Deposition of cubic tungsten carbide coating on metal substrates at sputtering of electric discharge plasma

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Abstract. Hexagonal modifications of tungsten carbide are widely used in various metalworking products and tools. However, the cubic tungsten carbide phase is still poorly understood due to significant difficulties in its synthesis, both in the form of powdered products, and in bulk form. This leads to the impossibility of conducting direct studies of its physical and mechanical properties. This paper shows the opportunity to obtain bulk coatings with a thickness of up to 70 μm, mainly consisting of cubic tungsten carbide using the plasma-dynamic method. The coating formation occurs when spraying the electric discharge tungsten-carbon containing plasma on a metal substrate made of a titanium and aluminum alloy due to the high rate of sputtering and crystallization. This allows synthesizing a stable coating adherent to the substrate based on cubic tungsten carbide with a purity of its yield of at least 85 wt.%.

1. Introduction

Tungsten carbide is the main material in the manufacture of cutting, drilling, milling tools and for catalytic systems due to its extreme hardness, resistance to high temperatures and high catalytic activity [1–5]. There are three main crystalline tungsten carbide modifications such as "higher" hexagonal phase (WC), lower "hexagonal" phase (W_2C), and cubic phase (WC_{1-x}) also known as β-WC or γ-WC_{1-x} [6]. The cubic phase is considered as a metastable one. There is an extensive literature on the synthesis of powders, ceramics and hard alloys based on hexagonal phases and their possible applications [7]. The cubic tungsten carbide is difficult to be synthesized because of the narrow range of synthesis temperature (between 2789 and 3028 K) [8] and the phase transition to the "higher" hexagonal WC phase at a temperature of 700–800°C [9]. This leads to difficulties associated with obtaining this phase in general and, especially, with a high purity (more than 90%).

For a long time, cubic tungsten carbide has been considered as unstable at the room temperature and existing only at extremely high temperatures that made experimental work on this phase very complicated. In spite of this, some reports give the information that the WC_{1-x} phase can be stable at the room temperatures in the nanocrystalline state [6], when it is crystallized from the melt with the high cooling rate equal to not less than 10^8–10^{11} K·s^{-1} [8,10]. Thus, the methods, based on plasma generation and electric discharge processes, are widely-used for synthesizing WC_{1-x}. In the literature, there are several main known methods such as thermal plasma synthesis [11], the production using an electric discharge followed by annealing in a nitrogen atmosphere [3], and magnetron sputtering with

direct and alternating current [12–16]. The authors of these studies obtained WC_{1-x} samples, both in the form of nanopowders [16] and in the form of thin films with the thickness of not more than 1 μm [12–15]. Cubic tungsten carbide can also be obtained in the form of minor inclusions (less than 20 wt.%) in hard alloys, cemented carbides under the influence of a high-current electron beam [17] and in samples obtained by the spark plasma sintering [6], respectively.

The formation of cubic tungsten carbide only in dispersed form or in the form of thin films does not allow evaluating the complex of physical and mechanical properties for this phase that prevents form extensive studying the properties of this cubic WC_{1-x} modification and expanding the general scientific ideas about the tungsten-carbon system. Thus, the urgent task is to obtain cubic tungsten carbide in bulk form.

This paper shows the possibility of obtaining volumetric coatings based on WC_{1-x} formed on a metal substrate at a high-speed sputtering of carbon-tungsten electric discharge plasma generated by a coaxial magnetoplasma accelerator. The features of the proposed process (high sputtering rate of more than 1 km·s^{-1} and high crystallization rate of 10^7–10^8 K·s^{-1}) make it possible to form a stable coating the main volume of which consists of large (up to several 10 μm) grains of cubic tungsten carbide.

