The effect of structural factors on tribological behaviour of copper-zinc gas-dynamic coatings

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Abstract. The paper studies the effect of the structure of copper and brass coatings, obtained by gas-dynamic spattering, on their tribological behaviour. Using durometrical, chemical and X-ray analyses, as well as the wear tests, the authors have determined that the copper coating structure hardness is 102.7 HV, it has pores up to 2 μm in diameter, brass coating consists of 106.5 HV copper, 49.7 HV zinc and 168.7 HV non-metallic compositions (γ – and ε – phases), distributed by mass as 62:7.9:24.2 % correspondingly. The both coatings have presented good results in sliding friction couple tests.

1. Introduction
In the process of coating application by gas-dynamic spattering using low-pressure equipment, the mechanical mixture of pure metals and aluminum oxide is used [1]. A chemical compound (corundum – Al₂O₃) is injected into the mixture of powders to improve the mechanical properties of the coating (adhesion and cohesion). Corundum, striking a part (item), cleans the surface from non-persistent pollutants, oxides, etc., activating it, changing the micro-relief and, therefore, improving the cohesion hardness of the applied metal coating. In the process of interaction of corundum particles with the metal surface and collision between each other, they destroy and partly fix in the coating.

Tribological tests of copper coating applied by gas-dynamic spattering using the mixture of copper and corundum powders, in the media of liquid and consistent grease joined with the counterbody of steel 52100 thermally processed at 58-62 HRC, have revealed that the wear of the applied copper coating was comparable with the wear of steel 52100 after glow-discharge nitriding [2]. In this case the quality of the surface of the counterbody made of steel 52100 thermally processed at 58-62 HRC rises by one class if joined with the coating of copper.

The authors suggest the model of friction surface interaction, according to which the copper coating with the inclusions of fine particles of corundum affects the counterbody as an abrasive tool (emery stone), which results in the improvement of the counterbody surface quality.

The results of tests of the coating based on the mixture of copper, zinc and corundum (“brass”) particles, applied on the base coat of 40Cr steel under the conditions of dry friction at the ambient temperature, have shown that its wear is four times lower than that of copper coating [3]. However, the intensity of the counterbody wear is by an order lower if coupled with the “brass” coating. Micro-X-ray spectrometry of the counterbody surface after the test shows the presence of mass transfer of zinc and copper from the coating to the counterbody [4].
The test results are to be assessed as positive, which presupposes the continuation of the study of the possibility of using the coatings, applied by gas-dynamic spattering, in sliding friction units. Tribological behavior of the coatings based on copper and the mixture of copper and zinc particles (“brass”) is certainly related to the specific features of formation of the applied metal structure, which may determine the conditions of use and operation of the coatings based on metals and chemical compositions.

The objective of this paper is to study the changes in the coating structure depending on the composition of the spattered mechanical mixture using the particles of copper, zinc, mixture of copper and zinc particles (“brass”) and assess the effect of structural factors on tribological behavior of the applied metal coating.

2. Methods and equipment
The coating is spattered on the base coat of steel 5140 using gas dynamic facility DIMET-404 at the rate of interchangeable nozzle displacement in relation to the sample surface 10 mm·s⁻¹ and the distance from the face of the nozzle to the surface 10 mm. The air flow temperature is 360° C when spattering a mechanical mixture of particles of copper, zinc and corundum (grade C-01-11), copper and corundum (grade C-01-01), zinc and corundum (grade C-00-11). A mixture of metal particles and a chemical compound is used as received, and the ratio of ingredients by weight is - Cu:Zn:Al₂O₃ = 35%;35%; 30%; Cu:Al₂O₃ = 55-60%;45-40%; Zn:Al₂O₃ = 55-60%;45-40% [1].

The phase composition of the coatings is examined at a Rigaku Ultima IV multifunctional X-ray diffractometer using CuKα-radiation and a parallel beam. X-ray optics in the form of a multilayer parabolic mirror is used to form a parallel beam. Diffraction patterns are taken in symmetric mode, scanning range 2θ from 20 to 120, step 0.05°, detector rate 3° min⁻¹.

The diffraction patterns are analyzed on the basis of the PDXL (Rigaku) software product using the PDF-2 database. The quantitative analysis is performed using the Rietveld method implemented in the PDXL (Rigaku) software package.

