Structure and Properties of Al-Ni Coatings Before and After Irradiation by Charged Beam Particles

A.D. Pogrebnjak[1], B.P. Gritsenko[2], N.A. Pogrebnjak[1],
V.V. Ponariadov[3], Sh.M. Ruzimov[4], M.K. Kylyshkanov[5]

1 Sumy Institute for Surface Modification, 40030 Sumy, Ukraine, e-mail: apogrebnjak@simp.sumy.ua
2 Institute of Physics of Strength and Material Science, RAN, Tomsk, Russia
3 Belarus State University, Minsk, Belarus
4 National University, Tashkent, Uzbekistan
5 East-Kazakhstan Technological University, Ust-Kamenogorsk, Kazakhstan

Abstract – Using a Rutherford back scattering (RBS) of ions, an analysis of nuclear reactions, a scanning electron microscopy (SEM) with a micro-analysis, an X-ray structure analysis (XRD), measurements of a micro-hardness, an adhesion, we studied the coatings of Al-Ni deposited using a high-velocity pulsed plasma jet on a substrate of a copper with a subsequent W ion implantation (60 kV) The irradiation dose was $5 \cdot 10^{17}$ cm^{-2}, a maximum concentration was W≈7at.%. After this the surface was once again subjected to an action of an electron beam till melting. The efficient diffusion coefficient (D_{eff}W) of the W-implant was derived from the distribution profiles . For the 4 and 6 regimes the D_{eff} was $2.9 \cdot 10^{-7}$ and $1.1 \cdot 10^{-5}$ cm^2/s, respectively

Introduction

At the end of a previous century the beam technologies (like a laser irradiation, electron and ion beam irradiation as well as plasma flows) found their wide application because they allowed one to increase a reliability and life of the construction materials. One of the most promising ways to solve the problem seems to be a deposition of the essentially thick coatings of powder materials on a tool surface (reaching scores of μm to tenth fraction of mm) [1–4]. The powders on nickel base are considered to be one of the basic classes of powder materials, allowing one to protect the surfaces from corrosion, wear [1, 5, 6].

To form a surface with a wide complex of the necessary characteristics, they apply often pulsed plasma flows, allowing them a possibility to heat both the deposited material and the substrate at the place of their contact to a temperature, which is necessary for a good adhesion [1–3]. The purpose of this work was to product the coatings forming the nickel and aluminum inter-metalloids, which would have essentially high servicing characteristics, as well as to study an effect of an ion implantation with a subsequent electron beam melting.

Experimental Methods

The powder PT-NA-001 (95 %Ni, 5 %Al) was used as an initial material to produce the corrosion-resistant coatings. The powder particle dimensions in their initial state were 29 to 59 μm. To deposit the coating, we applied a modified version of the plasmatron "Impulse-5". The expenditures of the combustion mixture components amounted 2 m^3 per hour under 4Hz initiation frequency of detonations. The rate of the plasma flow reached 8km per hour with a temperature of the plasma jet $3 \cdot 10^4$ K. To increase the temperature, a current of to 2kA was conducted over the plasma jet. An electrode of a Ni-Cr alloy was used as an eroding one in the plasmatron [2]. The thickness of the produced coating, which was deposited using the high-velocity pulsed plasma jet to the Cu substrate, was 100 to 120 μm. An implantation of W ions was realized using the accelerator "Diana" having 60 kV accelerating voltage, under $5 \cdot 10^{17}$ cm^{-2} dose, in about 105 Torr vacuum. An electron irradiation was realized using a facility Y-112 under 30 kV voltage, the energy density being kept such that provided a partial melting of the system and a full melting of the coating. Studies of the surface morphology were performed using a scanning electron microscope REMMA-102.A qualitative and a quantitative surface micro-analysis was performed using the X-ray wave spectrometer WDS-2 [7]. To check the obtained results, we performed the additional studies of the element composition of the powder coatings using a Rutherford back-scattering method [8]. An analysis of the light impurities, a carbon first of all, then of oxygen was performed by a method of resonance nuclear reactions. A phase composition of surfaces was studied using an X-ray analysis on the X-ray diffraction facility DRON-2 in a copper emission [9]. Additionally we prepared the transversal cross-sections and performed mechanical tests of the modified samples (micro-hardness measurements) using the apparatus

PMT-3 under 20 to 100 g/mm^2 loads. An adhesion was measured in scrubbing by a diamond pyramid over the coating and substrate surfaces.

