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Ablation of a WC−Co alloy by impact to high-power nanosecond ultraviolet laser pulses to modify the surface prior to diamond coating

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Ablation of a WC−Co alloy under exposure to high-power nanosecond ultraviolet laser pulses on purpose to modify the surface before application of diamond coating The surface of a WC−Co hard alloy was modified by scanning radiation from focused beams of a nanosecond ultraviolet (UV) laser. After exposure, chemical etching was carried out using the Murakami and Caro method and subsequent magnetron sputtering of a tungsten layer 600 nm thick. The optimal mode of preliminary laser heat treatment of the WC−9% Co alloy for the purpose of the upcoming application of diamond coating has been determined. This is We $= 1-2\,\mathrm{J/cm^2}$.

Keywords: laser heat treatment, carbide (WC−Co), tungsten carbide, surface modification, diamond coating (DC).

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Wear-resistant tools based on tungsten carbide (WC) tools are widely used for machining various materials. To improve the mechanical properties of WC, an alloy with cobalt (WC− Co) [1] was created. To strengthen it, various methods are used, for example, by radiation [2], plasma [3], as well as laser treatment [4]. Strengthening is achieved by changing the phase composition [5] of the near-surface layer and its micro- and nanostructure.

The development of industrial technologies stimulates the use of new, promising materials, for example, carbon fiber-reinforced polymer materials; silumin with high silicon content (up to 20%), etc. Due to the difficulty of these materials machining, WC−Co-based tools with a durable polycrystalline diamond coating (DC) are often used. The use of DC significantly increases the service life of the tool [6]. However, the process of DC application is associated with a number of significant problems related to the presence of Co, which, interacting with carbon, catalyzes the formation of the graphite phase. In the work [6] various methods of preparing WC−Co surface for DC application, caused by the need to isolate diamond from contact with cobalt, are discussed in detail. The process consists of several rather complex technological operations, so we search for its optimization; for example, the work [7] reported on the successful use of ion implantation with niobium and zirconium before DC application.

Laser technologies are actively used for materials treatment [4,8]. It is known that there are two modes of action that noticeably change the properties of the surface. At an energy density $\geq 1\,\mathrm{J/cm^2}$ a well-studied optical breakdown occurs with crater formation on the surface [9]. The paper [10] reports the discovery of a much less noticeable optoplastic effect observed at energy density of $\sim 0.1-1.0\,\mathrm{J/cm^2}$. There, the effect of powerful nanosecond UV laser pulses action on thermomechanical processes occurring in the condensed state of the metal was studied in detail.

In the paper [11] the process of WC−Co exposure to UV laser pulses in the single spot mode was studied. The optimal exposure mode was selected. This paper reports on the preliminary modification of WC−Co surface using high-power nanosecond UV laser pulses in scanning mode in order to increase the effective surface area. It is expected that this shall lead to DC adhesion imp[rovement.

As in papers [12,13], heat treatment was carried out with Nd:YAG laser (third harmonic, wavelength $\lambda = 355\,\mathrm{nm}$, pulse width $\lambda = 10\,\mathrm{ns}$, pulse energy density We $\sim 0.2-2.0\,\mathrm{J/cm^2}$). The radiation was collected onto a polished WC−9% Co sample with a quartz lens with a focal length of 250 mm into a spot with size of $100-200\,\mu\mathrm{m}$.

The exposure was carried out by a series of pulses at frequency $f = 100\,\mathrm{Hz}$. The sample moved on a computer-controlled three-coordinate table in a stationary beam along a raster trajectory („snake“). The overlap coefficient of treatment spots is $K = S/D = 0.1$, where the spots spacing

Elemental composition (percent by weight)

Zone-Spectrum	We, J/cm^2	C	O	Al	V	Cr	Co	W	Total
1–1	0.2	3.18	24.14	3.85	2.65	23.17	0.03	45.63	100.00
1–2	0.2	10.91	2.01	3.85	2.65	1.02	0.01	83.40	100.00
2–1	0.34	10.51	5.03			1.17	0.04	83.25	100.00
3–1	1.035	10.54	3.80			0.82	0.02	84.83	100.00
3–2	1.035	10.31	4.68			0.91	0.02	84.09	100.00
4–1	2.02	10.68	2.88		0.69	0.62	0.01	85.12	100.00

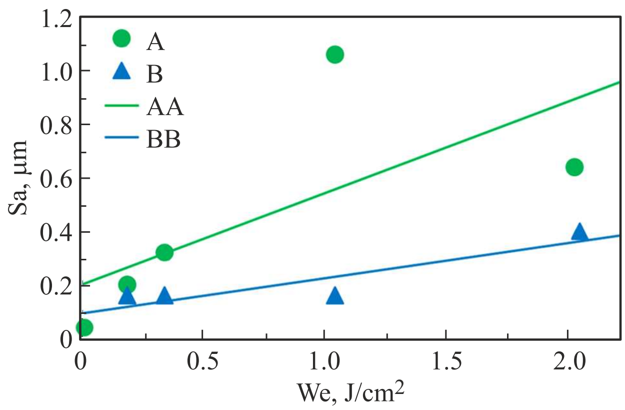

Figure 1. Average roughness of WC–Co over area Sa vs. radiation energy density. A — after laser exposure, B — after next etching and tungsten layer application.

is $S = 20\,\mu$m, and the spot diameter is $D = 200\,\mu$m [14]. In this case, the same area was exposed to ~ 30 laser pulses.

