PAPER • OPEN ACCESS

The structure and properties of the coating based on particles of copper and zinc deposited by gas-dynamic spraying

View the article online for updates and enhancements.

The structure and properties of the coating based on particles of copper and zinc deposited by gas-dynamic spraying

V E Arkhipov, A F Londarsky, G V Moskvitin and M S Pugachev

Mechanical Engineering Research Institute of the Russian Academy of Science, Moscow, 101990, Russia

vearkhipov@mail.ru

Abstract. The results of the study of the structure and properties of the coating based on a particulate mixture of Cu and Zn deposited by the method of cold gas-dynamic spraying are presented. The presence of diffusion during the deposition of a coating with the formation of a solid solution of copper in zinc is shown. The process of predominant diffusion of copper into zinc with a slight exposure time in the furnace with the formation of intermetallic compounds $Cu_5 Zn_8$ and $CuZn$, the mass fraction of which reaches 44% and 28%, respectively, is revealed. The diffusion coefficient of copper to zinc is not less than 1.56×10^{-13} $m^2 \cdot s^{-1}$. An increase in the exposure time leads to a decrease in the content of beta (β') and gamma (γ) phases to $\approx 15\%$ and the formation of a solid solution of zinc in copper (α phase, 58%) with a different ratio of initial components. The formation of electronic compounds reduces the cohesive strength of the coating metal by almost two times, and an increase in the proportion of the phase leads to an increase in the cohesion above the initial value.

1. Introduction

Copper and brass coatings are applied using a variety of chemical and physical processes, such as flame spraying methods. In the last decade, considerable attention has been paid to the technology of applying coatings using the method of gas-dynamic spraying, which is distinguished by substantially less heating of the substrate and, as a result, the absence of deformation of the product and changes in the mechanical properties of the substrate [1]. In foreign scientific centers, they are actively engaged in the research of gas dynamic coating processes for tribotechnical purposes using brass powders, copper powders and a mixture of copper particles with zinc particles. Positive results were obtained on the deposition of a brass coating and an assessment was made of the effect of heat treatment of powders and coatings on the quality and mechanical properties of the applied metal layer [2,3,4,5,6].

In the Russian Federation, manufacturers of the "DYMET" series equipment used for gas-dynamic spraying of various functional coatings, in the nomenclature of powder materials, offer a mechanical mixture of copper and zinc particles to obtain a coating of brass [1]. Testing of the coating based on copper and zinc particles under dry friction conditions at room temperature showed very low values of sample wear with the coating and especially the counter body compared to copper coating, which is caused by the mass transfer of copper and zinc to the surface of the counter body [7]. However, an increase in the test temperature to 250°C significantly increases the wear of the coating and the counter body, which may be due to a change in the structure and properties of the coating.

The purpose of this work is to study the sequence of structural-phase transformations in the coating based on a mechanical mixture of copper and zinc particles deposited by cold gas-dynamic spraying and their influence on the cohesive strength of the coating metal.

2. Materials, methods, equipment.

The coating on the 40X steel substrate was sprayed using the DYMET – 404 gas-dynamic installation at an air flow temperature of 450°C, a moving speed of the replaceable nozzle relative to the sample surface 10 mm/s and a distance from the nozzle section to the surface 10 mm. Since the width of the applied coating layer when moving the nozzle in one direction does not exceed 6 mm, the deposition on the entire surface of the substrate is carried out with a successive displacement of the nozzle relative to the previously applied metal layer by 3 mm (overlap 50%). The mechanical mixture of particles of copper and zinc (C – 01 – 11) is used in the delivery condition and the ratio of ingredients by weight is – Cu : Zn : Al_2O_3 = 35%:35%:30% [1].

Heat treatment of the coating with the substrate is carried out in a SNOL laboratory furnace at a temperature below the melting point of zinc (405-415 ° C) and exposure times of 3, 5, 10, 20, 40, 60 and 180 minutes.

The phase constitution of the Cu – Zn system coatings is investigated on a multifunctional X-ray diffraction meter Rigaku Ultima IV using $Cu_{K\alpha}$ radiation and a parallel beam. To form a parallel beam, X-ray optics in the form of a multilayer parabolic mirror is used. Diffraction patterns are taken in a symmetric mode, the scan range 2θ from 20 to 120, step 0.05°, the speed of the detector 3°/min.

Analysis of diffractograms is carried out on the basis of the PDXL software product Rigaku using the PDF-2 database. Quantitative analysis is carried out using the Rietveld method that is implemented in the PDXL software package Rigaku.