2. Experimental details

The deposition of WC_{1-x} coatings was performed by the plasma dynamic method in the system based on the coaxial magnetoplasma accelerator (CMPA). The CMPA-based system consists of three main elements such as capacitive energy storage (C), CMPA with the graphite electrodes and working chamber (figure 1). Coaxial magnetoplasma accelerator is a typical Z-axis pinch accelerator (1–5, 7) placed inside an external inductive system (6), the main function of which is to make the electroerosive wear uniform along the length of the acceleration channel. The electrode system is formed both by the graphite accelerating channel (7) and the graphite insert (4), located at the end of the central non-magnetic metal electrode (1), which is connected through the power keys (8) with the energy storage. The plasma is initiated into the plasma formation zone (5) formed by the fiberglass insulator (2) and the graphite insert. All of these components are strongly fixated by non-magnetic metal elements (3). Before the experiment, between the metal fixator, which has a direct connection with the barrel-electrode, and central electrode an Ohmic voltage divider is placed. Also for recording the discharge current a Rogowski coil is used. The current and voltage waveforms are registered by the Tektronix 2012TDS oscilloscope and using these data the discharge power and released energy are calculated.
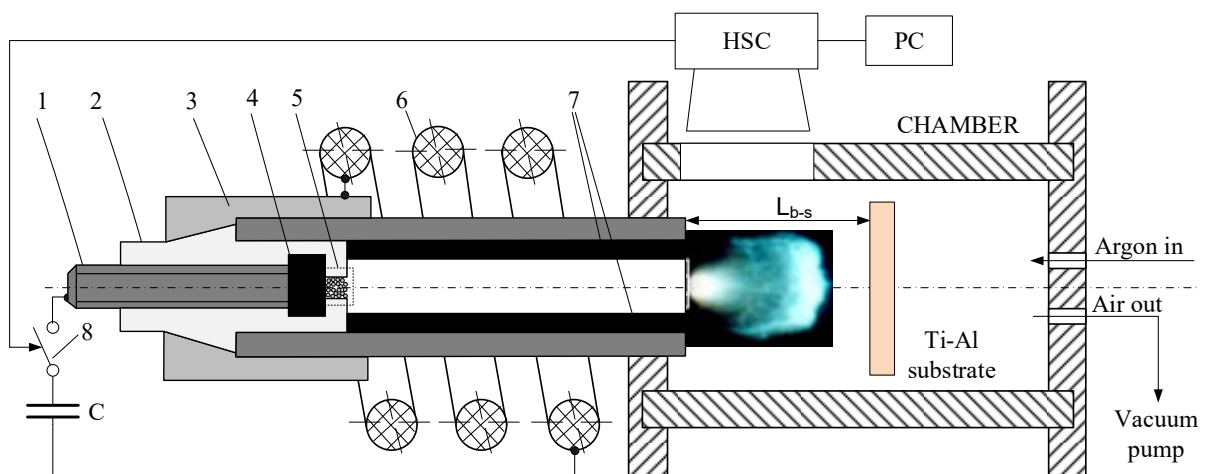

Figure 1. The sketch-map of the CMPA-based system for depositing WC_{1-x} coatings.

Before the experiment, the CMPA is placed through the barrel in the flange of the working chamber. The substrate is rigidly fixated at some distance from the edge of the barrel-electrode L_{b-s},

inside the chamber. The working chamber is preliminary evacuated by means of the vacuum pump and filled with argon at normal atmospheric conditions. The chamber is equipped with a window to record the plasma flow movement by using a high speed camera (HSC) Photron FastCAM 1.1.

The start of the working cycle is controlled from PC. When pushing a special button "record" in a HSC software, an electronic signal from HSC goes to a pulse generator (PG), which creates an analogue signal coming control blocks of power keys. This signal is amplified and ignites the discharge inside the controlled power keys (ignitrons) placed in the discharge circuit. After igniting this discharge they start to provide the energy from the capacitive energy storage to the load, which is CMPA. The energy release is characterized by increasing the voltage between the graphite insert of the central electrode (4) and barrel-electrode (7). After some level there is a breakdown of this gap and arc discharge plasma is formed inside the plasma formation zone (5). The capacitive energy storage is starting to discharge and a growing current appears in the circuit. The current is flowing through the central electrode (1), graphite insert (4), plasma structure formed in the plasma formation zone (5), barrel-electrode and external inductive system (6). It is also should be noted that before the experiment the plasma formation zone is filled with the precursor, which is the mixture of the carbon black and tungsten in the atomic ratio C/W = 0.8. During current increasing the precursor is converted into the plasma state and accelerated by the forces of conductive and inductive electrodynamics. Additional carbon is added to the plasma flow due to electric erosion from the internal surface of the barrel-electrode under the heat influence of the plasma flow. After quitting from the accelerating channel the tungsten-carbon containing plasma interacts with the substrate, located at the length of 65 mm from the barrel-electrode edge.

