Nanostructured Hard Coatings: the Key to Safe Operation of Equipment in Extreme Conditions

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Abstract—Two main classes of hard coatings based on tungsten and tungsten carbides prepared by chemical gas-phase sedimentation are considered in this work. The coatings possess high hardness (11–40 GPa) and thickness (12–100 μm). Results on abrasive and corrosion resistance in solutions of hydrogen sulfide, inorganic acids, and other aggressive environment are presented. All these coatings are promising for use in extremely severe conditions of abrasive, corrosion, and erosive wear owing to a unique combination of chemical stability, hardness, viscosity, and crack- and impact-resistance.

Keywords: chemical gas-phase sedimentation, hard coating, tungsten, carbide
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INTRODUCTION

The safety of operation of oil and gas or chemical equipment in many respects depends on factors of the impact on critical details (abrasive, erosive, and corrosion media). The number of materials working in extreme conditions is very limited. Therefore, the main means of protection of products against cumulative influence of the aggressive media is the application of hard and superhard coatings. This especially concerns friction knots, where hard coatings have to provide the certain admission on the working surfaces.

Gas-thermal technologies traditionally are used for this purpose. They allow one to precipitate thick coatings (more than 100 μm with a microhardness up to 13 GPa) consisting of hard disperse particles (usually tungsten monocarbide) with a soft, rather fusible link (usually nickel or cobalt). The nanocrystal structure in gas-thermal layers, which is known to provide the best mechanical and anticorrosive properties, is problematic to create because of the adhesiveness of nanodispersed powders.

High-velocity oxygen fuel (HVOF) [1] or detonation guns (D-Gun) [2] are some of the most promising methods. The fundamental impossibility of depositing the coating on products of a difficult form, for example, the “shaded” surface sites, can be noted among the disadvantages of these methods.

It is impossible to use gas-thermal coatings in friction knots directly after the precipitation owing to their rough morphology, additional labor-consuming machining (cutting, grinding, and polishing) needs to be done after the deposition. In addition, powder coatings are restrictedly applied in chemically aggressive media owing to their porosity.

The improvement of new formulations and methods of the deposition of powder coatings have practically exhausted its possibility. Therefore, searching for new methods of hardening working surfaces of friction knots, especially using nanotechnologies, is the main area of development of modern materials science. The low-temperature method of chemical gas-phase sedimentation of hard nanostructured coatings based on tungsten carbides allows one to solve the problem of hardening of products of difficult forms and significantly (by dozens of times) increases the potential and safety of the operation of components of oil and gas equipment.

The purpose of this work is to develop pore-free coatings of constructional function having a coating thickness of more than 12 μm with a hardness higher than 11 GPa. The technology has to provide deposition of a pore-free coating of equal thickness on products of a difficult form; at the same time, the thickness of the coating has to be set and controlled and the morphology of the coating surface has to be smooth in order to be easily led to the necessary purity.

POSSIBILITIES OF THE CVD METHOD OF DEPOSITION OF COATINGS

A new method of the precipitation of hard nanostructured W–C coatings from gaseous mixture of tungsten hexafluoride, propane, and hydrogen (CVD) at a low temperature of the substrate (370–600°C) and pressure (1–10 kPa) is presented in [3, 4]. Depending
The essential role of fluoride oligomers in the course of chemical heterogeneous reactions, superficial diffusion, and crystallization has been shown previously [5]. The excellent mobility of reagents in the gas environment provides deposition of coatings on any difficult forms, which it is impossible to do by gas-thermal methods. The low temperature of the deposition process promotes preservation of the geometry of the product and mechanical properties of material of the substrate.

According to their functional and mechanical properties, W–C coatings can be conditionally divided into two main classes.

1. Especially hard carbides and their mixtures.
2. The composite coatings containing hard carbide particles distributed in a tungsten metal matrix.

**CHARACTERISTICS OF CARBIDE-TUNGSTEN COATINGS**

Microhardness, crack resistance, thickness, adhesion to substrate material (mainly, to carbonaceous, tool, and stainless steels), porosity, resistance to abrasive wear, erosion, and corrosion are the key parameters of hard, especially hard, and superhard coatings of the constructional function.

It was found by the direct method of the transmission electronic and microscopic study of the films that not all carbide coatings belong to nanostructured materials. The size of subgrains of cubic monocarbide WC_{(1–x)} takes the value of 2–3 nm, that of hexagonal monocarbide WC is 4–5 nm, and that of semicarbide is 200–400 nm. A mixture of tungsten mono- and semicarbides is an especially hard nanocomposite system in which the size of monocarbide grains remains invariant and semi-carbide grains sharply reduce their size to 3–5 nm. Nanodimensional clusters of carbides in pure form or in their mixtures favorably affect the mechanical properties of these especially hard coatings, especially their microhardness.

Hard nanocomposite layers consist of a tungsten matrix with a size of grains of 1–2 μm and carbide inclusions (1–3 nm) distributed in it. The unique small size of carbides in pure form and in the form of inclusions in the metal matrix promotes dispersive hardening and controllable increase of microhardness.

Dependence of microhardness of carbide-tungsten layers from the content of carbon is presented in Fig. 1. Microhardness varies from 0.45 (hardness of pure tungsten) to 40 GPa. Especially hard carbides and their mixtures possess the microhardness of 29–40 GPa (see Fig. 1b). Carbide WC_{(1–x)} has the maximum microhardness (40 GPa), and it can be considered a superhard material.

The absence of cracks on the surface of the carbide layers grown on the steel substrate is noted at the maximum thickness of the layer of 14–25 μm depending on the stehiometrical composition of carbides. This fact indicates that the internal tension of growth at this thickness, which lead to no destruction of the carbide layer, increases with an increase in the content of carbon in carbide (from W_{2}C to WC).