Study of adhesion characteristic of a surface alloy formed by a low-energy high-current electron beam

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Abstract. In the present work, the adhesive strength of the surface alloy with different transition layer thickness was measured. A Ni-Cu surface alloy is formed using successive operations of Ni film deposition followed by mixing in a melted phase with the Cu substrate by a low-energy, high-current electron beam (LEHCEB). A different thickness of the transition layer was obtained by varying the thickness of Ni film deposited during the formation of the surface alloy. The study includes characterization of formed Ni-Cu surface alloys by scanning electron microscopy, in-depth elements distribution and scratch test. The results obtained showed correlation with thickness of the transition layer and adhesive strength of the surface alloy.

1. Introduction
Ever since the treatment of material surfaces by deposition of functional metallic coatings and thin films has become a widely used, the adhesion of these coatings to substrates represents a scientifically interesting topic with a huge practical impact in industry. Adhesion is one of the most important characteristics of coating efficiency. As structural factors (such as the state of the substrate surface, substrate roughness, the thermal expansion coefficients, etc.), and factors associated with the deposition process (such as internal stresses, thickness and the presence of impurities and structural defects in the coating, etc.) affect the adhesion of the coating to the substrate. The influence of some factors can be avoided by using various methods of preparing the substrate surface, others using additional interlayers of materials that help reduce the internal stress of the coatings. However, in all these cases, the level of adhesion will be the result of the interaction of two surfaces at the interface - the surface of the coating and the surface of the substrate. The [1,2] report that the forming surface alloys method using by a low-energy high-current electron beam (LEHCEB) can drastically improve the adhesion of the coating to the substrate. The surface alloy is formed by alternating operations of deposited a film on a substrate, followed by LEHCEB liquid-phase mixing of the film with a substrate. This method of coating synthesizing leads to the formation of a transition layer between the coating and the substrate, in other words to the blurring of the interface between the coating and the substrate. Such a transition layer, which can be several microns thick. However, there is practically no information in the literature on the effect of this transition layer on the adhesive characteristics of surface alloy. Therefore, the aim of this work was to investigate the effect of thickness of the transition layer of surface alloy on its adhesive characteristics.
The adhesive characteristics of the surface alloy were investigated for the Ni-film/Cu-substrate system. This system of materials is a good model system for studying the adhesive characteristics of the surface alloy, because copper and nickel form a continuous series of solid solutions that is important for the formation of a transition layer. In addition, nickel is a harder material than copper, which means that the system as a whole (both the coating and the substrate) will work under loads.

2. Experimental

The electron-beam machine "RITM-SP" with an explosive-emission cathode and a plasma-filled diode generating the LEHCEB was employed in the work [3]. This electron-beam machine was equipped by a LEHCEB source and a magnetron sputtering system providing thin film deposition and LEHCEB surface melting in a single vacuum cycle. The parameters of LEHCEB were as followed: energy of electrons up to 30 kV, pulse duration from 2 to 4 µs, electron current up to 25 kA and electron beam diameter up to 80 mm.

A Ni-Cu surface alloy was formed by alternating the operations of Ni film deposition on a Cu substrate, followed by irradiation of the resulting film/substrate system with a LEHCEB in a single vacuum cycle. The substrates measuring 15×15×2 mm were manufactured from oxygen-free copper of the М00b grade (99.997 wt.%). The surface roughness of the initial specimens \( R_s \) was 1±0.25 μm.

Before film deposition, Cu substrates were irradiated with a LEHCEB in order to clean and homogenize the surface. Optimal electron energy in this operation was determined experimentally and was found to be 20 keV. Different thickness of the transition layer was obtained by varying the film thickness deposited during the formation of the surface alloy. The total thickness of deposited Ni layer was 5 μm. The modes of surface alloy formation are listed in table 1. For a comparative analysis of the resulting properties of surface alloy, a reference sample was prepared – a 5-μm nickel coating deposited onto a copper substrate by a magnetron sputtering process without irradiation by a LEHCEB (mode 5).