The analysis of diffraction lines broadening to determine the parameters of the fine crystal structure (block size, microstrains) was performed using the PDXL (Rigaku) software product by the Rietveld method. The instrumental broadening was recorded by the measurement of the reference - lanthanum hexaboride (LaB₆), that has no physical broadening.

The study of the structure and elemental composition of the coating is performed at FEI Quanta-650 scanning electronic microscope with an EDAX energy-dispersive X-ray spectrum analyzer. The study uses a back-reflected electron detector providing an image with atomic number contrast and visualizing various phases on the surface of the samples. A tungsten cathode served as a source of electrons in the microscope; the accelerating voltage was 25 kV.

The coating metal hardness is measured by Vickers method according to GOST 2999-75 at the load of 245 mN and a holding period of 10 s at the hardness tester SHIMADZU HMV-2. The study is performed from the surface of the coating by two structural components, having a red (copper) and light (zinc) shade.

3. Research results
X-ray phase analysis of coatings based on the mixture of copper and corundum, zinc and corundum, as well as the mixture of particles of copper, zinc and corundum shows that the copper coating contains almost no significant amounts of any compounds and phases.

When a zinc-based coating is applied, aluminum oxide (corundum) in the amount of 5.6% and zinc oxide with the mass fraction of 2.3%, are detected in the metal layer. The analysis of the coating based on the mixture of copper and zinc particles in the coating shows the presence of copper and zinc in the amount of 62.0% and 7.9%, respectively. The amount of corundum in the “brass” coating is almost the same as in the zinc-based coating. Moreover, in the process of coating application, the processes of diffusion of copper into zinc have taken place in the coating with the subsequent formation of
intermetallic compounds of γ - and ε - phases, which are formed on the process of cooling of copper and zinc liquid alloy with zinc content of more than 55 atom per cent [5].

The size of substructure of copper and zinc for all coatings exceeds 200 nm; in zinc coating, the oxide size is $242 \pm 49$ nm. In gamma-phase, the size of the substructure is $>200$ nm, just like in zinc; in epsilon-phase, it is much less: $82.8 \pm 41.5$ nm.

The lattice constant of copper (initial cubic face-centered lattice of constant of 3.608 nm) increases to 3.616 nm after the spattering of copper coating, which is associated with the metal deformation by the particles of corundum. After spattering of a coating based on the mixture of copper and zinc particles, the lattice size still slightly increases (3.620 nm). In the initial composition of a three-component mechanical mixture (Cu, Zn, Al₂O₃), the amount of corundum is significantly lower (30%) than that after spattering of a two-component mechanical mixture (Cu, Al₂O₃), where the amount of corundum is in the range of 40-45% (see the Experiment Procedure section), therefore, any additional effect of corundum on the copper deformation can be excluded.

The copper and zinc hardness do not significantly differ at normal temperature, and, as the metal particles temperature does not exceed 80°C [2] when reaching the base coat surface, the mechanical effect of zinc on copper with the increase of its deformation degree can be omitted. Therefore, the lattice constant increase should be referred to the processes of diffusion and the beginning of generation of solid zinc solution in copper (α is the solid of the solution).

The initial hexagonal close-packed zinc lattice of $2.6649/ 4.9468$ nm significantly increases after spattering of zinc coating, especially by one of the parameters – $2.6656/ 4.9494$ nm, which is preconditioned by the metal deformation by corundum particles. After the spattering of the coating based on the mixture of copper and zinc particles (“brass”), the size of the lattice increases even greater – $2.6664/4.952$ nm, which is preconditioned by the formation of hard copper solution in zinc (ƞ-phase) with the subsequent formation of electronic inter-metal compounds.

The copper coating structure contains a minor amount of pores of the size up to 10 μm, which have formed in the process of mechanical treatment of the applied coating of metal as a result of separation of corundum particles from the matrix, and numerous structural defects of the size not exceeding 2 μm (figure 1).

