Influence of parameters of gas-dynamic spraying on substructure of "brass" coating type

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Abstract. Investigations of the influence of the parameters of applying a gas-dynamic coating of copper-zinc on its substructure have been carried out. It was found that the coating has a gradient hardness and different phase composition. Increasing the temperature of spraying and coating with 3mm overlap leads to a decrease in the size of the substructures. The structure of the coating, which is gradient in phase composition and hardness, should provide high tribotechnical characteristics of the friction surface in contact.

1. Introduction
In the field of mechanical engineering, powder coatings of various application methods are widely used. The main areas of application of such coatings are friction pairs, sealing of joints, restoration of geometry, and anti-corrosion protection. One of the modern methods of forming a coating from a powder mixture is gas-dynamic spraying. It allows the application of coatings of ductile metals with a relative elongation of more than 40%, zinc, nickel, aluminum and copper on a steel supporting structure. In this case, the supporting structure does not heat up more than 140°C. The coatings have high values of adhesion strength and cohesive strength of the coating metal.

The quality of such coatings depends on the technological modes of spraying: composition and fraction of the sprayed mechanical mixture, number of passes, spraying temperature, powder consumption, distance from the nozzle exit to the spraying surface, etc.

One of the factors that have a significant effect on the mechanical properties of the considered coatings is their substructure.

The aim of the work was to assess the influence of the parameters of gas-dynamic spraying on the substructure of the coating of the “brass” type.

2. Equipment and research method
The coating was sprayed on the backing of 5140H steel using gas-dynamic device DIMET-404 at air temperature 270°C, 360°C and 450°C, the rate of replaceable nozzle displacement in relation to the sample surface 10 mm·s⁻¹, the distance from the nozzle cut to the surface equal to 10 mm and nozzle displacement of 2 mm (contact ratio 94%) and 3 mm (contact ratio 55%) (table 1). To apply the coating, the authors used the mechanical mixture of copper and zinc particles and aluminum oxide (Al₂O₃) of as received grade C-01-11 with ingredients weight ratio Cu:Zn:Al₂O₃ = 35%:35%:30%, manufactured at Obninsk Powder Spray Center [1].
Copper-zinc (brass) coatings were applied to a 5140H steel supporting structure using a gas-dynamic device manufactured by DIMET-404 at air flow temperatures from 270°C to 450°C in 90°C increments, at a nozzle velocity along the sample of 10 mm·s⁻¹ and the distance from the end of the nozzle to the spray surface is 10 mm. In this case, to obtain a continuous coating of a flat surface, the nozzle moved relative to the previously deposited layer by 2 mm (with an overlap ratio of 64%) and 3 mm (with an overlap ratio of 55%) (table 1). The initial powder mixture of grade S-01-11 consisted of particles of aluminum oxide (Al₂O₃), zinc and copper with a powder mass ratio of Al₂O₃: Zn: Cu = 30%:35%:35%, produced in Obninsk [1].

The phase composition of the coatings was investigated on a Rigaku Ultima IV multifunctional X-ray diffractometer using CuKα radiation and a parallel beam. The analysis of diffraction patterns is carried out on the basis of the PDXL software product (Rigaku) using the PDF-2 database. The quantitative analysis and analysis of the broadening of diffraction lines in order to determine the parameters of the fine crystal structure (block size, microstrains) is carried out using the Rietveld method implemented in the PDXL software package (Rigaku). The hardness of the coating was measured by the Vickers hardness test in accordance with GOST 2999-75 at a load of 245 mN and a holding time of 10 seconds using a SHIMADZU HMV-2 hardness tester.