In the considered system there was made an experiment for depositing the cubic tungsten carbide coating on the surface of the metal substrate to confirm this possibility. The substrate was made of aluminum and titanium alloy and had dimensions LxWxH = $100 \times 100 \times 2$ mm^3. The substrate surface was used without any preliminary processing. The initial energy parameters of the process were as follows: the charge voltage was 3.0 kV, the charge capacity was 6.0 mF. Thus, the value of charge energy was equal to 27 kJ. The waveforms recorded during the process are shown in figure 2. The value of the released energy was found to be 21.5 kJ and the energy conversion efficiency was ~ 80%.
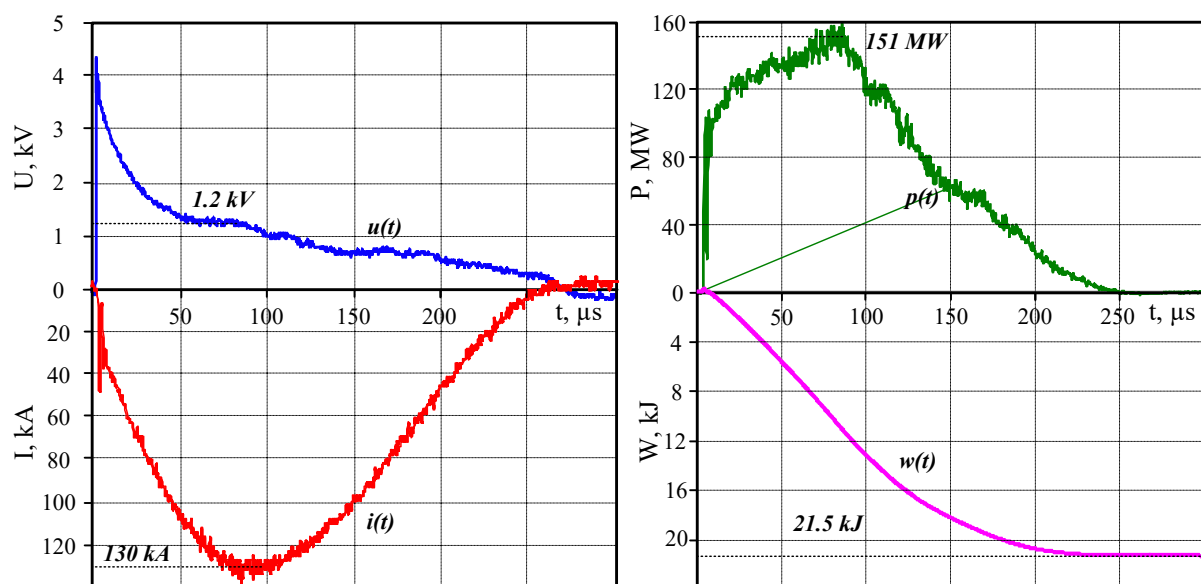

Figure 2. Typical waveforms of the voltage $U(t)$, discharge current $I(t)$, discharge power $P(t)$ and released energy $W(t)$ in experiments with the WC$_{1-x}$ deposition on the metal substrates.

The plasma flow movement in the working chamber until the moment of interaction with the substrate was recorded by means of the high-speed camera and is shown in figure 3. It was found that

the plasma flow speed at the edge of the barrel-electrode was ~ 3 km·s^{-1}. This value is typical for the system based on CMPA with the graphite electrodes at corresponding parameters [18]. During the movement into the chamber the plasma flow speed decreased exponentially and at the moment of interaction with the substrate it was equal to ~ 1 km·s^{-1}.
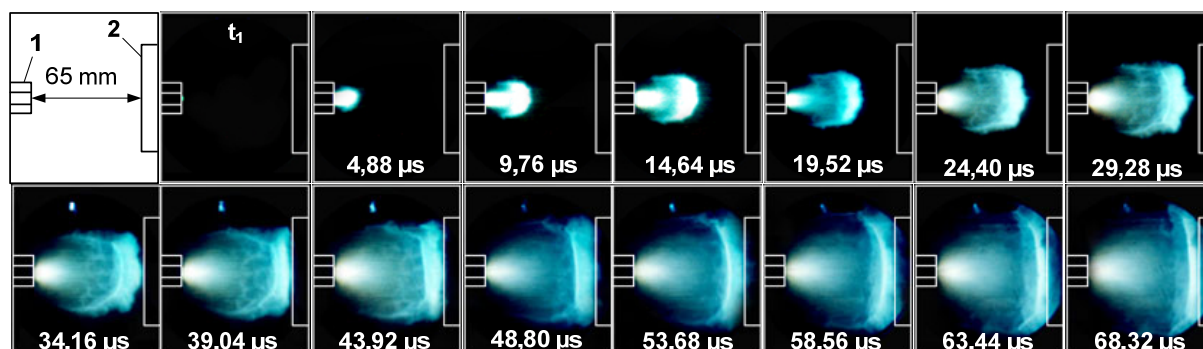

Figure 3. The photogram of the plasma flow movement in the working chamber: 1 – barrel-electrode; 2 – Ti-Al substrate.