The broadening of diffraction lines was analyzed to determine the parameters of the fine crystal structure (block size, micro strain) using the PDXL software Rigaku using the Rietveld method. Accounting for instrumental broadening was carried out using a standard survey — lanthanum hex boride (LaB_6), which does not have physical broadening.

X-ray fluorescence analysis is performed on a Rigaku spectrometer Primus II using an X-ray source an X-ray tube with Rh-anode in vacuum and range of elements from Ca to U. Quantitative analysis is carried out after recording and decoding the experimental spectra from the samples under study using special software from Rigaku ZSX using the SQX fundamental parameters method (without using reference samples).

The study of the structure and elemental composition of the coating is carried out on an FEI "Quanta-650" scanning electron microscope with an energy dispersive X-ray spectrometer EDAX. The study uses a detector of back reflected electrons, which allows obtaining an image with atomic number contrast and visualizing different phases on the surface of the samples. The electron source in the microscope is a tungsten cathode; accelerating voltage is 25 kV.

Coated samples are tested using the SHIMADZU universal servo hydraulic testing machine with a constant displacement rate of 0.002 mm/s.

The study of the cohesive strength of the metal coating is carried out using the method of "ring separation" [8]. The cohesive strength of the coating metal is calculated as the ratio of the ultimate load preceding the destruction of the coating to the area of the coating. Based on the calculated data, the dependence of the cohesion of the copper-zinc coating on the heat treatment time is constructed.

3. Results

The mass content of copper and zinc in the applied coating is 64.8% and 35.0%, respectively, which differs significantly from the initial ratio of components in the mechanical mixture of powders. In the structure of the coating, a rather uneven alternation of particles of zinc and copper is observed – areas of light and light gray, respectively figure 1. In addition, uneven in shape and size of the inclusion of corundum (dark areas) are clearly visible.
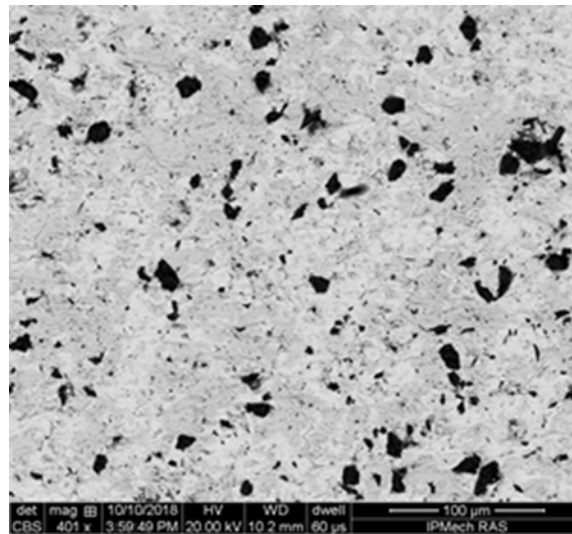
Figure 1. Coating structure based on copper and zinc particles: scanning electron microscopy using a back-reflected electron detector.

X-ray diffraction phase analysis reveals copper ($\approx 3.61A^0$), zinc ($\approx 2.66A^0$) and zinc-based solid solution ($\approx 2.75A^0$) in the initial coating structure (table 1).

Table 1. Phase composition of the coating based on copper and zinc.

Name of phases and compounds	Mass fraction of elements, chemical compounds and phases,%							
	Holding time, min							
	0	3	5	10	20	40	60	180
Cu	58	48	38	26	26	19	22	1
α – tv. rr	-	1	14	16	17	30	34	58
CuZn (β')	-	-	-	28	29	27	17	15
$Cu_5 Zn_8$ (γ)	-	44	44	22	20	14	17	14
Zn	23	7	-	-	-	-	-	-
ZnO			4	8	8	10	10	12
η - phase	19	-	-	-	-	-	-	-
Total content,%	100	100	100	100	100	100	100	100

Six phases can form in solid state of copper and zinc alloys: α – solid solution of Zn in Cu; β' – solid solution of electronic type based on CuZn compound; γ is an electronic solution based on $Cu_5 Zn_8$; ε is a solid solution of electronic type based on $CuZn_3$; δ is a solid solution (nature is not established); η is a solid solution of Cu in Zn. At normal temperature, the brass used in practice is single-phase and consists of the α-solid solution or the β'-phase or two-phase on the basis of α and β' [9].