Treatment of WC–9% Co was monitored by Zygo NewView 7300 optical profilometer and JSM-7001F scanning electron microscope (SEM), JEOL. After laser heat treatment, in a single process chemical etching of all studied samples of WC–9% Co was carried out using the Murakami and Caro method, and subsequent magnetron sputtering of a tungsten layer 600 nm thick. Etching time — 552 s (Murakami) and 4 s (Caro). This made it possible to reduce the concentration of Co on the surface (see Table) and to create a barrier layer that prevents Co diffusion from the bulk. The barrier layer thickness W = 600 nm was found experimentally, based on the results of DC deposition and full-scale testing of samples [6,7]. When applying W, we proceeded from the rate of magnetron sputtering in selected modes, measured in tens of angstroms per second. The experiments were carried out in the range of 200–1200 nm on unit for cold magnetron sputtering (50°C).

Figure 1 shows the dependence of surface roughness on energy density in the range 0.2–2.0 J/cm^2. The roughness value (Sa) [15] increases with energy density increasing. After etching and deposition of W layer, the value (Sa) of the surface decreased noticeably. This expands the technological capabilities of the preparatory process before the diamond film deposition, and makes it possible to obtain the required roughness by choosing the optimal laser mode, making the laser ablation method more promising compared to mechanical methods, such as widespread sandblasting. At the same time, it becomes possible to profile under

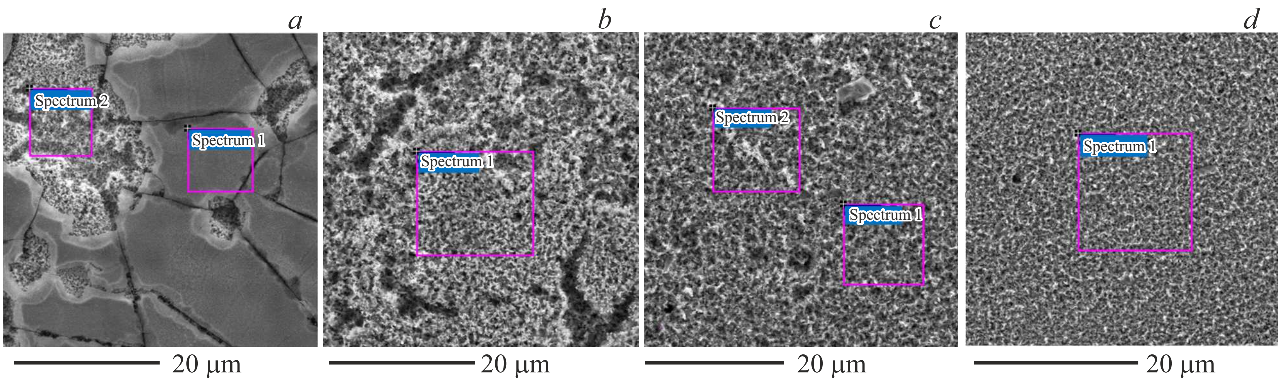

Figure 2. Areas of recording spectra for elemental analysis after chemical etching of cobalt with Murakami and Caro reagents, taking into account the evolution of surface morphology in the SEM image after exposure to a series of laser pulses; (*a–d*) zone-spectrum, cobalt content, wt%: (*a*) 1–1 — 0.03, 1–2 — 0.01; (*b*) 2–1 — 0.04; (*c*) 3–1 — 0.02, 3–2 — 0.2; (*d*) 4–1 — 0.01; radiation energy density, (J/cm^2): (*a*) 0.2, (*b*) 0.34, (*c*) 1.035, (*d*) 2.02.

monitoring WC–Co surface, creating channels in which, during deposition, stiffening ribs of specified sizes and depths are formed, the presence of which can have a positive effect on the adhesion of the diamond coating.

Figure 2 shows the locations of the spectra for elemental analysis after chemical etching of cobalt with Murakami and Caro reagents, taking into account the evolution of surface morphology in the SEM image after exposure to series of laser pulses; cobalt content, wt.%, zone-spectrum: (*a*) 1–1 — 0.03, 1–2 — 0.01; (*b*) 2–1 — 0.04; (*c*) 3–1 — 0.02, 3–2 — 0.2 (*d*) 4–1 — 0.01; radiation energy density, (J/cm^2): (*a*) 0.2; (*b*) 0.34; (*c*) 1.035; (*d*) 2.02. It should be taken into account that due to the features of the SEM operation, the carbon content in the given data is somewhat overestimated [16], therefore the actual Co concentration will be slightly higher. Since the influence of the elements (oxygen, aluminum, and chromium) was not decisive for the process of plasma-chemical deposition of DC, their presence was not discussed in detail. The presence of a noticeable amount of them may be due to surface contamination after treatment.

Studies of profilograms of WC–Co surface treated with the laser showed that it has uniform over area nature. The surface roughness Sa after treatment increases monotonically with increase in laser energy density. Elemental analysis of SEM images after chemical etching of cobalt showed that the optimal laser irradiation mode recommended for preparing WC–Co surface for diamond coating application can be in the range We $= 1 - 2\,\mathrm{J/cm^2}$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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