The Ti-Al substrate coated with the tungsten carbide was studied using X-Ray diffractometry (XRD) method. The XRD analysis was carried out using Shimadzu XRD7000S diffractometer with the counter monochromator Shimadzu CM-3121. The database PDF2+ and the software PowderCell 2.4 were used to provide respectively qualitative and quantitative analyses of XRD patterns. After this the cross-sections of the specimen were prepared by filling them with the epoxy resin with the following polishing using the "Forcipol 300 1V" grinding and polishing machine. The cross-section was used to study the coating structure and thickness using the Hitachi TM-3000 scanning electron microscope and Quanta 200 3D system with the focused ion beams.

3. Results and discussion

Figure 4a shows the X-ray diffraction pattern of the coating obtained on a Ti-Al substrate. It is compared with reference diffraction patterns of various phases in the W-C systems (figure 4b). This allows uniquely identifying the most intense maxima that relate to the cubic tungsten carbide phase. At the insignificant level, traces of crystalline phases WC, W_2C and graphite C are also present in the coating material. The predominant content of the WC_{1-x} phase is also confirmed by the results of quantitative estimates obtained by carrying out full-profile structural-phase analysis using PowderCell 2.4 software (table 1).

Table 1. Main energy parameters of the working cycles in the series of experiments.

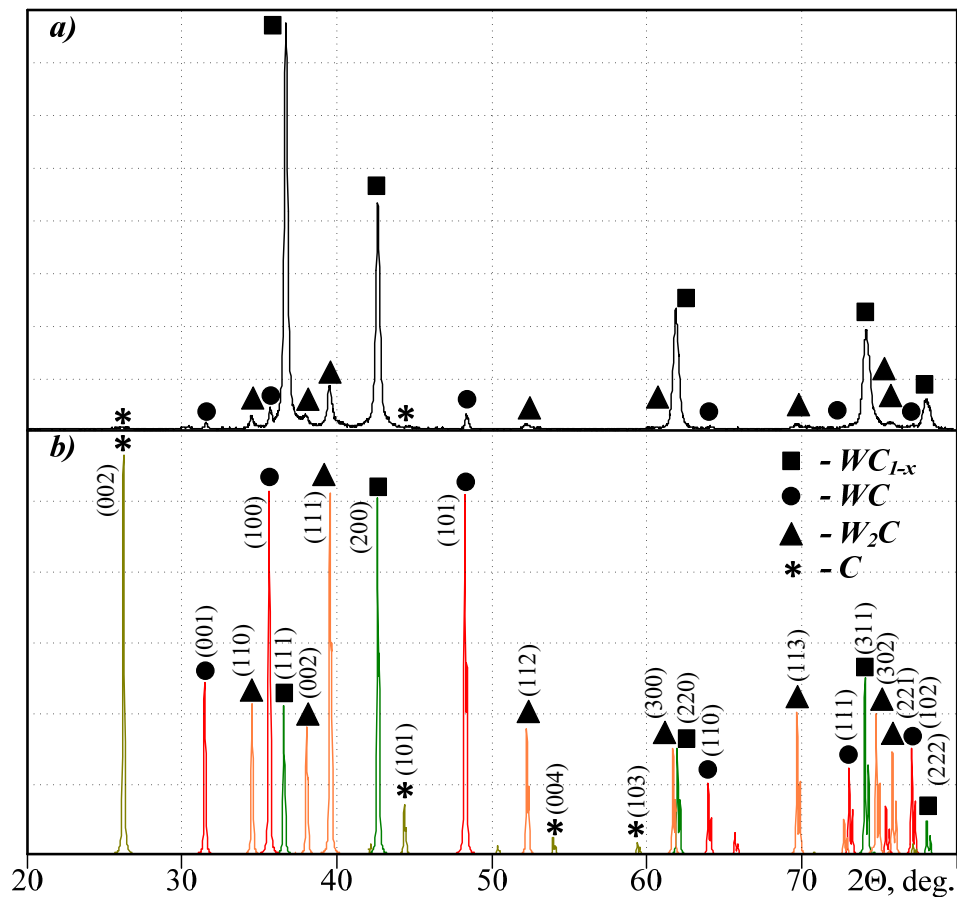| Crystalline phase			WC_{1-x}	WC	W_2C	C
Phase content (wt.%)			85.6	2.9	8.9	2.6
CSR (nm)			73.02	112.97	115.42	25.14
$\Delta d/d \cdot 10^{-3}$			1.87	0.60	4.21	1.60
Lattice parameters (Å)	a	cal.	4.2406	2.9030	3.0029	2.4109
		ref.	4.2355	2.9063	2.9920	2.4700
Lattice parameters (Å)	c	cal.	-	2.8409	4.7384	6.8331
		ref.		2.8375	4.7250	6.7900