Thus, it can be argued that in the process of spraying a coating based on a mixture of particles of copper and zinc at a temperature of 450°C the deposited metal layer undergo initial diffusion processes, which leads to the formation of η-solid solution of Cu in Zn.

The following factors can influence the diffusion process and the formation of a solid solution of copper in zinc during the deposition of a coating. The results of the study of electrical resistivity and X-ray analysis of the copper coating show the presence of plastic deformation of particles with an increase in the number of vacancies [8]. However, the most important factor should be considered to increase the temperature of the coating (used metals) to a temperature close to the temperature of the

airflow (≈450°C) [8]. In this case, zinc particles are in a state close to melting, when the bonds between the lattice atoms weaken and the number of vacancies increases significantly, which leads to the possibility of diffusion passing through the vacancy mechanism [10].

A slight exposure of the coating based on copper and zinc particles is accompanied by the beginning of the formation of a solid solution based on copper with a period different from pure copper (a-phase; ≈3.72A^0), a decrease in the content of pure zinc (up to 7%) and the formation of an electronic compound – gamma phase $Cu_5 Zn_8$, the mass fraction of which is 44% table 1. It can be seen from the copper-zinc state diagram that the gamma phase is formed when the zinc content in the melt is from 50% to 78% (β′+γ, γ, γ+ε) [9].

Spectral analysis of the surface of the coating was carried out along the route, which includes a zinc particle (≈15 μm), limited to copper particles figure 2.
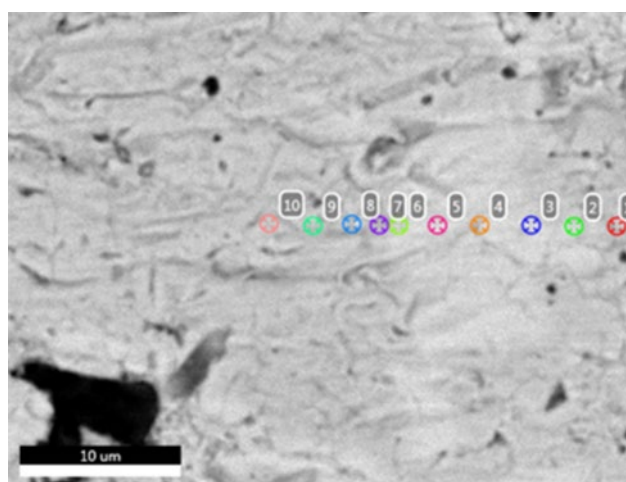

Figure 2. The trace of the analysis of the chemical composition of the surface area of the coating after heat treatment for 3 minutes.

At the edge of dark tint particles, the copper concentration is within 95.21-96.82 at.% (error 2.05%), and the rest is zinc. The result obtained indicates the presence of diffusion of zinc into copper and the formation of a solid solution of zinc in copper (α phase). The diffusion of copper atoms into a zinc particle takes place on both sides fairly evenly (throughout the volume); the copper concentration decreases to the center of the zinc particle and reaches 26 at.% figure 3.

Diffusion coefficient [10], which is ≈1.56x10^{-13} m^2/s is calculated by the simple relation of $D_x = x^2/2t$, using copper diffusion distance (half-size zinc particle) and a heat treatment time (180 s).

In zinc particles in different parts of the surface of the coating, 19 measurements were made of the content of the starting components. Based on the copper-zinc state diagram: 12 (63.2%) measurements are in the region of existence of the γ phase; 3 (15.8%) measurements on the concentration of copper and zinc correspond to the region of existence of the γ+ε phases; 2 (10.5%) measurements correspond to the existence region of the γ+β ′ phases and 2 (10.5%) measurements on the atomic content of the components correspond to the phase of existence of the α+β′ phases.
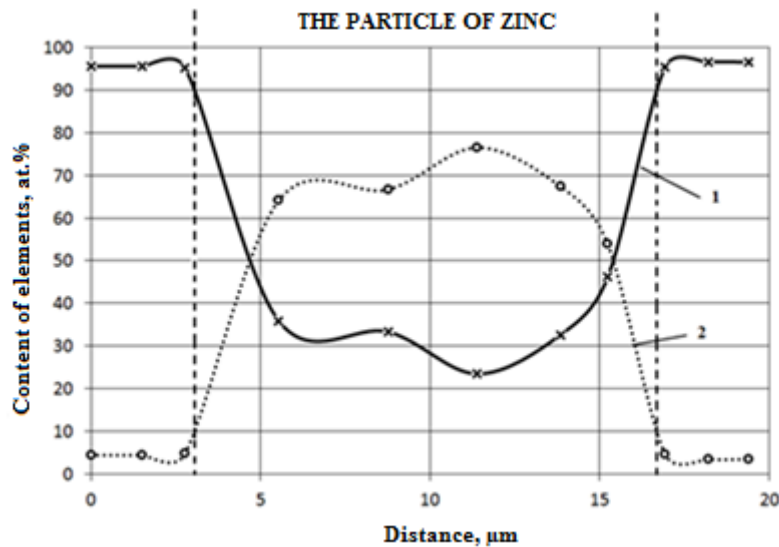
Figure 3. Changes in the concentration of copper (1) and zinc (2) in
the coating after heat treatment for 3 minutes