The authors have analyzed the content of copper, aluminum and oxygen by the path that visually contains no corundum, at the points located on the copper particles (№ 1-3, 8, 9) and at the particles interface (№ 4, 7) (figure 1). The copper content in the spectra № 1-3, 8, 9 is stable enough, ≥98.5 atom per cent, and the presence of aluminum can be described as the “traces”. At the interface between the particles the copper content significantly decreases (91-94 atom per cent), and the aluminum and oxygen content rises (spectra 4 and 7). Considering the stoichiometric ratio of aluminum and copper, it is safe to say that at the copper particles interface (spectra № 4, 7) there are the aluminum (corundum) and copper oxides.

From the ratio of the content of components in the points adjoining the interface (spectra № 5, 6) it is possible to judge about the presence of finer particle of aluminum oxide and copper oxide. The size of spectrum initiation zone at micro-X-ray spectrum analysis varies for different elements (it depends on atomic weight, atomic number, density, etc.), it is in the range from 0.2 to 2 μm. The calculations performed show that for copper, the size of spectrum initiation (excitation) zone is ≈2 mm. Considering the structure of the coating (figure 1) and the ratio of the spectra of metals (spectrum 4), it is highly likely, that the aluminum oxide particle size is less than 1 μm.

It should be pointed out that the presence of copper oxide at the interface of copper particles is preconditioned by the use of copper particles which are coated with oxide film at the initial state.

The values of copper coating hardness vary greatly from 72 HV to 122 HV, and the average hardness value is ≈ 102.7 HV.

Considering the results obtained, the following can be noted:

- numerous works in tribology show that the pores play the roles of reservoirs for grease which, in the course of wear of the material and the friction heating and heat expansion of a part (coating) are pressed out from its volume and pass to the friction area, providing the
restoration of grease film thus providing the conditions of interface grease and operability of
the joined couple [6, 7];
• the surfaces of sliding friction bearings (parts) are normally processed by a tool to 9-10 degree
of finish, when the size $R_z = 1.6 - 0.8 \mu m$ (0.32-0.16 Ra) and, therefore, so fine particles of
corundum, even when separated from the matrix (copper), should not affect the wear and the
counterbody surface quality deterioration.

Zinc coating presents more defects (pores), than the copper coating, a number of which contains
corundum particles; in average, the size of the structure defects is larger than in copper coating (figure
1, 2). The authors have analyzed the content of zinc, aluminum and oxygen by the pass that visually
contains no corundum particles; the spectra in the points located on the particles of zinc ($\# 1-3, 6-8$)
and at the interface between particles ($\# 4, 5$) (figure 2) have been excited.

![Figure 1](image1.jpg)

**Figure 1.** The order of spectra location in the coating based on copper and corundum.

![Figure 2](image2.jpg)

**Figure 2.** The order of spectra location in the coating based on zinc and corundum.
Zinc content at points № 1-3, 6-8, located on the particles, varies significantly from 55 atom per cent to 97 atom per cent. Considering the change in the content of aluminum and oxygen in the spectra, we can state that corundum particles of different sizes are located at these points. At point 8 it is possible to assume the presence of zinc oxide from the ratio of the content of aluminum, oxygen and zinc. At the interface between zinc particles (spectra 4, 5), there are larger corundum particles than over the body of the particle.

The hardness of zinc coating does not significantly vary, the hardness of the coating is ≈49.7 HV.

In the coating applied using a mixture of copper and zinc particles (“brass”), the pores and corundum particles are visible along the interfaces of copper particles, the size of which does not exceed 5 μm. The corundum inclusions of such size are not observed when analyzing the structure of copper-based coatings (figure 1), the detection of such inclusions during the study of the structure based on a mixture of copper and zinc particles (figure 3) is possible due to the presence of zinc in these zones, which “captures” the corundum particles. X-ray diffraction phase analysis of a coating based on zinc and a mixture of copper and zinc particles showed almost equal corundum content, which indicates the predominant arrangement of corundum particles in zinc particles.

The amount of zinc as well as zinc-based phases in the structure is not so great, only 7.9%, therefore the micro-X-ray spectral analysis of elements distribution (spectra № 1-8) was performed for copper particles, including the interface between them (figure 3).