Figure 4. XRD-patterns of the obtained coating (a) and the reference cards from PDF4 database (b).

These results allowed establishing that the content of the cubic phase in the coating material is not less than 85% with an average size of coherent scattering regions (CSR) of about 73 nm, which indicates the nanocrystalline particles structure for this phase. The insignificant microstresses level may be caused by the mismatch of the lattice parameters with the reference one, which, apparently, may be due to an unclear correspondence of the WC_{1-x} stoichiometry obtained in the coating material with that given in the standard. The results of X-ray diffractometry give a background to suggest that with the noted energy and design experimental parameters, it is possible to obtain a unique cubic tungsten carbide phase by implementing the plasma dynamic synthesis.

The study of the obtained coating structure was carried out with two independent scanning electron microscopes using the polished cross-section of the coating, which was preliminary filled with epoxy compound (figure 5). From the presented micrographs it can be seen that the coating is characterized by a tight fit to the substrate along the entire interface, which, as noted earlier [19], is due to hydrodynamic mixing during plasma dynamic synthesis and is one of the main advantages of this method. It is also worth noting the uneven coating thickness and the presence of local pores that also characterizes the processes of high-speed material sputtering. From the presented images it can be seen that the coating thickness varies from 40 to 70 µm. Taking into account the results of XRD, indicating the predominant content of the WC_{1-x} phase, it can be argued that the obtained coating has the sufficiently substantial dimensions that will allow in the future carrying out a whole range of studies to reveal the physical and mechanical properties of this unique phase.
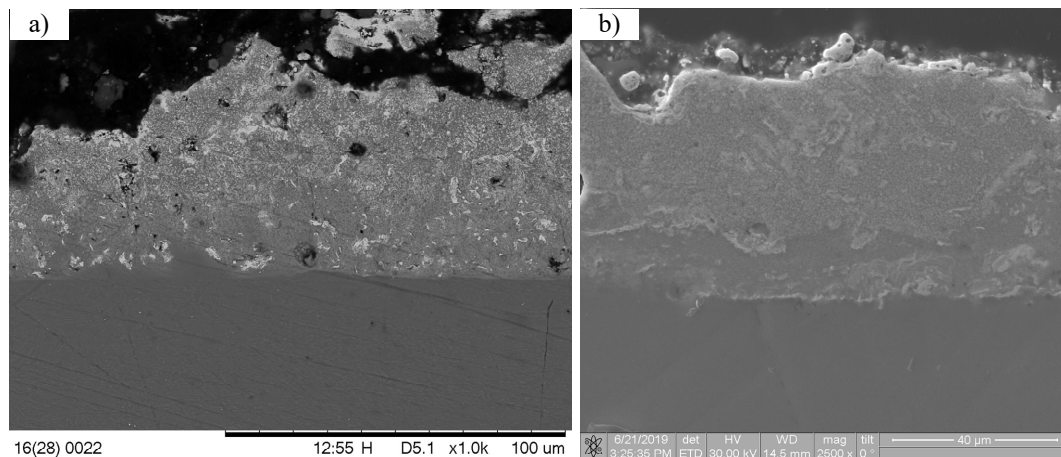
Figure 5. SEM-images of the deposited WC_{1-x} coating obtained with two microscopes: a) Hitachi TM-3000; b) Quanta 200 3D system.

4. Conclusion

In this work, studies have been carried out to confirm the possibility of obtaining a cubic tungsten carbide modification in the form of a bulk coating. It was established that when spraying an electric discharge tungsten-carbon plasma jet onto the surface of a metal substrate, it is possible to form a tightly adherent coating with a thickness of up to 70 μm. By means of XRD analysis it has been established that such a coating mainly consists of the WC_{1-x} phase with the content of ~ 85 wt. %. The obtained results can be further used to conduct direct measurements of the physico-mechanical properties of this phase.

Acknowledgements

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