The effect of process parameters of gas-dynamic spray on generation of brass-type coating structure

V E Arkhipov, G V Moskvitin and M S Pugachev
Mechanical Engineering Research Institute of the Russian Academy of Sciences, Moscow, 101990, Russia
GVMoskvitin@yandex.ru

Abstract. The study results have shown the effect of coating temperature and contact ratio on generation of phase structure of the coating based on the mixture of Cu and Zn particles and Al₂O₃ applied by cold gas-dynamic spray method. The x-ray diffraction and micro-spectral analyses have shown the presence of copper and zinc in the structure and generation of electronic compound based on CuZn₃ (ε – phase) and Cu₅Zn₈ (γ – phase), which is preconditioned by copper diffusion into zinc. The mass fraction of intermetallic compositions in the coating structure depends on the coating temperature and contact ratio, it reaches 12% and 33%. The analysis of surface processing by solid and plastic particles flow has shown the effect of copper particles deformation on diffusion rate.

1. Introduction
Gas-dynamic spray coating is the advanced method of obtaining high-quality coatings in adverse conditions. The sprayed copper and zinc-based layer has high adhesion strength of not lower than 50 MPa and cohesion strength of 80 to 150 MPa, whereas the temperature of steel backing heating does not exceed 140°C.

The objective of this work is to study the changes in the brass coating structure depending on process parameters of gas-dynamic coating.

2. Methods and modes of obtaining the coating
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].

Table 1. The results of particle surface treatment analysis.

| Nozzle displacement, mm | Contact ratio,% | Number of particle surface treatment, times |
|-------------------------|-----------------|--------------------------------------------|
|                         |                 | 1 (time/surface)                            |
|                         |                 | 2 (time/surface)                            |
|                         |                 | 3 (time/surface)                            |
| 2                       | 64              | 14 s / 20 mm²                               |
|                         |                 | 28 s / 90 mm²                               |
|                         |                 | 42 s / 112.5 mm²                            |
| 3                       | 55              | 12 s / 74 mm²                               |
|                         |                 | 24 s / 148.5 mm²                            |

Table 1: The results of particle surface treatment analysis.
3. Research results

Chemical analysis of the coating composition has shown a significant dependence of the components content on the spray temperature. Rising the air flow temperature from 270°C to 360°C and 450°C was accompanied by generation of a coating where zinc mass fraction increases from 8.15% to 22.3% and 37.6%. The copper content in the coating composition at gradual air flow temperature increase decreased from 91.7% to 77.5% and 62.2%.

The metals (copper, zinc), aluminum oxide and solid electron-type solution based on CuZn3 (ε – phase) (table 2) were revealed in the coating applied at the air flow temperature of 270°C. Copper-zinc state diagram shows that ε and ε+η – phases were generated in case of zinc presence in the melt in the amount of ≥ 78 at.% [2]. The increase of nozzle displacement distance from 2 mm (K_cont 64%) to 3 mm (K_cont 55%) resulted in copper content reduction from 87.9% to 83.8%, which could be explained by the increase of weight ratio of ε – phase, which includes copper (table 2). The study of the coating applied using the mechanical mixture of copper, zinc and aluminum oxide particles by gas-dynamic coating reveals the presence of the process of copper into zinc diffusion with generation of electron type compound. However, many researchers of diffusion process in copper-zinc system have theoretically and practically proven that zinc into copper diffusion coefficient exceeds the copper into zinc diffusion coefficient by several times; sometimes this ratio, for example, calculated for ε – phase, is of abnormal nature (D_{Zn} : D_{Cu} = 47) [3, 4]. In this case we could suppose the presence of other conditions that affect the diffusion process at gas dynamic spray of the coatings.

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

Rising the spray temperature to 360°C is accompanied by the major decrease in the mass fraction of copper and the increase of zinc and the intermetallic compound in ε - phase (table 2). When the coating is sprayed with the contact ratio of 64% (2 mm displacement), a new phase is revealed in the coating structure – the electronic-type solid solution based on CuZn5 (γ - phase), with mass fraction of 17.0% (table 2). When smelting brass, this phase is generated when zinc content in the solution is within the range of 52-78 at.% (γ + β'; γ; γ + ε) [2]. Analyzing the ratio of metals and compounds in the coating with an increase in contact ratio, it is possible to observe that the decrease of pure copper content from 69.0% to 62.0% and zinc from 12.6% to 7.9% is due to the generation of a new γ - phase (CuZn5) compound. The mass fraction of ε - phase decreases as well, which is also associated with the process of copper into zinc diffusion and the generation of a new electronic compound.

