Antifriction wear-resistant coatings process development for sliding bearing friction surfaces of submersible pumps

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Abstract. The tribotechnical coating structure using a mechanical mixture of copper and zinc particles obtained over a wide temperature range of air flow under ultra-high-speed gas-dynamic spraying is studied. Comparative tests were carried out to assess the tribotechnical properties of various composition gas-dynamic coatings and industrial compact antifriction alloys, which showed the advantage of gas-dynamic coatings of copper-zinc-corundum composition. The antifriction wear-resistant coatings production process by cold gas spraying can be recommended for sliding bearings of submersible pumps.

1. Introduction
Copper and its alloys (brass, bronze) are widely used in mechanical engineering, in particular for the manufacture of friction bearings, as they have high antifriction properties. To obtain the necessary composition of brass, metallurgical processes are used, followed by resurfacing and plastic working of the semi-finished products to obtain the final products [1,2].

The example of copper alloys application is thrust bearings for the borehole submersible pump shafts consisting of a pin and a thrust bearing. A known disadvantage of such bearings is the large heat evolution in the friction zone due to the high rotational speed of the thrust cap relative to the thrust bearing, which reduces the reliability and load capacity of such thrust bearings. The gas-dynamic coating use based on copper on steel backplates should increase both the tribological properties of the friction assembly and their bearing capacity.

The aim of this work was to study the phenomenology of the copper-zinc coating structure and properties deposited on a steel backplate by cold gas spraying at different airflow temperatures.

2. Materials, methods, equipment
A coating was sprayed on a 40X steel backplate using a DIMET-404 gas-dynamic facility at a nozzle moving speed relative to the sample surface of 10 mm/s and a distance from the nozzle exit to the surface of 10 mm. The airstream temperature was 270°C, 360°C, and 450°C when spraying a mechanical mixture of copper, zinc and corundum particles (grade C - 01 - 11). A metal particulate mixture and a chemical mixture was used as-received condition and the ratio of ingredients by mass was – Cu: Zn: Al₂O₃ = 35%:35%:30% [3].

Corundum was introduced into the composition of the mixture to increase the particle quantity fixed on the sprayed surface and their compaction.

The phase composition of the Cu – Zn coating system was studied on a Rigaku Ultima IV
multifunctional X-ray diffractometer using CuKα radiation in parallel flux geometry. The quantitative analysis was carried out using the Rietveld method implemented in the PDXL software package (Rigaku).

The diffraction line broadening analysis in order to determine the parameters of the fine crystalline structure (block size, microstrains) is carried out using the PDXL software (Rigaku) by the Rietveld method. The instrumental broadening was taken into account by shooting the standard — lanthanum hexaboride (LaB6), which lacking intrinsic broadening.

X-ray fluorescence analysis was performed on a Rigaku Primus II spectrometer using an X-ray tube with an Rh anode as an X-ray source in a vacuum and an element range from Ca to U.

The coating hardness was measured by the Vickers method according to GOST 2999-75 at a load of 490.3 mN and a dwell time of 10 s on a SHIMADZUHMV-2 hardness-testing machine. The study was conducted from the coating surface according to two structural components having a red (copper) and light (zinc) shade.

Tribological studies were carried out on a CETR tribotester of the UMT-3 model according to the cylinder-plane linear contact pattern with the oscillating movement of the counter-sample at a given frequency [4]. The sample was cut directly from an Ø18mm pipe made of 12X18H10T steel. A coating based on a mechanical mixture of copper and corundum particles, as well as copper, zinc and corundum at a temperature of 450°C was sprayed onto the counterbody. A plate with a coating sprayed on it was fixed on a tribotester object table, which is kinematically connected with a reciprocating drive. The tests were performed under normal conditions without lubrication, with constant vibration speed: amplitude A = 0.5 mm; frequency f = 30 Hz, normal load N = 10 H. The test duration were 6 hours. During the tests, the friction coefficient was controlled, after tests by strip chart recording, the depth and width of the friction track on the test coating were determined, and the profile of the annular sample was measured.

The friction area S was determined by photometric measurement using the Image program from a fray photograph taken on an MBS-10 microscope with an attachment for image reading. The contact pressure was determined as q = N/S (MPa), where N — is the acting normal load (N), S — is the contact spot area (m²).

The friction path for conjugated samples was determined from the expression $L = 4.141 \cdot A_{rms} \cdot f \cdot t \cdot 10^{-6}$ [km], where $A_{rms}$ — is the mean-square vibration amplitude (mm), f — is the vibration frequency (Hz), t — is test time (s) [5].

The linear wear rate (I) and wear coefficient (K) were calculated in the traditional way, respectively, as $I = h/L$ и $K = I/q$, where h — is the wearing depth (km), L — is the friction path (km), q — is the contact pressure, MPa.