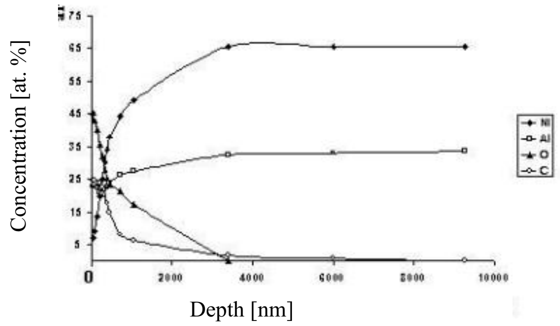


Fig. 1. The concentration distribution profiles for the coating elements over its depth, which were taken from the RBS and NRA

Investigation Results and Discussion

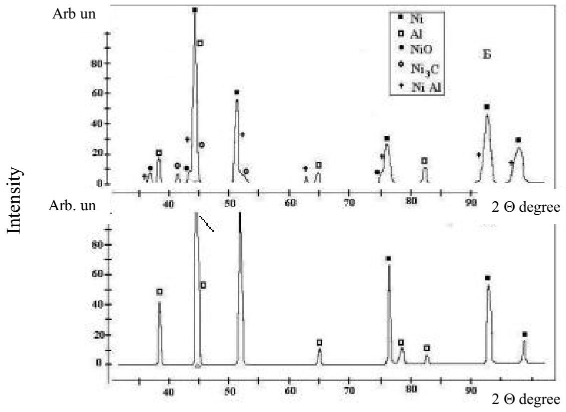
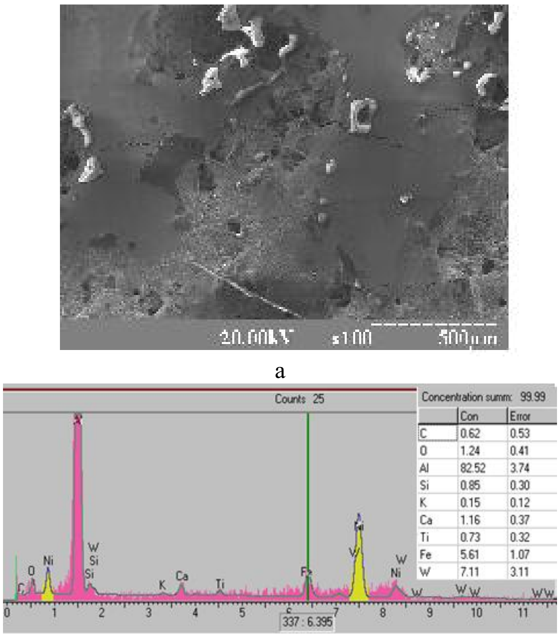


Fig. 2. X-ray patterns for the powder Al-Ni: A – for the initial state; B – for the powder coating surface (Δ – the peak was reduced by a factor of 3.7; *x* – the peak was reduced by a factor of 3.1)

