Forming of nanostructured Cu–Ni coatings of tool steel H12M after surface machining attrition treatment

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Abstract. Surface machining attrition treatment (SMAT) was performed on a copper-nickel coating of tool steel H12M to form a nanostructured (NS) layer on the surface of the sample. Tribotechnical, metallographic, physical and chemical properties of nanostructured copper-nickel coatings were investigated. The results showed that a significant increase (2.3 times) in the wear resistance of the coatings was achieved after high plastic deformation under a stress of 3.5 GPa. A structure was formed with a minimum size of coherent scattering regions (CSR) of 23 nm and a maximum crystal lattice microstrain value (CLM) of 1.25%.

Keywords: surface mechanical attrition treatment, severe plastic deformation; nanostructure, copper-nickel coating.

Introduction
Insufficient strength of copper-based alloys and coatings limits the scope of their application for engineering, electrical and other equipment operating under high mechanical loads. Therefore, the search for ways to improve the complex of mechanical and electrical properties while maintaining high strength, heat and electrical conductivity of copper alloys is an important task.

Modern approaches to improving the properties of alloys are grinding of their grain structure to ultrafine-grained (UFG) and nanocrystalline (NC) state by such methods of severe plastic deformation (SPD) as severe plastic deformation by torsion (SPDT) [1-4], equal channel angular pressing (ECAP) [5-6], rolling [7-12], friction stir welding [13-15], selective laser melting [16-20], surface mechanical attrition treatment (SMAT) [21-24] and other methods of SPD.

The positive effect of SPD on the properties of alloys, as a rule, is associated with the peculiarities of their structure: high diffusion coefficient; significant distortions of the crystal lattice; grinding of grains and subgrains; increase in intergranular and interfacial boundaries and density of dislocations in the body of grains.

The aim of the work was to improve the properties of nanostructured Cu – Ni coatings of tool steel H12M after SMAT.
Methods and Materials.
The materials for the research were prepared using the technology of the Kuban State Technological University. Fig. 1 shows the setup for diffusion metallization in an environment of low-melting liquid metal solutions.

Installation consists of the lower and upper water-cooled chambers. Between the chambers there is a hermetic shutter, which allows to unite and divide the cavities of these chambers. In the lower chamber there are heating elements, an object table, on which a bath with a low-melting solution is installed, heat shields, a movable screen, as well as a vacuum line with a stop valve, an inert gas supply line. In the upper chamber there is a shutter drive mechanism, a movable rod, on which the coated products are fixed. On the side surface of the upper chamber there is a loading door. A vacuum line with a shut-off valve is mounted in the lower part of the upper chamber, and an inert gas supply line is mounted in the upper part. The vacuum line and the inert gas supply line are interconnected by a pipeline of the inert gas circulation system, which, in addition to the pipelines, contains a heat exchanger and a pump that circulates the inert gas in the upper chamber and the heat exchanger.

A bath with a fusible solution is installed on the stage of the lower chamber. Through the loading hatch in the upper chamber, the products are placed in this chamber and fixed on a movable rod, which serves to move products from one chamber to another. After that, the loading door closes and the upper chamber is sealed and the lower and upper chambers are evacuated. After reaching a given
vacuum, the upper and lower chambers are filled with argon. Next is heating the bath with a metal solution for diffusion metallization of the surfaces of products. Coatings based on copper or nickel were applied on tool from steel H12M. After that the materials were subjected to additional SPD at stresses of 3.0; 3.5; 4.0; 4.5 GPa. The research of the microstructure of steel H12M was performed using a microvisor of reflected light μVizo-MET. X-ray microanalysis was performed using “Camebax micro” microanalyzer, equipped with an INCA ENERGY 350 energy dispersive spectrometer. Phase identification in the samples was carried out by X-ray diffraction analysis (XRD) using Bruker-D8 Diffractometer. Wear tests were conducted using friction machine SMTs-2 with "block - roller" configuration with frequency of rotation of the bottom roller of 300 rpm. Tribotechnical tests were carried out on samples of steel H12M before and after applying coatings.

**Results and discussion**

Optical metallography and micro X-ray spectral analysis of the coating in the initial state. The results of the study of coatings microstructure and the distribution of alloying elements after diffusion metallization at temperature of 1000 C, 2 hours (initial state) are presented in Fig. 2 and Table. 1. In the boundary layer of the applied coating, we see the crushing of grains, the appearance of particles of secondary phases (carbides and intermetallic compounds).
Figure 2. The microstructure of the intermediate coating layer of the H12M steel after diffusion alloying at a temperature of 1000°C, 2 h., obtained using an optical microscope \( \mu \)Vizo-MET. \( \times 2500 \) (a). \( \times 400 \) (b).