Thus, based on the results of micro spectral analysis, the main phase formed as a result of the diffusion of copper into zinc is $Cu_5 Zn_8$, which coincides with the results of X-ray structural analysis. In this case, after heat treatment of the coating for 3 minutes, a four-phase structure is formed on the basis of copper (≈48%), zinc (≈7%), gamma phase (≈44%) and a-phase (≈1%).

Heat treatment of the coating for 5 min is accompanied by a decrease in the copper content from ≈48% to ≈38% and an increase in the content of the solid solution based on copper from 1% to ≈14%. The amount of gamma phase does not change, but zinc oxide is additionally detected in the amount of ≈4% (table 1). The gas-dynamic coating of copper and zinc has an open porosity in the range of 3-4%, which can contribute to the oxidation of zinc over the depth of the deposited metal layer when it is heated in a furnace with the formation of zinc oxide [8].

An increase in the heat treatment time of the initial coating to 10 min leads to a further decrease in the copper content from ≈38% to ≈26% and to a slight increase in the amount of solid solution based on copper (up to 16%). In the same time interval, the content of the γ - phase decreases by half (22%) with an increase in the amount of zinc oxide to ≈8% (table 1). In this case, X-ray phase analysis shows the presence of a new e-compound of β' phase CuZn in an amount of ≈28% (table 1).

A further increase in the exposure time of the coating in the furnace to 180 minutes is accompanied by a decrease in the copper content to ≈1%, an increase in the a-phase content to 58% and a decrease in the β' and γ phases to 14% and 15%, respectively (table 1). An increase in the solid solution of zinc in copper and a decrease in the content of electronic compounds indicates a predominant diffusion of zinc into copper. At the same time, the zinc oxide content increases from 8% to 12%.

Microspectral analysis of elements in the coating after 180 minutes of heat treatment was carried out at points and on the area of plots (grains, particles), which are limited to dark tint lines and differ in size (from 10 μm to 20 μm) figure 4.
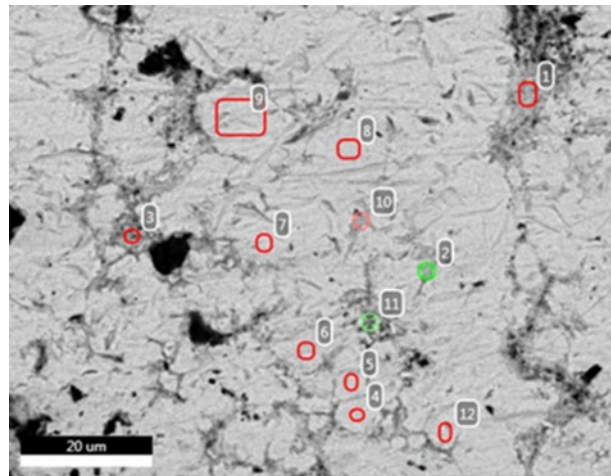
Figure 4. The order of analysis the chemical composition of the surface area of the coating after heat treatment for 180 minutes

Analysis of the results shows that the grains (particles) of an insignificant size (8–12 μm) contain zinc in the range of 37.21–38.24 at.%. In this case, in the structure of the coating after heat treatment with a maximum exposure time, there are areas that, by mechanical properties, correspond to single-phase brass L63, that is, they have high strength with good ductility [9]. In particles (grains) of a larger size, zinc content from 44.82 at.% to 47.14 at.% is observed, which according to the copper-zinc state diagram can be interpreted as the presence of two-phase brass, where α solid solution and β′ phase are present. Two-phase brass with such a zinc content has the highest strength with low ductility. In addition, zones with a zinc content of about 8.59 – 17.99% are noted in insignificant amounts, which indicates the presence of structural components that, by mechanical properties, correspond to single-phase brass of type L90 (low brass) and L80. The identified distribution of components in a solid solution of zinc in copper (α phase) is undoubtedly due to the uneven distribution of copper and zinc particles in the coating figure 1. There are also areas with zinc content in the range of 66.55-70.53 at.%, Which according to the copper-zinc state diagram corresponds to the region of existence of the γ phase. It should be noted and the presence of a certain number of points where the zinc content within the measurement error is close to zero. Microspectral analysis of the surface areas of the coating in general confirms the results of the study of the phase composition of the coating obtained by X-ray structure analysis.

