Modification of the WC-Co carbide surface with high-intensity pulsed ion beam

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Abstract. The paper presents the results of WC-Co surface modification with high-intensity pulsed ion beams at high energy density 7-8 J/cm² per one pulse. One, five and ten pulses regimes of irradiation have been studied using scanning electron microscopy of both the surface morphology and cross-section, X-ray diffraction analysis and a nano-hardness tester. Beam irradiation with high energy density resulted in phase transformation from hexagonal α-WC to cubic β-WC₁₋ₓ. XRD analysis shows that the volume content of new formed cubic phase in the modified layer is ~ 97%.

Keywords: High-intensity pulsed ion beam, high energy density, cemented carbide, surface remelting, cubic tungsten carbide

1. Introduction.
Hard alloys based on tungsten carbide remain the main material in the production of drilling and mining tools. This is due to the fact that tungsten carbide cemented alloys considerably exceed other alloys in hardness, wear resistance and heat resistance, however, they are more brittle. To improve tool durability, reduce friction coefficient, increase crack resistance of cemented carbide tools, new methods [1] of hardening are used, such as laser irradiation [2], irradiation with pulsed ion [3] and electron beams [4].

High-intensity pulsed ion beams (HIPIB) have been used as a unique pulsed energy source for the surface modification of materials. The shallow range (0.1–10 µm) and high energy density (1 – 50 J/cm²) of these short-pulsed beams make them ideal flash-heat sources to rapidly melt or vaporize and solidify the near surface layer of treated materials with heating and cooling rates up to 10⁹-10¹¹ K/s. These rates are sufficiently high to promote mixing, rapid diffusion, and the formation of new metastable high-temperature phases

2. Experimental set-up and diagnostics.
WC-Co (98 wt.% WC and 2 wt.% Co) samples irradiation was performed with the TEMP-6 [4]. The samples measuring 10 mm ×10 mm ×3 mm were preliminary polished with an abrasive paper and diamond paste. Detailed information on the operating principle of the accelerator, diagnostics used to measure ion beam parameters can be found elsewhere [6]. We used the following beam parameters to treat the samples: ion beam composition 15 % H⁺ and 85 % C⁺, ion energy 250-300 keV, energy density 7-8 J/cm² per pulse, pulse duration 130 ns, number of shots 1, 5 and 10 pulses.
The surface and cross-sectional morphology of the samples were observed using a JCM-6000 scanning electron microscopy (SEM). The surface hardness was measured with a Vickers indenter using the G200/XP Nano Indenter system under a load of 0.25N for a holding time of 30s. The phase composition of irradiated WC-Co samples was analyzed by X-ray diffraction (Shimadzu XRD-7000).

3. Results.
Surface hardness measurements were taken at 6 different points. The average hardness was calculated for both treated and untreated surfaces with different number of irradiation pulses, the results are summarized in Figure 1a.

![Figure 1. a) Average surface hardness of WC-Co samples irradiated with HIPIB with 7-8 J/cm² at varied pulse numbers; b) Surface XRD patterns of irradiated WC-Co sample at varied pulse number.](image)

Hardness of the surface treated with 5 and 10 pulses is much higher than for 1 pulse experiment. Based on the XRD results, a possible explanation for this effect is related to formation of a harder cubic tungsten carbide phase, the concentration of which grows with increasing pulse number at fixed energy density. XRD patterns of the treated samples with different pulse number and energy density of 7-8 J/cm² are shown in Figure 1b.

XRD pattern of original sample is given for reference. One can see that original sample consists of hexagonal WC-phase (96.8 vol.%) and cubic Co phase (3.2 vol.%). HIPIB treatment considerably affected the phase composition of the surface layer. Besides hexagonal α-WC phase, new phases such as cubic β-WC1-x are clearly seen on the XRD pattern. With increasing pulse number from 1 to 10 pulses, the intensity of diffraction peaks corresponding to β-WC1-x remarkably increases while the intensity of α-WC phase decreases. Diffraction from cobalt becomes very weak, below detectable level, at all regimes of treatment. As for Co content in the surface layer after irradiation, XRD data also confirms the fact that cobalt binder is almost completely ablated from the modified layer. As for tungsten carbides one can see that HIPIB treatment resulted in phase transformation from hexagonal α-WC to cubic β-WC1-x. This effect is especially noticeable when treated with 5 and 10 pulses. In that case β-WC1-x phase becomes dominant in the surface layer, its volume fraction amounts to ~94% for 5 pulses and ~97% for 10 pulses. Similar phase transformations were found after HIPIB treatment of tungsten carbide hard alloys in [8].

In our experimental conditions with the energy density 2 times higher, we obtained approximately the same value of β-WC1-x / α-WC for one shot. Further increase in the number of shots dramatically increases the content of transformed cubic phase giving 93.8 % and 96.9 % for 5 and 10 pulses, respectively.

4. Conclusion.
Surface treatment of WC-Co cemented carbide with high - intensity pulsed ion beams at high energy density of 7-8 J/cm² has been studied. Surface irradiation resulted in obvious change in...
surface morphology, transformation of phases and softening of the surface layer. Phase transformation from hexagonal $\alpha$-WC to cubic $\beta$-WC$_{1-x}$ was found at varied pulse number. The content of formed new cubic phase rapidly increased with increasing pulse number. After 10 pulses of irradiation the phase volume fraction of $\beta$-WC$_{1-x}$ in the modified layer was 96.9%. While providing a favorable condition for effective formation of the cubic WC phase, the beam treatment with high energy density negatively affected the surface hardness. After one pulse of irradiation with 7-8 J/cm$^2$ hardness of the treated surface decreases dramatically and then increases again with 5 and 10 pulses, however, remains to be lower than the surface hardness of the initial sample.

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