Since the material properties depend in many things on the state of this material state, we studied the coating surface morphology. The obtained results demonstrated the formation of such a surface, which was typical of for the coating resulting from an action of a high-velocity pulsed plasma jet. Coatings, which were formed as a result of such a deposition, have a pronounced relief with a high roughness. An alternation of the silver-grey regions with the embedded gray hills reminding glued and not fully glued melted powder particles was observed in the surface. Under higher magnification one can definitely observe many valleys of an indefinite form, which are present in the surface. We found also bright glowing regions. According to the data of a micro-analysis, a dominating element of these regions is aluminum, and in the above regions its concentration was one order higher than that of a basic component – a nickel powder. Figure 2 shows the spectra taken from the coating surface at the points indicated in Fig. 1, *b*. An integral characteristic of this region indicates that the main components of this coating are Ni and Al. In addition, in the surface there are many such elements as Fe, Cr, Cl, Ca, Si. Fe, Cr, and Si can deposit in the surface in the combustion plasmatron chamber. Ca seems to be an uncontrolled impurity, which deposited into the coating surface when the samples were taken into an air. Ratio of the Ni and Al concentration essentially changed depending on the surface region (the dark and grey regions showed higher Ni concentration in comparison with Al). The obtained results one can find that a dominating element of the surface of to 1μm thickness is Ni. An element analysis was additionally studied using an RBS and nuclear reactions. It shows the energy spectra of an elastic resonance of nuclear reactions (with an initial energy of the α – particles 1.768 MeV) and a back-scattering of the protons (with an initial proton energy 2.02 MeV). These energy spectra demonstrated that a thin near-surface coating layer consisted of the main components of the initial powder – the aluminum and nickel. A high carbon and oxygen concentration were found in the coating. The step in the spectra and non-coinciding calculation and experimental data demonstrate the formation of the intermetalloid nickel/aluminum compounds, a stoichiometry of which was close to Ni_4Al. We also assume that a compound Ni_3Al and pure Ni are present in the coating and this, in complex, demonstrates this stoichiometry. The obtained spectra allowed us to calculate the efficient profiles of all the elements and to determine the concentration distribution of the coating-containing elements over its depth. Fig. 1 shows the concentration profiles for the element distribution over the coating thickness. These results demonstrated that the coating surface was highly saturated by oxygen and carbon, which concentration started sharply to decrease to the surface depth (to 1 μm). A low nickel concentration (7.2 % at h=37 nm) was found in the coating surface. However, closer to the substrate its concentration increased significantly (to 65 %) and it became a main component of the coating matrix. The concentration of aluminum in the surface seems to be explained by the fact that aluminum is a lighter fraction with a lower melting temperature and in the plasma jet it is mainly present in a melted state.

When the plasma jet interacts with a surface, it takes place a dynamical effect, and Ni powder particles are deformed. The melted gas-plasma phase of Al finishes the deposition and covers the surface According to our studies, 93.5 % of nickel and 6.5 % of aluminum form the initial PT-NA-001 powder. The lattice parameters of the coating main components are respectively: a(Ni)=3.524 Å (a_{table}(Ni)=3.5238 Å [9]); and a(Al)=4.054 Å (a_{table}(Al) = 4.0484 Å [9]). The period of coating formation is accompanied by a number of phase transformations occurring in the initial powder material. Figure 2 shows schematically the fragments of X-ray diffraction patterns for the powder composition in the initial state (a) and those for the already formed coating (b). When calculating the X-ray diffraction patterns, we found that the coating surface consists mainly of Ni atoms (85 %). Together with the main phase of the powder matrix, in the coating we observed the formation of such phases as NiO (4 %) and Ni_3C (3 %). And the regimes, which were selected for the coating deposition, affected positively on the formation of the intermetalloid nickel-aluminum compounds found in the surface. We revealed that the coating surface contained about 5 % of Ni_3Al. The X-ray diffraction pattern also shows a low concentration of a pure aluminum (to 3 %). The adhesion power of the coating with the substrate changes essentially from region to region. Our tests demonstrated that the adhesion power alternated within 28±2.2 to 45±3 MPa. A micro-hardness measured over the surface and the transversal cross-section of the coating demonstrated a significant difference of this measured value. In the studied coating regions the obtained micro-hardness value ranged within 65±3.5 kg/mm^2 to $3.0\cdot10^2\div4.2\cdot10^2$ kg/mm^2. We assume that the maximum value of micro-hardness was observed in those regions where the concentration of intermetallic compounds of nickel with aluminum and nickel carbides was dominating.