3. Research results

The coating chemical analysis showed a significant dependence of the component content on the spraying temperature. An air flow temperature increase from 270°C to 360°C was accompanied by the coating formation, where the zinc mass fraction increased from 8.15% to 22.3%; a further temperature increase gains the zinc proportion to 37.6%. Since the particle temperature before reaching the surface with increasing air flow heating did not change significantly (≤80°C), the zinc content increase in the coating is due to a particle energy increase and the possibility of their additional joining to the surface [6]. The copper content in the coating composition decreased from 91.7% to 77.5% with increasing air flow temperature from 270°C to 360°C; a further increase in gas temperature led to a copper proportion decrease in the coating composition to 62.2%. If the coating with the revealed equivalence ratio is remelted, the result will be an alloy similar in properties to brass grades L90 (low brass), L80 and L63 (C27400) [1,2]. In particular, L63 brand brass is used for the manufacture of sliding bearings, therefore, to study the tribological properties of the copper and zinc coating, a spray temperature of 4500°C was chosen.

The X-ray phase analysis results of the coating sprayed with a minimum air flow temperature testify that during the galvanizing the transfer processes (diffusion) of copper atoms to zinc took place.
with the formation of the intermetallic compound CuZn$_3$ (ε-phase) having a close-packed hexagonal lattice [2], where mass fraction was 5.3%. The copper particles hardness in the coating was 103.6 HV. It was not possible to measure the hardness of zinc particles because of its insignificant amount (8.15%).

The spraying temperature increase to 360°C was accompanied by a slight increase in the content of the ε-phase (7.9%) and the formation of a new intermetallic compound Cu$_5$Zn$_8$ (γ-phase) with a face-centered cubic lattice [2], the mass fraction of which is 17.0%. The hardness of copper particles in the coating structure did not change (103.2 HV), and the hardness of the zinc transmutation product was $\approx$ 178.7 HV.

The further spraying temperature increase to 450°C was accompanied by an increase in the content of electronic compounds based on CuZn$_3$ and Cu$_5$Zn$_8$ to 11.2% and 33.0%, respectively. At this spraying temperature, zinc was oxidized with the zinc oxide formation, the mass fraction of which is 4.3%. The hardness of copper particles changed slightly (106.5 HV), as well as the hardness of intermetallic compounds (168.7 HV). The spraying temperature increase led to the aluminum oxide (corundum) decrease in the coating: 5.4% → 2.2% due to the flow rate increase, which may have a positive effect on the surface wear of the conjugate pair (table 1).

In a coating based on a mixture of particles of copper, zinc and corundum, pores are observed that are formed during resurfacing due to the corundum desolidization from the matrix. In addition, the presence of the fine pores is due to the technological features of the coating method, when pores are formed due to insufficiently hard contact of metal particles. The pore size is a range within 2-12 microns and in some of them, inclusions of up to 3 microns are noticeable. The accessible porosity of the copper and zinc coating is about 3% [6].

The coating structure consists of areas (particles) having a light (zinc, electron compounds) and a dark shade (copper). Their maximum size does not exceed 30 microns; structure fragments of 3-5 microns in size can be visually observed in separate areas of dark and light shades (figure 1).

In tribology, many studies have shown that pores act as reservoirs for a lubricant, which, as the material wears out, as well as frictional heating and thermal expansion of the part (coating), is squeezed out of its volume and enters the friction zone, contributing to the restoration of the lubricating film, which ensures the conditions boundary lubrication and matched-pairs performance. In addition, the presence of a structure having a fine grain (≤30 μm) is also attributed to positive factors that improve the wear resistance [7, 8].

![Figure 1. Structure of copper-zinc particles mixture coating deposited at 450°.](image-url)
The size of the substructure at the minimum spraying temperature of the spray coating is more than 200 nm for copper and more than 100 nm for zinc. In the ε-phase, the size of the substructure is about 70 nm, which is close enough to the size of the zinc substructure, on the basis of which the electronic phase is formed. With spraying temperature increase, the size of the substructure does not change in copper and increases in zinc and products based on it. The size of the substructure of all structural components (copper, zinc, ε-phase, γ-phase) with an increase in spraying temperature from 360°C to 450°C sharply decreases from ≈200 nm and is within the range 60.0-90.0 nm (table 1). Grinding the size of the substructure of all structural components can have a positive effect on the tribological properties of the deposited metal coat.

Table 1. The value of the coating substructures

| Spraying temperature, °C | Copper | Zinc | ε-phase | γ-phase |
|--------------------------|--------|------|---------|---------|
| 270                      | >200   | >100 | 70.5±4.7| -       |
| 360                      | >200   | >200 | 82.8±41.5| >200    |
| 450                      | 89.8±19.5 | 63.7±6.2 | 96.5±76.7 | 62.0±15.3 |

Compelling results are revealed by the spectral analysis of copper particles, which show the zinc presence, evenly distributed over the surface, the content of which ranges from 1.04 at % to 3.52 at %. A slight deflection of the zinc values allows us to assume that the surface of the copper particle is covered with a zinc film, which, if we consider the oxygen content, is zinc oxide (table 2). The depth of the spectrum initiation zone in the electron microprobe analysis has the same value as the spot size of 0.2-2 microns. If we take the ratio of the volume of the metals (copper and zinc) revealed in the analysis and the spectrum initiation depth ratio with the film thickness, it can be calculated that its thickness is in the range from 38 nm to 380 nm. If we consider the spraying process and surface subsequent mechanical treatment for research, then its appearance can be associated only with the mass transfer process (displacement) of zinc during surface treatment on sandpaper and polishing wheel. In this case, a zinc mass transfer possibility can be noted when the coating is exposed to a conjugate surface. The oxide films presence on the surface allows improving the conformability of the conjugate friction pair surfaces.