Different techniques like scanning electron microscopy (SEM) and energy dispersion x-ray analysis (EDX) have been used for characterization of the surface morphology and elemental composition of the surface alloys. Much attention in the work has been paid to investigation of cross-sections and in-depth elements distribution of surface alloy. The comparative evaluation of adhesion was performed from at least 3 scratch tracks on each of the samples. The scratch adhesion test was done using scratch tester Revetest (CSM Instruments) with loads increasing linearly from 0 up to 30 N. The length of scratch track was 10 mm. Each coating was analyzed after the scratch test using optical microscope. The critical load values were evaluated from the scratch tracks as follows: the first critical load \( L_{c1} \) (the load value at which first cracks appeared in the coating), the second critical load \( L_{c2} \) (the load value at which first delamination appeared in the coating), and the third critical load \( L_{c3} \) at which total delamination of the film occurred and the substrate was fully exposed inside the scratch track. The cracks at the critical load \( L_{c1} \) represent fractures within the coating itself, i.e. a cohesive fractures, while the critical loads \( L_{c2} \) and \( L_{c3} \) are adhesive fractures at the coating-substrate interface.

| Mode | Charge voltage (kV) | LEHCEB energy density (J/cm²) | Thickness of Ni film deposited per cycle (μm) | Number of cycles | Number of irradiation pulses |
|------|---------------------|-------------------------------|-----------------------------------------------|-----------------|-----------------------------|
| 1    | 25                  | −5                            | 1                                             | 5               | 4                           |
| 2    | 25                  | −5                            | 0.5                                           | 10              | 4                           |
| 3    | 25                  | −5                            | 0.25                                          | 20              | 4                           |
| 4    | 25                  | −5                            | 0.125                                         | 40              | 4                           |
| 5    | −                   | −                             | 5                                             | −               | −                           |

Table 1. Surface alloy formation modes.
3. Results and discussion

Figure 1 presents SEM images from the surfaces of samples with the Ni-Cu surface alloy formed at different modes and reference sample. An examination of surface morphology showed that the samples have a similar surface morphology and the main differences lie in the various elemental composition. According to the EDX analysis, the Ni concentration on the surface of the reference sample was 100 at.%. For a sample with a surface alloy formed in mode 1, the concentrations of Ni and Cu in the surface layer are found to be 89.4 and 10.6 at.%, respectively. With a decrease in the thickness of the sprayed film and, accordingly, an increase in the number of cycles for the formation of a surface alloy the nickel concentration in the surface alloy decreases. For samples with surface alloy formed in modes 2, 3 and 4 the content of Ni in the surface layer was 85.5, 83.3 and 78.1 at.%, respectively. A decrease in the nickel content in the surface layer indicates a better mixing of thin Ni films with the substrate and a better diffusion of Ni into the substrate.

![Figure 1](image1.png)

**Figure 1.** SEM-images of the surface of reference sample – (a) and sample with Ni-Cu surface alloy formed in mode 1 – (b), 2 – (c), 3 – (d) and 4 – (e).

The comparison of the interface between the substrate and the coating was carried out by examining the polished and etched samples cross sections with SEM. Figure 2 presents SEM-images of cross section for reference sample and samples with Ni-Cu surface alloy formed in different modes. As can be seen from the images a Ni coating thickness is 4.5 μm and interface of coating looks as a line that replicates the of the substrate surface profile. In the case of surface alloy, the interface is a very rough and wavy line. The average thickness of the surface alloy formed in modes 1 and 2 was 8±2.4 μm, of which 2–3 μm was the dimension of the irregularities contained at the interface. For modes 3 and 4, the average thickness of the surface alloy was 6.5 μm and the dimensions of the irregularities were 1–2 μm.

