Peculiarities of the “brass” coating formation applied by gas-dynamic spraying

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Abstract. A research of the "brass" type coating structure generation process, obtained by gas-dynamic spraying from a particulate mixture of copper, zinc and corundum. The formation mechanisms of the phase and chemical composition of the obtained coating are determined. During the coating formation, mass-transfer of zinc microvolumes by corundum particles occurs and their interstitial dissolution into copper particles, while diffusion processes occur by the motion of vacancies, of copper to zinc with the formation of intermetallic compounds.

1. Introduction
Copper alloys are widely distributed in various fields of technology, for example, in rubbing bearings, due to the high tribological properties. However, bearings made of copper alloys obtained by the metallurgical method have such disadvantages as heat evolution in the friction zone due to the high rotational rate, as well as the creation of secondary stresses in the alloy material during pressing, which reduces the maintainability, reliability and load capacity of the entire tribotechnical system. In Russian and foreign scientific centres, studies are being carried out on the application of tribotechnical coatings using brass particles of different chemical composition and a mixture of copper and zinc particles with and without solid particles, as well as with preliminary and subsequent heat treatment to change the physical and mechanical characteristics of the applied metal layer [1].

This work aims to study the process of coating structure forming based on copper and zinc particles supported on a steel substrate by gas dynamic cold spraying at an airflow temperature of 450°C.

2. Methods and equipment
To spray the “brass” coating, a mechanical mixture of particles of copper, zinc and aluminium oxide (corundum) is used in the ratio by weight of Cu:Zn:Al₂O₃ = 35%: 35%: 30% (grade C - 01 - 11) [2]. The coating is applied at a nozzle moving speed relative to the sprayed surface V = 10 mm/s, from a distance L = 10 mm from the nozzle exit to a sample 15 × 15 × 3 mm in size using an air flow heated up to t ≈ 450°C. According to the experimental conditions, the net coating time does not exceed 14 s.

The X-ray structure analysis of the phase composition of gas-dynamic coatings Cu-Zn is studied on the Rigaku Ultima IV multipurpose X-ray diffractometer using CuKα radiation. The microspectral analysis of the coating composition is carried out on the FEI “Quanta-650” scanning electron...
microscope with an EDAX energy dispersive X-ray spectral analyser and using a back-scattered electron detector.

3. Research results

X-ray phase analysis reveals copper, zinc and two intermetallic (electron) compounds based on CuZn3 (ε-phase) and Cu5 Zn8 (γ-phase) in the coating, the mass fraction of which is 58%, 9%, 11% and 33%, respectively (table 1).

| Phase composition | Lattice distance d, nm | Coherent scattering region size, nm | Weight percent, % |
|-------------------|------------------------|------------------------------------|------------------|
| Copper            | 0.3617                 | 89.8                               | 58               |
| Zinc              | 0.2666/0.4946          | 63.7                               | 9                |
| ε-phase           | 0.2754/0.4296          | 96.5                               | 11               |
| γ-phase           | 0.8900                 | 62.0                               | 33               |

According to the copper – zinc state-transition diagram, these phases are formed at a zinc content of ≥ 55 at% [3]. The lattice distance of copper and zinc (table 1) is significantly increased, which may be due to the process of deformation of flexible metal particles upon impact on the surface and their collision with corundum solid particles. It is also impossible to exclude the influence on the parameter changes of the lattice diffusion (inter diffusion) of metals during the formation of solid solutions.

The area of two copper particles (spectra 1–6 and 14–19) and one zinc particle (spectra 7–13) are used to study the concentration distribution of coating components (figure 1). With a fairly uniform distribution of the content of elements in copper particles (97.59 at.% and 2.41 at.%), an abnormal change in concentration was detected when, at a distance of ≈3 μm, the copper concentration changes from 39.11 at.% to 98.45 at.% (figure 2, point 10 and point 11). Heating of the coating metal with the net effect on the surface of the heated gas is ≈ 90% of air temperature with a slight decrease closer to the substrate [4]. At this temperature (≈ 410°C), zinc has low mechanical properties when the tensile strength is close to zero and corundum solid particles pass through zinc particles and, capturing metal particles with their sharp edges, transfer and alloy them into copper particles. In the work [5], the study of a “set” of metal composed of rolled aluminium in thickness of 100 μm, after gas-dynamic treatment with corundum particles, revealed deformation marks (holes) with a depth of up to 230 μm, which allows to count on the running of the process described above.

Figure 1. Analysis of the chemical composition of the coating surface area after spraying at a temperature of 450°C (areas of elemental analysis are highlighted).
The microspectral analysis of the component content, studied along the route, including two copper particles and a zinc particle, shows that the diffusion of copper passes almost the same route on both sides of the zinc particle. The concentration of copper in zinc decreases to 16.30 at.% on one side and to 18.94 at.% on the other side of zinc particle (figure 2). Inside the zinc particle, the copper content rises to 25.56 at.%, which is associated with the process of interdiffusion.

During the inter (reactive) diffusion, by measuring the depth of the diffusion coating, it is possible to determine the diffusivity coefficient by the formula [6]:

\[ D = \frac{X^2}{2t}, \]

where \( X \) – is the average depth of the diffusion coating (for calculation, half the depth of the diffusion coating is taken), cm; \( t \) – is the diffusion process time, s.

The diffusivity coefficient from a liquid-alloy of zinc into copper at a temperature of 427°C is \( \approx 0.45 \times 10^{-13} \) m²/s. In another work, the diffusivity coefficient of zinc into copper was calculated for the \( \gamma \) phase at a temperature of 350°C and it was \( \approx 1.3 \times 10^{-9} \) cm²/s [7]. Using the diffusivity coefficient and the coating spraying time (14 s), the distance that diffusion could pass does not exceed 16 nm, which is significantly less than the result obtained \( \approx 7.9 \) μm (figure 2). If half the length of the scan path (15.88 μm) is put in the formula, then taking into account the spraying time, the diffusivity coefficient of copper into zinc will be \( \approx 1.14 \times 10^{-8} \) cm²/s, which significantly exceeds the values obtained in studies of the diffusion of copper into zinc and zinc into copper [7].

The tensile strength of copper at a temperature of \( \approx 400\degree\text{C} \) decreases almost twice, which is \( \approx 220 \) MPa. Under the corundum particles influence, copper particles are deformed and, if the deformation of the particles is accompanied by the formation of stresses, then their relaxation will take place due to the coordinated atomic displacement, which will significantly increase the diffusion rate of copper into zinc. In this case, the high value of the diffusivity coefficient during gas-dynamic spraying of a coating supported on copper and zinc particles should be attributed to a significant increase in point defects (vacancies) in zinc heated to a temperature of 410°C and diffusion through the vacancy mechanism, as well as occurrence and strain relaxation - stress in copper particles.

4. Conclusions

As a result of studies, the presence of mass-transfer of zinc microvolumes by corundum particles and their interstitial dissolution into copper particles was established.

In the coating, conditions for the predominant diffusion of copper into zinc are formed with the formation of intermetallic compounds inherent in brass.
Corundum particles during spraying deform particles of copper, which leads to an increase in the diffusivity coefficient of copper in zinc.

The studies of the structure of the gas-dynamic coatings based on the mixture of copper-zinc particles are preliminary, to assess the possibility of their use as an analogue of bronze and brass, it is necessary to conduct further tests for friction and wear.

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