### Table 1. Results of the analysis of surface treatment by particle flow.

| Nozzle displacement, mm | Surface exposed to particles, times | | |
|-------------------------|------------------------------------|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|
Table 2. Phase analysis of coverage.

| Nozzle displacement, mm | Cu   | Zn   | ε-phase | γ-phase |
|-------------------------|------|------|---------|---------|
|                         | T=270°C |      |         |         |
| 2                       | 87.9±1.0 | 1.44±0.17 | 5.3±0.9 | -       |
| 3                       | 83.8±0.8 | 1.3±0.1 | 8.5±0.9 | -       |
|                         | T=360°C |      |         |         |
| 2                       | 62.0±0.9 | 7.9±0.6 | 7.9±0.8 | 17.0±2.0 |
| 3                       | 69.0±0.7 | 12.6±0.6 | 10.4±0.5 | -       |
|                         | T=450°C |      |         |         |
| 2                       | 40.5±0.8 | 9.0±0.6 | 11.4±0.7 | 33.0±0.2 |
| 3                       | 56.0±0.8 | 24.0±0.6 | 12.0±0.7 | -       |

Measurements of the lattice parameters of copper and zinc show that a change in the technological modes of spraying does not affect the lattice period of metals. A decrease in the displacement distance of the nozzle from 3 mm to 2 mm leads to a significant increase from 0.3870 nm to 0.4303 nm in the size of one of the faces of the crystal lattice of the electronic compound of the ε-phase (Table 3). This result can be interpreted as the beginning of the rearrangement of the structure of the electronic compound (ε-phase), which has a hexagonal close-packed lattice, into another crystallographic system with the formation of a new compound.

Table 3. Parameters of metal lattice, phases and compounds.

| Nozzle displacement, mm | Cu       | Zn       | ε     | γ     |
|-------------------------|----------|----------|-------|-------|
|                         | T=270°C  |          |       |       |
| 2                       | 0.3619   | 0.2667/0.4953 | 0.2760/0.4303 | -     |
| 3                       | 0.3617   | 0.2666/0.4945 | 0.2759/0.3870 | -     |
|                         | T=360°C  |          |       |       |
| 2                       | 0.3620   | 0.2666/0.4953 | 0.2757/0.430 | 0.8888 |
| 3                       | 0.3615   | 0.2666/0.4944 | 0.2759/0.4505 | -     |
|                         | T=450°C  |          |       |       |
| 2                       | 0.3617   | 0.2666/0.4946 | 0.2754/0.4296 | 0.8900 |
| 3                       | 0.3620   | 0.2665/0.4943 | 0.2753/0.4298 | -     |

Measurements of the lattice parameters of copper, zinc and intermetallic compounds (ε and γ-phases) revealed that an increase in the deposition temperature from 270°C to 360°C with a nozzle displacement by 3 mm does not lead to changes in the lattice size for copper and zinc (Table 3). In the electronic compound of the ε-phase, the change in the temperature of the air flow is accompanied by a significant increase in the size of one of the lattice faces from 0.387 nm to 0.4305 nm. The change in the parameters of the crystal lattice of the ε-phase is associated with additional enrichment with copper atoms, its rearrangement in accordance with the copper-zinc state diagram and subsequent transformation into the gamma phase.
When using a nozzle offset of 2 mm, an increase in the spraying temperature has no significant effect on the lattice parameters of all structural components (table 3).

Changing the technological parameters of spraying (L = 3 mm → 2 mm) does not significantly affect the lattice parameters of copper, zinc and corundum. In the electronic compound of the ε-phase, one of the lattice faces decreases in size and its parameters become close to those given in the technical literature. For the newly formed compound γ-phase, which has a body-centered cubic lattice, the parameters also correspond to those given in the literature (table 3) [3].

An increase in the spraying temperature from 360°C to 450°C with a nozzle displacement of 2 mm does not significantly affect the lattice parameters of all structural components (table 3). The use of a technological displacement of the nozzle relative to the previously deposited metal layer of 3 mm also does not significantly affect the lattice parameters of all structural components except for the ε-phase. For this electronic compound based on CuZn3, with an increase in the deposition temperature, one of the lattice periods significantly changes its size (0.4505 nm → 0.4298 nm) and the lattice itself has parameters that are given in scientific papers (table 3) [3].