Concentration summ: 99.99

	Con	Error
C	0.62	0.53
O	1.24	0.41
Al	82.52	3.74
Si	0.85	0.30
K	0.15	0.12
Ca	1.16	0.37
Ti	0.73	0.32
Fe	5.61	1.07
W	7.11	3.11

a

б

Fig. 3: a – The surface structure of the Al-Ni powder coating, which was deposited by a plasma jet with a subsequent implantation by W ions of E=60 kV, a dose of $5\cdot10^{17}$ cm^{-2} and a pulse duration of 200 μs (the points 1 and 2 indicate the regions subjected to a micro-analysis)

We performed the micro-analysis both for the implanted regions and for the electron irradiated ones. After high-current electron beam irradiation (HCEB) till melting the roughness decreased and in some regions a smooth surface was formed. In the image of regions after W implantation one can see that the roughness of these samples is very high as-corresponding to the plasma-detonation way of coating deposition, Fig. 3. A micro-analysis was performed at various surface points, and Al was little, about 3.5 at.%, but Ni concentration reached about 92 at.%. In these regions W concentration was 4 at.%. In the regions where Al concentration was 30 to 50 at.% W concentration was lower – 2.7 at.%. We studied also the regions where Al concentration reached 82 to 92 at.%. In these regions we found about 7.11 wt.% of W. In other words, to formulate some regularities in the surface morphology as a result of W ion irradiation seems to be impossible. In addition, there is an essential difference in W concentration in the surface. After electron beam melting we found the regions containing only aluminum with rare traces of Ni. The micro-hardness measured over the Al-Ni coating surface after W implantation demonstrated that at low pyramid loads the difference in the values decreased in comparison with those found immediately after the coating deposition. However, when the load was increased, the regions, which had the maximum hardness before the implantation, demonstrated its increase of 25 to 32±2.5 %. But in the other regions we again found the essential difference in the values. Due to the HCEB melting the W concentration in the surface layer decreased, and in various regions its values were different. In some regions the W concentration lied within the range of the detection limits. In others it reached 2.2±2.5 % (first of all in those where the Al concentration was very high). Due to the fact that the surface coating layer temperature was essentially higher than that of Al melting because of the forces of the surface tension, in some regions Al was accumulated in "drops". In these regions the Al concentration reached 92 % (very light regions).

Figure 4 shows helium ion back scattering spectra for W-implanted Al-Ni coating. The Figure shows that partial yields of the implanted W and the coating elements changed essentially after the beam treatment. Broadening of the implantation profiles may be interpreted as an efficient diffusion or a mass transfer in the near surface layers of Al-Ni coating. As far as temperature increased tungsten diffused bulk deeper and deeper into the coating bulk. Then it started to move back to the coating surface, and the peak concentration decreased. Under the latter two regimes W uniformly dissolved in the $NiAl_2O_3$ layer and its concentration was only 0.1at. %.

Figures 5 (regime 4) shows selected concentration profiles of the W-implant distribution over the bulk of Al-Ni coating subjected additionally to the electron beam irradiation. The profiles were approximated for two and one Gaussians. The Gaussian peak in seems to be a result of finely divided precipitates the content of which includes the implant. The second broader

Gaussian corresponds to an isotropic W distribution in the Al-Ni coating layers. The microanalysis data confirm the same, i.e. the occurrence of regions of 4 wt.% to 2.14 wt.% concentration. In the case of annealing (melting) under the regime 4, we observed only isotropic bulk distribution of the implant, an essential decrease in the peak concentration, the peak shifting towards the sample (coating) bulk and a decrease in the distribution width. In the latter case, the formation of inclusions was not found, which was probably related to their decay and ablation from the surface after electron beam melting (and probably partial Al evaporation) under higher power densities. In the case of sample irradiation under the regime 2 (the regime 6), the W concentration continued its decreasing, the implant distribution and diffusion from the sample (coating) bulk to the surface spread.

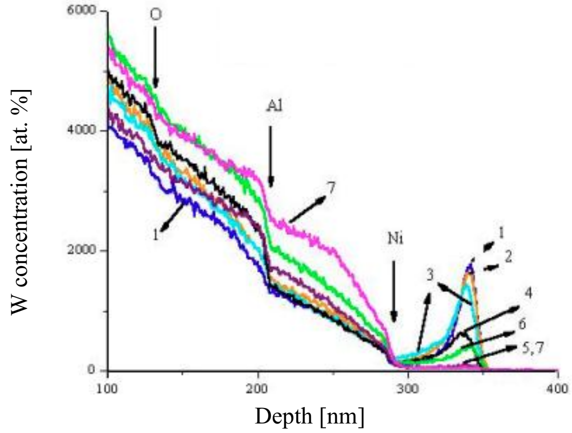


Fig. 4. Partial yields of the implanted W and the coating elements after the electron beam treatment