In the areas (lines) of dark gray color, an elevated oxygen content of 31.19–40.79 at.% was revealed and it can be said with confidence that it is zinc oxide that forms along the boundaries of metal particles and in structure defects (pores) figure 4.

The analysis of the results obtained shows that the cohesive strength of the coating metal in the initial state has a value of 78 MPa. Heat treatment for 3 minutes reduces the cohesion to ≈64.6 MPa, which is due to the formation of the electronic compound – gamma (γ) of the $Cu_5 Zn_8$ phase, figure 5 (table 1). With an increase in heat treatment time up to 10 minutes, the cohesive strength of the coating metal increases slightly to ≈75.4 MPa, which is associated with an increase in the content of solid solution of zinc in copper (α phase) (figure 5, table 1). A further increase in the exposure time in the furnace (20 min) is accompanied by a maximum decrease in cohesion to the level of ≈42.6 MPa, which is caused by the formation of another electronic compound beta (β′) phase based on Cu Zn (figure 5, table 1). It is known that the formation of an electronic compound in alloys of copper and zinc (brass) is accompanied by a sharp decrease in strength and ductility [9]. Increasing the heat treatment time to 60 minutes or more increases the cohesive strength of the coating metal, which reaches a value of 93 MPa.
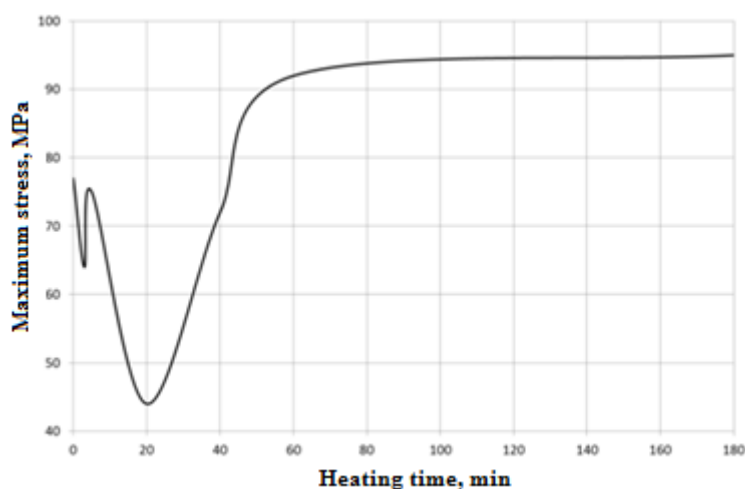
Figure 5. The dependence of the cohesive strength of coatings based on a mixture of copper and zinc particles on the heat treatment time at a temperature of 405-415 °C.

With an increase in the exposure time in the oven from 40 minutes. up to 60 min. content of the main structural components, namely copper, and α, β', γ phases varies slightly, which should not have a significant effect on improving cohesive strength of the coating metal (figure 5, table 1). However, in this time range of heat treatment of the metal of the coating, the size of the substructures of the main components of the coating significantly changes figure 6. Therefore, a sharp increase in the size of substructure fragments, especially the alpha phase, which becomes the dominant component in the structure of the coating with an increase in the exposure time, has an effect on increasing the cohesive strength of the coating metal (figure 6, table 1).
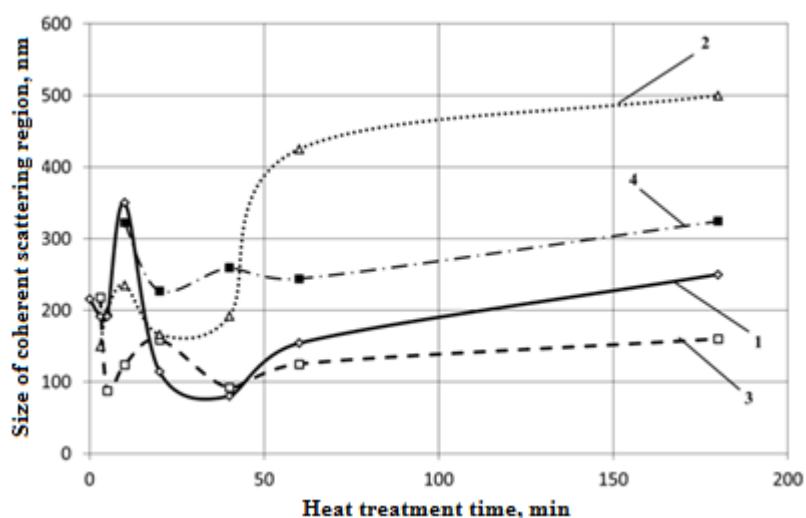
Figure 6. Dependence on heat treatment time at 405-415°C for: 1. – copper, 2 – α phase; 3. – γ phase; 4. – β′ phase.