The distribution of the Ni and Cu across the coating for reference sample and samples with Ni-Cu surface alloys, formed in different modes, are presented in figure 3. The data presented are obtained by EDX analysis of samples cross-section. In general, all the curves obtained show the inversion of Ni and Cu at crossing the interface. It is obvious that the magnetron Ni coating should be characterized by 100% Ni content at the full depth of the coating and the absence or very narrow a transition layer. What we can see from figure 3a. The thickness of a transition layer in this case is about 1 μm and its presence is due to the large spatial resolution of the EDX analysis.
Figure 2. SEM-image of cross-section of reference sample – (a) and sample with Ni-Cu surface alloy formed in mode 1 – (b), 2 – (c), 3 – (d) and 4 – (e).

For the Ni-Cu surface alloy formed in modes 1 and 2 can also be observed constant composition layer (87 Ni and 13 at.% Cu) was about 4 microns and then gradual decrease of the concentration of Ni to 0 at.% (figures 3b and 3c). The thickness of a transition layer in this case is about 3 μm. For the surface alloy formed in modes, 3 and 4 the thickness of the constant composition layer is about 2–2.5 μm with a Ni content of 88 and 82 at.%, respectively (figures 3d and 3e). The thickness of a transition layer for these modes is about 4–5 μm.

Figure 3. The distribution of the Ni and Cu across the coating for reference sample sample – (a) and sample with Ni-Cu surface alloy formed in modes 1 – (b), 2 – (c), 3 – (d) and 4 – (e).
The comparative evaluation of adhesion was performed for reference sample and samples with Ni-Cu surface alloy formed in different modes. According to the data obtained during the scratch test, a reference sample or a 5-μm Ni magnetron coating showed the lowest results in adhesion of all the samples in the considered load range. The first cracks (corresponding to the lower critical load $L_{c1}$) were observed when the load was 6 N. The value of the critical load $L_{c2}$, at which the first localized delamination occurred in the coating, was 9 N. The critical load $L_{c3}$ at which total delamination of the coating occurred and the substrate was fully exposed inside the scratch track was 17 N. The measured values of critical loads showed that the level of adhesion for the surface alloy formed in different modes was approximately equal. The critical loads $L_{c1}$, $L_{c2}$ and $L_{c3}$ were 13, 13.4 and 25 N for the Ni-Cu surface alloy formed in mode 1 and 13.5, 13.7 and 26 N for mode 2, respectively. For the surface alloy formed in mode 3, the values of critical loads $L_{c1}$ and $L_{c2}$ were 14.3 and 15.8 N, respectively, total delamination was not observed. The best adhesion results were obtained for a sample with a surface alloy formed in mode 4. In this case, the first cracks were observed at a critical load of $L_{c1} = 15.8$ N, the first localized delamination in the surface alloy was at $L_{c2} = 17.3$ N, and total delamination was not observed.

4. Conclusions
The effect of thickness of the transition layer of Ni-Cu surface alloy on its adhesive characteristics was investigate. Different thickness of the transition layer was obtained by varying the film thickness deposited during the formation of the surface alloy. According to in-depth elements distribution, the Ni-Cu surface alloy formed in the modes under consideration has a very rough and wavy interface. It was observed that the formation of the surface alloy by mixing thinner Ni films with the substrate leads to the formation a wider transition layer and therefore the best adhesion. It was shown that the surface alloy formed in any of the examined modes has the best adhesion in comparison with the magnetron coating. The best adhesion results were obtained for a Ni-Cu surface alloy formed with a deposition of a Ni film with a thickness of 0.125 μm. In this case, the first cracks were observed at critical load $L_{c1} = 15.8$ N, the first localized delamination in the surface alloy was at $L_{c2} = 17.3$ N, and the total delamination was not observed.

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References
[1] Markov A B, Yakovlev E V and Petrov V I 2013 IEEE Transac. on Plasma Science 41 2177
[2] Jiang W, Wang L and Wang X 2018 Nucl. Instrum. and Meth. in Physics Research Section B 436 63
[3] Markov A B, Mikov A V, Ozur G E and Padei A G 2011 Instrum. and Experim. Tech. 54 862