The fit was realized both by two Gaussians (the regimes 1—3) and by one Gaussian (the regimes 4, 6). The efficient diffusion coefficient ($D_{eff}W$) of the W-implant was derived from the distribution profiles [8]. For the 4 and 6 regimes the D_{eff} was $2.9 \cdot 10^{-7}$ and $1.1 \cdot 10^{-5}$ cm^2/s, respectively. The value of D_{eff} (under the regime 4) was found to be similar to an atomic diffusion of metals in melts, which was confirmed by SEM analysis.

Conclusion

The deposition of Al-Ni coatings to the Cu substrate using the high-velocity jet did not result only in the formation of NiO, Ni_3C, Ni_3Al, Ni and Al with a high adhesion to the substrate, but also induced a high roughness and a significant difference in the hardness values. The W ion implantation resulted in a non-significant increase in the hardness, however, due to the high roughness and the characteristic relief, we failed to understand the effect relating to the implantation, since in some regions of the surface layer the W concentration reached more than 7 at.%.

The subsequent HCEB irradiation of the Al-Ni coating under two various regimes with melting resulted in smoothing of the surface relief and decreasing of the peak W concentration in the surface layer. However, the drops of the pure Al were formed in the surface, the adhesion of the coating to the substrate increased, and the coating hardness left much to be desired.

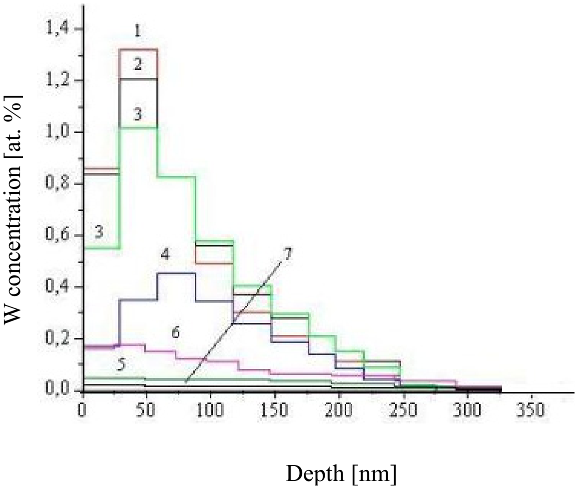


Fig. 5. Selected concentration profiles of the W-implant distribution over the bulk of Al-Ni coating subjected additionally to the electron beam irradiation

Acknowledgement

This work was partially funded by the project N3078 STCU. The authors are also thankful to A.P.Kobzev (Joint Institute for Nuclear Physics, Dubna, Moscow) for his help in RBS measurements and NRA Analysis, to Yu.A. Kravchenko and V.S. Kshnyakin for their help in performing of some experiments.

References

[1] Pogrebnjak A.D., Kul'ment'eva O.P., Kshnyakin V.S., Surface 6, 36 (2003).

[2] Pogrebnjak A.D., Kul'ment'eva O.P., Kshnyakin V.S., Fiz. I Chimiya Obrabotki Materialov 1, 40 (2002).

[3] Pogrebnjak A.D., Il'yashenko M.V., Kul'ment'eva O.P., Pis'ma v Journal. Tech. Fiz. 71/7, 111 (2003).

[4] Pogrebnjak A.D., Il'yashenko M.V., Kul'ment'eva O.P., Vacuum 66, 21 (2001),.

[5] Vol'pe B.M., Evstigneev V.V., Miljukova, Fiz. I Chimiya Obrabotki Materialov 1, 50 (1996).

[6] Klimenov V.K., Panin V.E., Bezborodov V.P., Fiz. I Chimiya Obrabotki Materialov 6, 68 (1997).

[7] Gouldsten J, Newberry J. *Scanning Electron Microscopy and X-Ray Micro-Analysis*. Moscow, MIR, 1984, 303P.

[8] Fel'dman A., Mayer D. *Fundamentals of Surface Analysis and Thin Films*. Moscow, MIR, 1989, 490P.