4. Conclusion

1. Gas dynamic spraying of a coating based on a mechanical mixture of copper and zinc particles is accompanied by the formation of a metal layer based on copper (58%), zinc (23%) and solid solution based on zinc (η – 19%).

2. Heat treatment of the coating at a temperature of 405-415°C for 3 minutes is accompanied mainly by the diffusion of copper into zinc and the formation of an electronic type compound, the gamma phase of $Cu_5 Zn_8$ (44%). The share of solid solution of zinc in copper (α – phase) is at the level of ≈1%. The diffusion coefficient of copper to zinc is not less than 1.56 x 10^{-13} $m^2 \cdot s^{-1}$.

3. Increase the exposure time to 10 min. leads to an increase in the proportion of the a-phase (16%), a decrease in the content of the γ phase (22%) and the formation of an electronic compound — the β' phase of Cu Zn (28%).

4. Heat treatment for 180 minutes is accompanied by the formation of a solid solution of zinc in copper (58%), which has a different ratio of components. Furthermore, in the coating are present intermetallic compound CuZn and $Cu_5 Zn_8$ (β' and γ phase), the mass fraction of which is ≈15%.

5. Along the boundaries of the particles (grains) and in the defects of the structure (pores), zinc oxide is formed, the mass fraction of which increases to 12% at the maximum exposure time.

6. Heat treatment of the coating based on copper and zinc particles at a temperature of 405-415°C and a holding time of 3 minutes and 20 minutes significantly reduces the cohesive strength of the coating metal from 78 MPa to 64.6 MPa and to 42.6 MPa, which is due to loss of γ and β' phases.

7. An increase in the size of the substructure of the main structural components of the coating after heat treatment for 60 minutes and more contributes to an increase in the cohesive strength of the coating metal.

References

[1]   DIMET *The use of technology and equipment* [Electronic resource] – Access mode: http://www.dimet-r.narod.ru/ (Date of access 23.11.2018)

[2]   Shinichi NISHIMURA, Yukitaka HAMADA 2017 Feasibility study of High-Strength Brass Coatings by the Cold Spray Process *Journal of the Society of Powder and Powder Metallurgy* **64** 661-6

[3]   Gershman Iosif S et al 2016 *Description of Seizure Process for Gas Dynamic Spray of Metal Powders from Non-Equilibrium Thermodynamics Standpoint, Entropy* p 315

[4]   Marple William J 2012 *The cold gas-dynamic spray and characterization of microcrystalline and nanocrystalline copper alloys* (United States Naval Academy, NAVAL POSTGRADUATE SCHOOL December Graduate Thesis for Master of Science in Mechanical Engineering)

[5]   Kowalski M and Spencer P J 2015 Thermodynamic Re-evaluation of the Cu-Zn System *J. Phase Equi* **14** 432–8

[6]   Warren B E and Warekois E P 1955 Stacking Faults in Cold Worked Alpha-Brass *Acta Metallurgica* **3** 473–9

[7]   Sachek B Ya, Mezrin A M, Arkhipov V E and Londarsky A F 2018 Modifying the surfaces of tribo -spraying by spraying metal coatings as a means of increasing their fretting resistance *Friction and Wear* **39** 24-8

[8]   Arkhipov V E, Londarsky A F, Moskvitin G V, Pugachev M S 2017 *Gas-dynamic spraying: structure and properties of coatings* KRASAND p 240

[9]   Efremov B.N. BRASS 2016 *From phase structure to structure and properties* INFRA-M p 314

[10] Bokshtein B.S. 1978 *Diffusion in metals* Metallurgy p 248