The spectral analysis of copper particles provides very interesting results: they show the presence of zinc, which is distributed over the surface quite uniformly. Its content ranges from 1.04 atom per cent to 3.52 atom per cent, and a slight deviation in zinc values suggests that the surface of a copper particle is covered with a zinc film, which, in terms of oxygen content, is a zinc oxide. X-ray phase analysis of the coating based on copper and zinc particles did not show the presence of zinc oxide, unlike the coating based on zinc particles. Hence, it is possible to conclude that it is very insignificant, and then the film is of insignificant thickness. The depth of the spectrum initiation zone in micro-X-ray spectral analysis is the same as the spot size 0.2-2 μm. Considering the ratio of the amount of metals (copper and zinc), revealed during the analysis, and the ratio of the spectrum initiation depth to the film thickness, it is possible to calculate that its thickness does not exceed 78 nm. Considering the process of spattering and the subsequent mechanical treatment of the surface for the study, it is possible to say that its appearance can only be associated with the process of zinc mass transfer (displacement) during the treatment of the surface with emery stone and a polishing wheel. In this case, we can note the possibility of mass transfer of zinc when the joining surface affects the coating.
At point 6, which is located at the interface of the particles, we observe the decrease in the copper content and an increase of oxygen and aluminum content, which can be interpreted as the presence of a corundum particle. The amount of aluminum in the other spectra should be considered insignificant, and the increased oxygen content can be attributed to the presence of zinc and copper oxide. The electrochemical potential of zinc is -0.763, and that of copper is +0.552, which, at all other conditions of coating application being equal, preconditions the preferable possibility of zinc oxide generation of coating deposition.

The average hardness of copper particles at significant scatter of values is ≈106.5 HV, which does not differ much from the hardness of copper at spattering of a coating based on a mixture of copper and corundum particles. The hardness of copper does not differ at spattering a mixture of different compositions, whereas the hardness of zinc in the structure of a coating based on a mixture of copper, zinc and corundum particles can be considered equal to the hardness of zinc when spraying a coating based on the mixture of zinc and corundum particles, that is, ≈49.7 HV. The diffusion process taking place during the spattering of the coating results in the formation of intermetallic compounds based on zinc - gamma and epsilon phases with the hardness of ≈168.7 HV.

Studying the structure of coating based on the particles of copper and zinc (“brass”), the authors detected the presence of the structure gradient in terms of composition and hardness, the film of zinc oxide on the copper particles surface and the porousness. Assessing the results obtained, we can point out the following [6, 7]:

- the presence of porousness can also be estimated as a positive factor of “brass” coating operation under the conditions of friction couple grease;
- the materials (alloys) containing both hard inclusions, preventing the basis destruction due to the effect of the abrasive, and plastic ones, which absorb the abrasive, thus improving the conformability of friction surfaces, are widely known in tribology. Therefore, the presence of two phases of various hardness (zinc and electronic compositions) can be assessed as a positive factor under dry friction conditions;
- mass transfer of metals is considered in tribology as a positive factor, as this mechanism provided the cure of the defects that were present or occurred on the surface due to the work of the joined friction couple;
- the presence of zinc oxide film on the surface of the particles may improve the conformability of the joined friction couple.

4. Conclusions
In the process of spattering of a coating with the use of a mechanical mixture of particle of copper and aluminum oxide (corundum), a structure of the hardness ≈102.7 HV is formed. Numerous pores are observed in the structure of the applied metal coating, the typical size of the pores does not exceed 2 μm; the corundum particles of minor size are revealed only over the interfaces of the particles. Such coating can have a good wear resistance in the process of operation of sliding friction surfaces under grease condition due to the presence of grease pockets. The presence of minor (below 1 μm) corundum particles should not affect the wear of the joined couple and the surface quality.

In the process of spattering of a coating with the use of a mechanical mixture of particle of copper, zinc and aluminum oxide (corundum), a structure is formed:

- on the basis of copper – hardness ≈106.5 HV, zinc - ≈49.7 HV, intermetallic compounds (γ - and ε - phases) - ≈168.7 HV, of the weight content of 62.0%, 7.9% and 24.2% correspondingly;
- a low-thickness zinc oxide film is detected on the copper particles which suggests the mass transfer of zinc; a non-significant number of corundum particles of the size below 2 μm is present over the interface of copper particles;
- the “brass” coating of gradient structure may quite efficiently prevent the surface destruction under the effect of hard particles.
The coatings based on copper and the mixture of copper and zinc ("brass") particles need the further study of their tribological properties and characteristics for assessment and specification of conditions of their operation.

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