Structure and properties of metal-carbon a-C coatings alloyed with Ti, Zr and Al with a high concentration

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Abstract
The paper presents a comparative analysis of the structure and mechanical properties of carbon coatings, highly alloyed with metals Ti, Zr and Al. Coatings were deposited from combined flows of metal and carbon plasma with approximately the same mass content. The influence of the nature of the metal on the size of Csp^2 clusters and the degree of ordering of the carbon matrix has been determined by means of Raman spectroscopy. Using scanning electron microscopy, the features of the morphology of coatings due to the formation of a carbide phase have been evaluated. It is shown that the values of the Young modules (E) and the coefficient of elastic recovery (η) of the coatings are also determined by the nature of the metal phase: a higher hardness is achieved when alloying with titanium, and the η is achieved when alloying with aluminum.

Introduction
A promising method for changing the structure and properties of carbon coatings is their alloying with metals characterized by different chemical activity in relation to carbon [1]. As a rule, during the formation of metal-carbon coatings, the change in their properties depends on the nature and concentration of the metal, which determines the ratio of the main phases formed with their participation: solid solutions, chemical compounds, metal micro-nanoparticles [1]. At a high concentration of the metal introduced into the volume of the carbon coating, one should expect a slight decrease in hardness due to the formation of metal clusters;

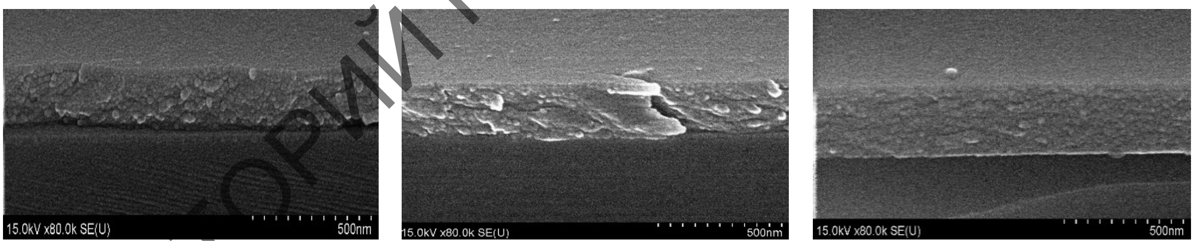
however, in this case, an increase in the elasticity of the coatings, their thermal conductivity, and a decrease in internal stresses are possible. The role of the nature of the metal in such layers is manifested in a different effect on the phase composition and structure of the carbon matrix, changes in the size and ordering of sp^2 and sp^3 clusters. In this regard, the study of the morphological features, properties of carbon coatings, highly alloyed with metals of various nature, and their comparative analysis is of particular interest. The aim of this work is to determine the structural and morphological features, mechanical properties of highly alloyed Ti, Zr and Al carbon coatings.

Deposition technique

a-C:Me coatings were deposited from ionized flows of carbon and metal. Metals (Zr, Al, Ti) were used as the alloying metal. The deposition of the carbon component was carried out from a pulsed cathode plasma generated by a source with a frequency of 5 Hz. Metal evaporation was carried out by an electric arc method at currents of an arc evaporator, providing the same deposition rate of the metal component. The structure of the coatings was studied using a Senterra Raman microscope (Bruker). The morphology and the elemental composition of the coatings were investigated by scanning electron microscopy with EDS (S-4800 FE-SEM, Hitachi). The mechanical properties of the coatings were studied using a NanoScan 4D (Russia).

The results obtained and their analysis

The Raman spectrum of the a-C:Me coatings presents an asymmetric peak ranging from 1000 to 2000 cm^{-1}. The results of processing Raman spectra using Gaussian functions are shown in Table 1 and show the dependence of ratio I_D/I_G, position and width of the G peak on the type of alloying metal. a-C:Ti coating is characterized by a high value of I_D/I_G ratio, while the width of the G peak is minimal, and the position of its center is shifted to the region of low wavenumbers, which is a consequence of a decrease in the size of Csp^2 clusters and an increase in the degree of ordering of the carbon matrix [2]. The significant broadening of the G peak upon doping with aluminum is apparently associated with a higher content of solid solutions in the coating. In this case, there is a correlation between the values of the ratio I_D/I_G and the hardness of the coatings (Table 1).



a b c

Fig. 1. SEM cross-image of coatings: a) a-C: Zr, b) a-C: Al, c) a-C: Ti

Fig. 1 shows the influence of the nature of the metal on the morphology of the coatings. Thereby for coatings doped with Ti and Zr (Figs. 1a and 1c), the formation of a structure with a grain of a spherical shape is characteristic, while the carbon coatings doped with Al have a fine-grain structure, characteristic of layers more homogeneous in their chemical composition.

Table 1. Elemental composition, structure and mechanical properties of coatings

Coating	C, wt.%	Me, wt.%	O, wt.%	d, nm	G peak position, sm^{-1}	Width G peak, sm^{-1}	Ratio I_D/I_G	H, GPa	E, GPa
a-C:Ti	53.8	45.0	1.2	262	1532.2	187.1	1.28	24.8	195.2
a-C:Zr	42.2	56.5	1.3	183	1535.5	211.2	0.78	20.2	178.6
a-C:Al	57.4	38.6	4.3	254	1487.3	235.8	1.08	20.8	187.1

The hardness of the a-C:Me coatings decreases in comparison with the a-C coating, which is determined by a change in both the structure of the carbon matrix and the formation of carbide and metal phases. It was found that the hardness of a-C:Al coatings is higher than that of a-C:Zr coatings, possibly due to the formation of Al_yO_x in the surface layer. It is known [1] that the chemical activity of Zr with carbon is much lower than that of titanium; therefore, in the structure of the a-C:Zr coating, metal prevails, the occupied volume of which is much higher than for a-C:Ti coating. The change in hardness, E and η depending on the depth of indentation, was established. The results obtained indicate the dependence of these parameters on the nature of the alloying metal and the peculiarities of the processes of chemical interaction between the elements. It was found that for a-C:Al coatings the η is maximum. For a-C:Ti and a-C:Zr, the mechanical properties change slightly over the layer depth.

Conclusion

The work established morphological features, phase composition and mechanical properties of carbon coatings doped with Zr, Al, Ti with a volume concentration of 38 to 56 %. It was found that a decrease in the size of Csp^2 clusters and an increase in the degree of ordering of the carbon matrix takes place in coatings doped with Zr, Al, and Ti, respectively. It is shown that in highly alloyed carbon coatings, the nature of the alloying metal has a decisive effect on the structure of the coating; the fineness of the coating is the highest when alloyed with aluminum. The hardness of the coatings is highest when alloyed with titanium; a-C:Al coatings are characterized by higher viscoelastic properties.

References

[1] D. G. Piliptsov, A. S. Rudenkov, P. A. Luchnikov, A. V. Rogachev, Jiao Xiao Hung, Zhou Bin, “Composite carbon coatings deposited from pulsed cathode plasma” [Kompozitsionnyye uglerodnyye pokrytiya, osazhdennyye iz impul'snoy katodnoy plazmy] (Moscow: Radiotekhnika, October 2020, 283 p.).
[2] Robertson, J. “Diamond-like amorphous carbon”, Mater. Sci. Eng. R, 37, 4 – 6, pp. 129 – 281 (May, 2002).