The increase in the content of CuZn3 (ε-phase)-based electronic compound in the structure of the coating composition with the increase in the spraying temperature at a nozzle displacement by 2 mm from 5.3% to 7.9% and a nozzle displacement by 3 mm from 8.5% to 10.4 % is due to the increase of the spraying temperature [5]. Moreover, the increase in the content of the electronic phase (ε-phase) in both versions of gas-dynamic spray slightly differs by 2.6% and 1.9%.

The next increase in the spray temperature to 450°C is accompanied by generation of a coating, in which the amount of copper significantly reduces, and the mass fraction of zinc increases, which is due to the change in the metal content at spray temperature increase (table 2). The mass fraction of CuZn3-based electronic compounds (ε-phase) and Cu5Zn8-based electronic compounds (γ - phase) increases, which is related to the increase in the diffusion rate at increasing spray temperature.
Decreasing of the distance by which the nozzle is displaced when the coating is sprayed on the entire surface of the sample (3 → 2mm) results in significant copper (56.0% → 40.5%) and zinc (24.0% → 9.0%) content reduction which is associated with generation of gamma phase in an amount of 33%. At a spray temperature of 450°C, the change of nozzle displacement distance does not result in significant change in the ε-phase content (table 2).

The results of X-ray diffraction phase analysis show that when the coating was sprayed at air flow temperature of 360°C and 450°C, γ-phase was formed in the applied metal layer in an amount of 17% and 33%. And when the nozzle was displaced by 3 mm, at equivalent other spray parameters, this intermetallic compound was absent in the applied coating. In this case, the revealed trend indicates the presence of the effect of gas-dynamic spray parameters, in particular, the cover ratio, on the phase composition of the coating. A graphical assessment of processing options reveals that in the first case (2 mm) there are surface areas (S≈50%) exposed to the particle flow for the third time (table 1).

In this case, the observed effect of the diffusion process intensity increase with the generation of a Cu5Zn8 –based electronic compound (γ-phase) can be related only to the additional deformation of copper particles. In this case, deformation can change the shape (geometry) of the particle, which should be accompanied by the displacement of the boundaries of contact between copper and zinc particles, but not lead to the acceleration of the diffusion process. In case of generation of stresses, their relaxation will occur due to elementary acts of cooperative copper atoms displacement (jumps), which will accordingly affect the diffusion coefficient and rate [5].

Besides, the calculations have shown that in the process of spraying, the temperature of the applied metal coating in the area of direct air flow effect was 80-90% of the gas stream temperature, that is, 290-320°C and 360-405°C when the coating is applied at the temperature of 360°C and 450°C [6]. When zinc was heated to the temperature close to the melt temperature (≈419°C), the number of vacancies significantly rose, which provided more intense copper to zinc diffusion process according to the vacancy principle. Therefore, copper to zinc diffusion process with the generation of electronic compounds inherent to brasses, occurs due to the copper particles deformation with corundum particles, generation of stresses and micro-deformations with subsequent deformation thereof due to cooperative copper atoms displacement (jumps) and significant increase on vacancies in zinc.

Microspectral analysis of coatings applied at the spray temperature of 360°C and 450°C and nozzle displacement by 3 mm, was performed along the route that began on the copper particle, further passed by zinc particle and finished on copper particle (figure 1 (a), (b)).
Figure 1. Copper and zinc particles coating applied at the temperature: (a) – 360°C and (b) – 450°C.

The analysis of copper and zinc distribution along the scanning route has shown the presence of copper diffusion into zinc at both sides of zinc particle (figure 2). The results obtained show that in the process of spraying at air current temperature 360°C there exist two areas with different copper and zinc ratio: a more significant one, where copper amount is in the range of 7-10 at.% (90-93 at.% of zinc), and a less significant one, where copper content is 18-20 at.% (80-82 at.% of zinc). Judging from copper-zinc state diagram, the electronic compound ε-phase was generated at this copper and zinc ratio, which confirms the results of x-ray diffraction phase analysis. Moreover, in this case we can speak about the presence of electronic type phase, where zinc and copper atoms ratio differs.