Table 2. The value of the coating substructures

| The spectrum number | Chemical elements, atomic % |
|---------------------|----------------------------|
|                     | Zn  | Cu  | Al  | O   |
| 1                   | 2.88| 94.39| 0.20| 2.53|
| 2                   | 1.04| 95.49| 0.88| 2.60|
| 3                   | 1.21| 94.25| 0.56| 3.97|
| 4                   | 2.05| 97.50| 0.00| 0.45|
| 5                   | 1.20| 98.39| 0.01| 0.40|
| 6                   | 1.05| 79.43| 9.99| 9.62|
| 7                   | 1.70| 96.34| 0.30| 1.66|
| 8                   | 3.52| 93.00| 0.52| 2.96|

Based on GOST 15557-2004, despite the presence of intermetallic phases typical for copper-and zinc-based alloys, the obtained coating can not be attributed to brasses, since copper and zinc were
present in the deposit metal layer, the mass fraction of which was 40.3% and 9.0%, respectively. In this case, coatings applied by gas-dynamic spraying using a mechanical copper and zinc mixture is advisable to be called a brass-type coating.

4. Test results
A coating based on a mechanical mixture of copper and zinc particles had higher tribological characteristics compared to a coating based on copper particles (table 3) applied under the same technological spraying conditions. The brass-type coating wear rate is almost 4 times lower than the copper coating paired with a stainless steel sample. At the same time, the stainless steel counterbody wear is by two orders of magnitude less in a pair with a brass-type coating than in a pair with a copper coating. Metal physical studies have revealed the copper and zinc mass transfer presence, which should have an impact on the test result. However, it is possible to assume the influence on structure wear of a brass-type coating where along with copper (40.3%) hardness $\approx 103.2$ HV intermetallic compounds (44.2%) hardness $\approx 178.7$ HV were present.

**Table 3.** Study results of the tribotechnical characteristics of a coating based on copper and a copper-zinc particles mixture

| Evaluation parameter | Gas-dynamic spraying Cu | Gas-dynamic spraying Cu+Zn | Bronze C83600 | Brass C27400 |
|----------------------|-------------------------|---------------------------|----------------|--------------|
|                      | Coating - plate         | Coating - plate           | Counterbody - plate | Counterbody - plate |
|                      | Counterbody - cylinder  | Counterbody - cylinder    | Counterbody - plate | Counterbody - plate |
| h, micron — wear     | 166                     | 20                        | 12               | 234           | 15           | 262           | 12           |
| $\mu$ — friction coefficient | 0.6                      | 0.6                        | 0.88             | 0.88          | 0.3          | 0.3           | 0.8           | 0.8 |
| q, MPa — contact pressure | 0.6                      | 0.6                        | 5.9              | 5.9           | 0.6          | 0.6           | 0.6           | 0.6 |
| I∙10^{-8} — wear intensity | 3.7                      | 1.5                        | 1.0              | 0.01          | 5.2          | 0.34          | 5.9           | 0.27 |
| K∙10^{-8} MPa^{-1} — wear coefficient | 6.2                      | 2.5                        | 0.17             | 0.01          | 9            | 1             | 10            | 0.5 |

5. Conclusions
The increase in the spraying temperature from 270°C to 450°C was accompanied by a decrease in the mass fraction of copper from 91.7% to 62.2% and an increase in the mass fraction of zinc from 8.15% to 37.6% in the coating based on a copper-zinc particles mixture.

Coating phase analysis of revealed in addition to copper, zinc and zinc oxide the CuZn$_3$ and Cu$_5$Zn$_8$ intermetallic compounds presence, the mass fraction of which increased with an increase in the spraying temperature from 5.3% to 11.2% ($\varepsilon$– phase) and from 17.0% to 33.0% ($\gamma$– phase).
The increase in the airflow temperature did not affect the copper hardness (106.5 HV → 103.6 HV) and slightly reduced the zinc conversion products hardness (ε and γ phases) from 178.7 HV to 168.7 HV.

The wear intensity of copper-zinc particles coating is 3.7 and 5 times lower than coatings based on copper particles and compact industrial alloys, respectively.

Tribological properties preliminary studies of gas-dynamic copper-zinc particles coating show the prospects of their application in sliding bearings, such as submersible pumps instead of using bronze or brass ones.

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