Table 1. The distribution of alloying elements in the initial state, [weight].

| Analysis | Al   | Cr   | Fe   | Ni   | Cu   |
|----------|------|------|------|------|------|
| 1        | 2.59 | 0.06 | 19.49| 54.10| 23.55|
| 2        | 0.67 | 0.66 | 23.75| 54.01| 20.91|
| 3        | 0.90 | 1.01 | 32.43| 50.18| 15.23|
| 4        | 1.08 | 1.62 | 44.57| 43.21| 9.33 |
| 5        | 0.87 | 5.72 | 67.73| 21.73| 3.83 |
| 6        | 0.57 | 15.12| 74.51| 8.35 | 1.27 |
| 7        | 0.62 | 20.18| 76.32| 2.69 | 0    |
| 8        | 0.59 | 14.75| 83.56| 0.98 | 0    |
| Max.     | 2.59 | 20.18| 83.56| 54.10| 23.55|
| Min.     | 0.57 | 0.06 | 19.49| 0.98 | 1.27 |

In the initial state in the surface layer of the coating the content of copper, nickel and chromium was 23.55; 54.10 and 0.006%, respectively. At a distance of 25 μm from the surface (transition layer), the content of Cu and Ni decreased to 0 and 2.69%, respectively, see Fig. 3 and Table 1.

On the contrary, the Cr content in the transition layer increased to 20.18%. As shown by X-ray diffraction data, cubic carbide particles M23C6 and Sigma-phase FeCr are formed in these transition layers enriched in chromium and iron, Fig. 2, b and Table 1.

Thus, in the process of diffusion alloying of a tool made of H12M steel (initial state), counter flows of alloying elements appear in the surface layer. Copper and nickel penetrate on the surface of the tool from steel H12M. Chromium and iron from steel are redistributed into the (Cu – Ni) coating, especially to its boundary region, where secondary phases precipitate.

Optical metallography and micro-X-ray-spectral analysis of Cu–Ni coating after SPD. The results of micro X-ray spectral analysis of the distribution of alloying elements in steel H12M before and after SPD under the stress of 3.5 GPa are presented in Fig. 3.
As shown by the results, the distribution of the alloying elements after SPD was identical to the graph of the initial state. On a quantitative level, the concentration of Cu and Ni decreased to 1.3...3.4% after SPD in the surface layer and at the depth of the coating. The Cr concentration increased in the intermediate layer compared with the initial condition, but only after SPD at stress of 3.5 GPa, Fig. 3. Equally distribution of Cr and Fe was observed on the remaining samples in boundary region of coating. In this case we did not observe precipitation of cubic carbide M23C6 and sigma phase FeCr.

X-ray diffraction analysis of steel H12M before and after SPD.

We studied the width of diffraction lines (W), the size of the coherent scattering regions (CSR) and the value of microstrains (ε) of the crystal lattice before and after SPD under stresses of 3.0; 3.5; 4.0 and 4.5 GPa. CSR - is a part of the grain, separated from neighbor part through the defective wall. For very small grains, CSR determines the grain size. As grain grows, it is divided into a number of coherent scattering regions separated by dislocation walls.

The formation of cubic carbide M23C6 and the sigma phase of FeCr is represented as a multistage process in the initial state in the intermediate layer of the coating. It includes: 1. formation of segregations of atoms, 2. formation of coherent phases, 3. separation of secondary phases of carbide M23C6 and intermetallic FeCr, having a maximum CSR of 36 nm and a minimum ε of 1.25%.

The size of diffraction line width (W), coherent scattering regions (CSR) and crystal lattice microstrain size (ε) changed after SPD under stresses of 3.0; 3.5; 4.0 and 4.5 GPA, as shown in Table 2.

Table 2. Diffraction line width (W), size of coherent scattering regions (CSR), and crystal lattice microstrain size (ε), depending on the magnitude of stresses for SPD

| Sample № | Stress SPD [GPa] | Diffraction line width W, [angle degrees] | Size of coherent scattering regions (CSR) [nm] | Crystal lattice microstrain size ε, % |
|----------|-----------------|----------------------------------------|-----------------------------------------------|-----------------------------------|
| Initial  | 0               | CuNi (111) - - - 1,71                   | 36                                            | 1,15                              |
| 2        | 3,0             | CuNi (222) 0,42 0,77 1,95               | 34                                            | 1,17                              |
| 1        | 3,5             | CuNi (220) 0,53 0,91 1,97               | 23                                            | 1,25                              |
| 3        | 4,0             | CuNi (220) 0,41 0,75 1,90               | 30                                            | 1,19                              |
After the SPD under stress of 3.5 GPa, the maximum of diffraction line width W (220) was 1.97 degrees, the maximum size of the ε - 1.25%, and the minimum size of the CSR was 23 nm. Results obtained with a transmission electron microscope.