The distance by which the nozzle is displaced at the same temperature of coating spraying, taking into account the measurement and calculation error, has practically no effect on the magnitude of microstrains of copper and electronic compound.

An increase in the deposition temperature leads to a significant decrease in the magnitude of microstrain in copper when the nozzle is displaced by 2 mm (0.187% → 0.149%) and 3 mm (0.187% → 0.149%) (table 4). An increase in the temperature of the air flow from 270°C to 360°C is accompanied, though not significant, but an increase in the energy of the particle flow, which should lead to an increase in deformation [6]. Therefore, a decrease in the amount of deformation is due to the heating of the coating with air and the return (rest) processes in the structure. As a rule, the more significant the deformation, the lower the temperature at which the processes of migration of atoms and rearrangement of boundaries take place. An increase in the deposition temperature does not significantly affect the magnitude of microdeformations of zinc and an electronic compound (ε-phase). Zinc, as a brittle metal, collapses upon impact due to the displacement of the metal volumes relative to each other along certain crystallographic planes (extraplanes), and an electronic compound is formed on its basis, which should also not affect the magnitude of microstrains.

With a decrease in the displacement of the nozzle (3 mm → 2 mm) and the use of one air flow temperature of 360°C, the value of copper microstrains increases from 0.129% to 0.149%, which is associated with the additional effect of the particle flow on the coating metals (table 4). The change in the deposition parameters does not affect the magnitude of microstrains of the remaining structural components.

### Table 4. Deformation of metals, phases and compounds.

| Nozzle displacement, mm | The magnitude of microdeformations (microstrains), % | Cu       | Zn       | ε       | γ       |
|------------------------|--------------------------------------------------|----------|----------|---------|---------|
|                        | T=270°C                                          |          |          |         |         |
| 2                      | 0.187±0.04                                       | 0.10±0.11 | 0.11±0.08 | -       |
| 3                      | 0.189±0.011                                      | 0.00±0.016 | 0.10±0.04 | -       |
|                        | T=360°C                                          |          |          |         |         |
| 2                      | 0.149±0.04                                       | 0.03±0.12 | 0.13±0.04 | 0.307±0.016 |
| 3                      | 0.129±0.003                                      | 0.00±0.12 | 0.18±0.03 | -       |
|                        | T=450°C                                          |          |          |         |         |
| 2                      | 0.119±0.010                                      | 0.004±0.008 | 0.21±0.03 | 0.17±0.02 |
| 3                      | 0.13±0.002                                       | 0.005±0.10 | 0.20±0.03 | -       |
An increase in the spraying temperature with a displacement of the nozzle by 3 mm does not affect the magnitude of microstrains in all structural components of the coating based on a mixture of copper, zinc and corundum particles. A decrease in the displacement distance of the nozzle to 2 mm is accompanied by a significant decrease in the magnitude of microstrains in copper (0.149% → 0.119%) and an electronic compound based on Cu₅Zn₈ (γ-phase) from 0.307% to 0.17%.

With a decrease in the displacement of the nozzle (3 mm → 2 mm) and the use of one air flow temperature of 450°C, no significant changes in the magnitude of microdeformations are observed.

Calculation of the size of the substructure of metals and electronic compounds shows a significant effect of the technological parameters of spraying on the value of the CSR of the structural components of the coating based on copper, zinc and corundum. An increase in the mixing of the nozzle from 2 mm to 3 mm leads to a significant refinement of the substructure from > 200 nm to 21.4 nm for copper and from >100 nm to 22.4 nm for zinc (table 5). The size of the substructure of the electronic compound with an increase in the displacement of the nozzle decreases almost twofold from 70.5 nm to 36.2 nm and differs slightly from the size of the zinc substructure.