Figure 2. Copper and zinc distribution in the coating applied at the temperature of 360°C (1 – copper, 2 – zinc).
The rise of spray temperature (450 °C) was accompanied with generation of a coating, where and area with copper content of the order of 20 at.% and zinc content of ≅80 at.% (figure 3) is generated due to the copper diffusion into zinc particle. Copper-zinc state diagram shows that at this components content the ε-phase electronic compound was generated, which confirms the results of x-ray diffraction phase analysis (table 2). That is, the rise of spray temperature at equal other process parameters of spray accelerated the process of copper to zinc diffusion.

![Figure 3. Copper and zinc distribution in the coating applied at the temperature of 450°C (1 – copper, 2 – zinc).](image)

At mutual (reactive) diffusion, measuring the diffusion layer depth, it is possible to determine the diffusion coefficient using the formula [5]:

$$D = \frac{X^2}{(2t)}^{-1},$$  \hspace{1cm} (1)

where \(X\) is the mean diffusion layer depth (a half of diffusion layer depth is taken for calculation), \(m\); \(t\) is the diffusion process time, s.

Scanning route length was 24 μm; the section, where the copper to zinc diffusion process occurred, did not exceed 14.0 μm (14·10⁻⁶ m). In this case, if we consider the time of the direct impact of the flow of particles and heated air on the coating with a nozzle displacement of 3 mm equal to 24 s (table 1), the copper into zinc diffusion coefficient was ≈0.11·10⁻¹³ m²·s⁻¹.

The coefficient of diffusion from liquid zinc melt into copper at the temperature of 427°C is ≈0.45·10⁻¹³ m²·s⁻¹. In another work, the coefficient of diffusion of zinc into copper for γ-phase at the temperature of 350°C was calculated, it equaled to ≈1.3x10⁻¹³ m²·s⁻¹ [3, 4]. Therefore, the presented results obtained in this work, show that during gas-dynamic coating spray the coefficient of diffusion of copper into zinc is higher than that of zinc into copper from the melt.

Microspectral analysis was carried out on the coating applied at 450°C and nozzle displacement of 2 mm. From the area of two copper particles (spectra 1–6 and 14–19) and one zinc particle (spectra 7–13), we studied the coating components concentration distribution (figure 4).
The processing of the results for copper particles showed that the distribution of copper and zinc at 10 points was quite stable and their atomic ratio averaged to 97.59% and 2.41%. At two points, we observed an increase in zinc concentration up to ≈5.1%. Besides, we observed an abnormal change in the components concentration in copper particles, when at the distance of ≈ 3 μm the copper concentration varied from 39.11 at.% up to 98.45 at.% (figure 4, point 10 and point 11). This result can be interpreted as the presence of mechanical mixing of metals under the effect of corundum particles, which was noted in the study of a coating based on the mixture of aluminium and zinc particles [6]. In a zinc particle, the concentration of copper varies in a significant range from 13.26% to 52.86%. According to copper-zinc phase diagram, the regions with such zinc content corresponded to the existence of electronic type compounds of ε- and γ-phases, which is confirmed by the results of x-ray diffraction analysis (table 2).

4. Conclusions
An increase in the spray temperature from 270°C to 450°C is accompanied by a decrease of copper mass fraction from 91.7% to 62.2% and the increase of zinc mass fraction from 8.15% to 37.6% in a coating based on copper and zinc particles mixture.

It is shown that when the nozzle is displaced by 3 mm, the structure contains copper, zinc and a CuZn$_3$-based electronic compound (ε-phase), the mass fraction of which increases from 5.3% to 11.4% with the spray temperature increase from 270°C to 450°C.

It is shown that when the nozzle is displaced by 2 mm, alongside with copper, zinc and compound (ε-phase), a Cu$_5$Zn$_8$-based electronic compound (γ-phase) is generated in the structure, the mass fraction of which increases from 17% to 33.0% when the temperature of the air flow rises from 360°C to 450°C.

The analysis of the sample surface treatment with a heated air flow and a mechanical mixture of metal and corundum particles indicates the effect of copper particles deformation on the predominant diffusion of copper into zinc and the increase in the diffusion coefficient.

References
[1] Dymet Application of technology and equipment (electronic resource) Available at: http://www.dimet-r.narod.ru/ (accessed 23 August 2020)
[2] Efremov B N 2016 BRASSES from phase structure to structure and properties
[3] Zayt V 1958 Diffusion in metals
[4] Smiths K J 1980 Metals: A Handbook
[5] Bokshtein B S 1978 *Diffusion in metals*

[6] Arkhipov V E, Landarski A F, Moskvitin G V and Pugachev M S 2017 *Gas-dynamic coating: structure and properties of coatings*