It was found that in the initial state in (Cu-Ni) the coating has an elongated structure, with a cross-section size of 83...694 nm oriented perpendicular to the edge of the coating surface 6 (a). On electronograms were separate reflexes, Fig. 4 (b).

After SPD of the coating surface, an equiaxial nanostructure with a grain size of 14...110 nm is generated under stress of 3.0 GPa, in Fig. 4 (c). The electronograms varied considerably with the Fig. 4 (d). They were numerous reflexes along the circles, indicating high-angle disorientation of nanograins.

After SPD of the coating surface under stress of 3.5 GPa, an elongated nanostructure with a grit size of 14 cross-section was produced 125 nm, Fig. 4 (e). On the electronograms next to the reflexes appeared strands, indicating a small angle disorientation following subpellets separated from the next part by dislocation walls. As shown above, Table 2, CSR, was the lowest value of 23 nm. On the contrary, the value of crystal lattice microstrain size (ε) was the highest - 1.25 %, Table 2.

After SPD of the coating surface under stress of 4.5 GPa, has been generated fine-grained rather equiaxial nanostructure with the size of granules 13...173 nm, in Fig. 4 (f). According to electronograms the number of high-angle disorientation of nanograins was increased. Crystal lattice microstrain size (ε), which has appeared equal 1.15 %, Table 2, was diminished. On the contrary, CSR was increased and has averaged of 32 nm.

Tribological properties of materials.

The results of tribological tests are shown that after applying the Cu-Ni coating, the relative wear resistance significantly increases by 1.5 times and the surface roughness of the tool decreases by 2.4 times, compared to the surface properties of the uncoated surface.

When abrasion paired with steel H12M, the friction coefficient and relative wear resistance had values of 0.083 ± 0.028 and 1.54 ± 0.21, respectively. As a result of SPD of Cu-Ni coatings at stresses of 3.0; 3.5; 4.0 and 4.5 GPa; relative wear resistance increased by 2.5; 2.1; 2.6; and 3.5 times, respectively.
Figure 4. Electron microscopy photos (a, c, e, f) and electron diffraction pictures (b, d) of copper-nickel coating in the initial state (a, b), and after SPD with contact stresses of 3.0 GPa (c, d); 3.5 GPa (e); 4.5 GPa (f). x 60000 (a, c, e, f).

There was a correlation between a decrease in the relative wear resistance after SPD at stress of 3.5 GPa and the decrease in the size of CSR having low-angle dislocation boundaries in an elongated polygonized nanostructure. There was an increase in Cr concentration compared to the initial state in the transition layer of the coating. (Table 1).

It is assumed that chrome steel H12M redistributed by dislocation boundaries podturen. This leads to a change in the chemical and phase composition of the Cu–Ni coating and a decrease in its relative wear resistance. This redistribution leads to a change in the hardening chemical and phase composition of the coating, reducing the relative wear resistance.

Conclusion
The conducted studies allowed to conclude that in the process of deposition of copper-nickel (Cu-Ni) coating on a tool made of steel H12M and subsequent intensive plastic deformation at contact stresses 3.0; 4.0; 4.5 GPa, it was discovered nanostructuring of its surface layer and the corresponding redistribution of alloying elements. Significant increase in wear resistance and decrease in surface roughness after the application of copper-nickel coating on the instrument correlated with decrease in the size of coherent scatter regions (CSR) with low-angle dislocation boundaries in an elongated polygonized nanostructure at stress of 3.5 GPa, increase in the concentration of Cr was observed in the transition layer of coating as compared with the initial state.

1. Thus, ultrafine-grained structure is formed in the process of SPD of the copper-nickel coating at contact stresses of 3.0; 3.5; 4.0 and 4.5 GPa in the surface layer. It significantly increases the tribological properties of the surface of steel products H12M.

2. Plastic deformation under the action of external contact stresses from 3.0 to 3.5 GPa causes an increase in internal stresses, broadening of diffraction lines, and microstrain of the crystalline lattice. The minimum size of the CSR 23 nm, was achieved with abrasion paired with steel H12M at 3.5 GPa. The coefficient of friction and wear resistance have values of 0.078 and 2.13, respectively.

3. The application of nickel-copper coatings on the cutting tool and the use of SPD reduces the temperature of the cutting edge of the tool due to the high thermal conductivity and heat removal of the coating. This made it possible to increase the wear resistance of the tool during machining.

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