Table 5. Results of calculating the sizes of structural components.

| Nozzle displacement, mm | Cu Size of CSR, nm | Zn | ε | γ |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| T=270°C         |                 |                 |                 |                 |
| 2               | >200            | >100            | 70.5±4.7        | -               |
| 3               | 21.4±0.4        | 22.4±1.6        | 36.2±3.6        | -               |
| T=360°C         |                 |                 |                 |                 |
| 2               | >200            | >200            | 82.8±41.5       | >200            |
| 3               | 61.9±3.6        | 19.9±0.7        | 30.4±3.0        | -               |
| T=450°C         |                 |                 |                 |                 |
| 2               | 89.8±19.5       | 63.7±6.2        | 86.5±76.7       | 62.0±15.3       |
| 3               | 20.8±0.6        | 23.5±0.7        | 21.2±1.2        | -               |

An increase in the gas flow temperature leads to an almost threefold increase in the size of the copper substructure from 21.4 nm to 61.9 nm with a nozzle displacement of 3 mm, which is caused by an increase in the deposition temperature and a change in the mechanical properties of copper (table 5). The size of the substructure of other structural components, namely zinc and ε-phase, is not affected by an increase in the deposition temperature. When using the technological mode of spraying, in which the nozzle is displaced by 2 mm, an increase in the spraying temperature from 270°C to 360°C has practically no effect on the size of the substructure of the main structural components, with the exception of zinc, where it increases from >100 nm to >200 nm (table 5). The size of the substructure of the new electronic compound of the γ-phase does not differ from the size of the substructure of zinc, on the basis of which it is formed.

An increase in the deposition temperature from 360°C to 450°C with a nozzle displacement of 3 mm is accompanied by a significant decrease in the size of the CSR of copper and electronic compound ε-phase from 61.9 nm to 20.8 nm and from 30.4 nm up to 21.2 nm, respectively (table 5). The size of the zinc substructure does not change significantly with an increase in the deposition temperature: 19.9 nm and 23.5 nm.

A decrease in the distance to 2 mm is accompanied by a more significant change in the size of the substructure of the main phase components of the structure. The size of the CSR of copper, zinc, and intermetallic compound (γ-phase) sharply decreases from > 200 nm to 89.8 nm, > 200 nm to 63.7 nm and >200 nm to 62.0 nm, respectively. An increase in the deposition temperature from 360°C to 450°C
is accompanied by a more significant increase in the energy of the particle flux than an increase from 270°C to 360°C, which has a significant effect on the refinement of the structural components (table 4).

Spraying the coating at an air flow temperature of 450°C with a nozzle displacement of 2 mm and 3 mm is accompanied by the formation of a coating in which, with a smaller displacement of the nozzle relative to the surface, the size of the copper, zinc and ε-phase substructures is significantly larger than with a nozzle displacement of 3 mm (table 5). This difference may be due to the additional direct effect of the heated air flow on the coating.

4. Conclusions
Gas-dynamic spraying of a mechanical mixture of particles of copper, zinc and aluminum oxide (corundum is accompanied by the formation of a “brass” -type coating with a gradient in hardness and phase composition).

An increase in the deposition temperature significantly reduces the size of the substructure of the structural components: for copper from 200 nm to 89.8 nm, zinc from 200 nm to 63.7 nm, γ - phases from > 200 nm to 62.0 nm; the size of the ε-phase substructure changes insignificantly and is in the range of 75 nm - 86.5 nm. In this case, the deposition of the coating with a nozzle displacement of 3 mm leads to a greater refinement of the substructure of the phase components.

An increase in the deposition temperature leads to a significant decrease in the amount of deformation in copper from 0.187% to 0.119% and in an electronic compound based on Cu₅Zn₈ (γ-phase), from 0.307% to 0.17%. The value of microdeformations of the ε-phase increases slightly from 0.11% to 0.21% with an increase in the spraying temperature.

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