are covered by intermittent oxide films;
- the coating’s colour gradient could indicate that the copper distribution is non-uniformly as a result of the different quantity of zinc evaporation during the coating process.

The micro-hardness of M1 and L63 wires, which were used during EPS coating, amounts to 990 MPa, respectively, 1140 MPa. Hardness of sub-layers of Ni–chrome (Ni 20%, Cr 80%) and steel 65Mn (C 0.65%, Si 0.27%, Mn 1.1%, Cr 0.2%) amounts to 1530 and 5560 MPa, respectively. Furthermore, the sample steel 45 has a hardness of 2200 MPa.

The hardness gradient inside the coatings depends on their distance to the cooling surface—the closer to the surface, the harder is the coating (Fig. 5). The different rate of cooling of separate layers affects the showed behaviour. The closer to the surface, the faster is the rate of cooling and the less is the thermal effect to other layers.

![Figure 3](image1.png)

![Figure 4](image2.png)
4.2. Analysis of the coefficient of friction

The analysis was carried out with a friction pairings consisting of steel made roller and a block of rolled copper, which has been coated with brass by EPS. Fig. 6 shows the graphs of friction coefficient of a typical tested friction pair depending on the applied load and operation time. The used block was EPS coated with cooper M1. The friction behaviour has been analysed at a two-stage (a) and multi-stage (b) load state. Starting with an applied load of about 1500 N (Fig. 6), the coefficient of friction increases up to 0.035–0.045. After a running time of less than a minute the friction surfaces get adapted to each other and a reduction and stabilisation of the coefficient of friction occurs. When the load increases up to 3000 N the coefficient of friction increases as well, but when the surfaces get adapted themselves again to the changed friction conditions, the coefficient of friction decreases and get stabilised. During the long-time test the coefficient of friction converges at $f = 0.003–0.004$ and becomes stable ($\Delta f = 0.0005$). In tests with multi-stage load state (Fig. 6b) and in tests with EPS (brass L63) coated blocks (Fig. 7) an analogue behaviour of friction coefficient has been observed.

In Figs. 8 and 9, the results of test runs with blocks of rolled copper and brass at two-stage load state are shown. The friction pairing, containing a copper block shows a more stable behaviour of the coefficient of friction. In some tests...
Fig. 8. Load gradient and friction coefficient of a tested friction pair: steel shaft–copper block under two-stage load: (a) distinct sticking indications, high coefficient of friction and (b) relatively low coefficient of friction.

For friction pairings, whose blocks were made of copper, the probability of the existence of STP is low, nevertheless a protecting metal film could be formed, if a low coefficient of friction ($f = 0.007–0.015$) is dominating and surface activators are contained in the used lubricant.

In order to get a more precise explanation for the implementation of the selective transfer phenomenon in the tested friction pairings, the friction surfaces have been analysed by scanning with an electron and atomic force microscope.

4.3. Analysis of friction surfaces by the use of a scanning electron microscope

After the tribological tests the friction surfaces were analysed by the scanning electron microscope JSM-5600. Figs. 10–15 show pictures of various friction surfaces.

Fig. 9. Load gradient and friction coefficient of a tested friction pair: steel shaft–brass block (a) and copper block (b) under multi-stage load.
Fig. 10. View of rolled copper M1 surface after friction tests (22.5 MPa and friction way 8.5 × 10^4 m). ×2000, Rz = 0.22 μm.

Fig. 11. View of rolled brass L63 surface after tests (12 MPa and friction way 8.5 × 10^4 m). ×2200, Rz = 0.24 μm.

Fig. 12. View of EPS (copper M1) coating surface after friction tests (22.5 MPa and friction way 8.5 × 10^4 m). ×2000, Rz = 0.16 μm.

Fig. 13. View of EPS (brass L63) coating surface after friction tests (22.5 MPa and friction way 8.5 × 10^4 m). ×1900, Rz = 0.08 μm.

Fig. 14. View of EPS (copper M1) coat surface after friction tests (37.5 MPa, with friction way 2 × 10^5 m). ×2000, Rz = 0.06 μm.

Fig. 15. View of EPS coating (brass L63) surface after friction tests (37.5 MPa, with friction way 2 × 10^5 m). ×2000, Rz = 0.10 μm.
The surfaces of solid copper blocks (Fig. 8b) and those having an EPS (copper M1) coat have a porous structure. But, while the surfaces of the coated blocks are smoother and almost entirely porous, the surfaces of rolled copper reveal distinct zones of porous and non-porous zones.

The surface porosity is a typical characteristic of the selective transfer phenomenon [1]. That’s why the microscopic analysis does not discard the assumption that a protective metal film will be formed on friction surfaces during the self-adjusting process.

Rolled brass blocks worn intensively (abrasive wear) and friction pair seized when the comparative load was 22.5 MPa during the tests. Abrasive wear was less intensive and no seizing appeared at 10–12 MPa load, but all block surface was covered by segments of deformed brass material because of adhesive interaction of friction surfaces (Fig. 11).

A uniformly distributed porosity is typical for block surfaces coated by brass and is indicating the possibility of the existence of a selected transfer phenomenon (Figs. 12–15).

4.4. Investigation of friction surfaces by the use of an atomic force microscope

The atomic force microscope (AFM) has been designed as a tool for surface profiling [20]. Friction force microscopy (FFM) is now routinely used for tribological evaluation of surfaces of scientific and engineering interest at the atomic scale to the micro scale. The adhesion forces between the surface and the AFM cantilever tip can be investigated using AFM force spectroscopy (force–distance) mode. The different shapes of the force–distance curves correspond to the different interaction mechanisms on the surface and can be used to evaluate the elastic properties of the surface [21].

The force–distance curves were obtained in contact mode by Quesant Corp. Q-Scan 250 AFM during our experiments. Single crystal silicon cantilevers with integrated tip were employed (NT-MDT, Russia). The typical spring constant for vertical deflection of V-shaped cantilevers was 0.2 N/m. The obtained force–distance curves are presented in Figs. 16–18.

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The AFM force–distance curves were investigated at different points of the surface of the samples prepared at various tribological conditions. The force–distance curve of the block made of rolled copper and brass are presented in Fig. 16. It represents a typical dry solid body force–distance curve shape [21].

The force–distance curve of the block coated by EPS copper film is presented in Fig. 17.
5. Conclusions

1. The copper and brass coats are fine-grained and multi-layer with few hollows and other non-metallic inserts when they are built by electro-impulsive multiple spraying (comparative energy $E = 4.7-5.0 \text{ MJ/kg}$) at non-regulated environment.

2. The tribological tests at the marginal lubrication conditions show that coats have low and stable, close to the liquid conditions lubrication friction coefficient ($f = 0.003-0.004$) at the regular operation mode when they are double-stage or multi-stage loaded.

3. The investigations of friction surface after tribological tests with electronic scanning microscopy estimated that the electro-impulsive sprayed surface is continuous porous. At the friction surfaces made of solid rolled metal are visible porous and non-porous surface zones with some cases of seizing and transfer of metal.

4. During the investigations of surface interaction with the probe of atomic-force microscope according force-displacement curves was estimated that the local, viscous quasi-liquid film on friction pairs of electro-impulsive sprayed surfaces is forming.

5. Friction coefficient and microscopic investigations demonstrate that porous quasi-liquid protective metal film is self-forming when the electro-impulsive sprayed copper and brass coats are operating in friction pair at the marginal lubrication conditions. This film determines low friction coefficient, which is characteristic to the liquid lubrication conditions. According our opinion this film appears because of forming the selective transfer phenomenon in such friction pairs.

References


