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COATINGS FROM REFRACTORY COMPOUNDS ON GRAPHITE

By

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13. ABSTRACT

The technique and conditions for coating of graphite with TiC, ZrC, Nb_2C, and AlN were investigated, with the primary objective being the prepn. of coatings of max. d. and good wetability to the substrate. Two successive stages are included in the prepn. of carbide coatings on graphite: application of the metallic layer from the liquid phase in vacuum, and diffusion annealing, i.e. carburization of the metallic layer. These 2 stages are described in detail with respect to each of the 3 carbides and AlN. Expts. with Nb showed that both Nb_2C, with a microhardness of 2263 kg./mm.^{2}, and a solid soln. of C in Nb, with a microhardness of 282 kg./mm.^{2}, formed. Diffusion annealing at 1700-1900° results in the solid soln. gradually being transformed into the carbide, but also in an increasing C content in the remaining layer of the solid soln. The formation of the various carbides is explained on the basis of their electron configuration, which also explains why Nb_2C forms faster than TiC and ZrC. AlN coatings on graphite were obtained by plasma sputtering of Al with the subsequent nitriding of the metallic layer. The AlN coating formed on graphite contained 65.6 wt. % Al, 34 wt. % N, had a microhardness of 1200 kg./mm.^{2}, and a porosity of 12%.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Refractory Compounds						
Graphite						
Erosion						
Refractory Metals						
Silicon						
Boron						
Niobium						
Zirconium						
Tantalum						
Carbide-Silicide Coating						
Tungsten Coating						
Annealing						

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

COATINGS FROM REFRACTORY COMPOUNDS ON GRAPHITE

A. L. Burykina and T. M. Yevtushok

The possibility of practically using graphite in high-temperature processes is very limited because of vigorous oxidation, and also erosion and burn-out in gas flows. In connection with this, the protection of graphite from oxidation and burn-out is an important scientific-technical problem. Promising materials for coating can be refractory compounds, primarily the carbides, borides, nitrides and silicides of transition metals and alloys based on them. Besides protection from oxidation, coatings made from refractory compounds, which possess high hardness and wear resistance, allow raising the mechanical strength of graphite.

The creation of carbide coatings on graphite is possible by means of its thermal diffusion treatment with refractory metals, silicon or boron. The process can be conducted from the gas phase using halides, carbonyls or organic compounds of the indicated saturating elements.

Thus, coatings were obtained in work [1] from the carbides of niobium, zirconium and tantalum both on the external and the internal walls of long graphitic tubes by means of decomposing the vapors of metal chlorides.

Coatings made from oxides shield graphite well from oxidation, in particular coatings from beryllium oxide which is obtained by means of sintering to objects finely ground BeO powder applied from an aqueous suspension [2].

Many works are devoted to application on graphite of coatings made from the silicon carbide or silicon-bearing compounds. Their procedures are very diverse. Thus, for instance, coatings made from SiC are obtained by means of spraying molten silicon powder from a special sprayer and transforming the silicon layer into a carbide by local heating [3]. Thermal decomposition of silicon-organic compounds on the surface of objects in a hydrogen atmosphere leads to the formation of dense and uniform coatings made from SiC, which do not contain excess amounts of silicon and carbon [4]. A complex carbide-silicide coating which protects graphite from oxidation at a temperature of up to 1200° has been obtained by the sintering method [5]. The good shielding properties of silicon-bearing coatings are explained in particular by nearness of their coefficients' linear expansion to that of graphite.

Their high porosity and insufficiently good adhesion to a base are great disadvantages in the coatings obtained by the method of the sintering or precipitation from the gas phase. In connection with this, although they also increase the service life of graphite parts, they do not prevent their oxidation to a sufficient degree. This especially concerns objects of complex configuration [6]. Researchers who occupy themselves with the development of techniques of applying protective coatings are confronted with the problem of the obtaining of coatings with maximum possible density and good adhesion to a base. One of the ways of raising the shielding properties of coatings is the production of laminated coatings applied by the metallic coating method [6]. An especially promising method is surfacing (spraying) with the aid of a plasma torch. Thus, for instance, a tungsten coating on graphite or a coating made from tantalum first applied to the graphite will be applied by this method [7]. High speeds and temperatures imparted to the tungsten particles in the plasma jet ensure the high density of the coating and its strong adhesion to the graphite. Such a coating successfully protects graphitic nozzles from the erosive effect of combustion products which have a high temperature and flow rate.

This document gives the results of developing technology and study of the conditions of creating on graphite coatings made from the carbides of titanium, zirconium and niobium and aluminum nitride. In addition to this the goal of producing coatings with maximum density and good adhesion to a base was pursued.

The process of applying coatings from carbide on graphite by this technique includes two successive stages: the application of a metallic layer from the liquid phase in a vacuum and the homogenizing - carbidizing the metallic layer.

Samples were prepared from graphite of a different porosity in the form of plates, rings, pipes and were ground with a fine emery to get in the surface layer a fine-grained deformed structure. Then the samples were placed into a graphite cartridge with a double bottom and were covered with powdered metal at a rate of 0.3 g per 1 cm^2 of the surface. The cartridge was heated in a vacuum resistance furnace with a graphite heater to a temperature of 50-100° higher than the melting point of the metal (a vacuum of 10^{-3}-10^{-4} mm Hg holding 5-7 min.). Metal, having been melted, spread over the surface of the graphite and covered it with an even layer. The preconditioning of the surface, which leads to the deformation of the crystal lattice, facilitated the diffusion process of the flow [8].

The metallic coating formed on the surface was practically nonporous and was distinguished by its good adhesion to the base because of the presence of a transition layer -- the narrow band of carbon in the metal. A solid solution does not have a sharp boundary with the metallic layer, but when microhardness is measured it is possible to be persuaded that it regularly increases in a certain section when it approaches the boundary with carbide. With the application of niobium to graphite the transition layer consisted of the niobium carbide Nb_2C. The possible reasons for the formation of Nb_2C will be told below.

To apply the metallic layer to large graphite objects, it is possible to use any surface metallization method. For example with the aid of a plasma jet, good density and adhesion strength of a coating to a base are ensured by the high temperature and flow rate of the plasma jet. We used the plasma metal spraying method when applying to the graphite aluminum nitride coatings.

The second stage — homogenizing the graphite samples with metallic coatings — was done in a vacuum resistance furnace with a graphite heater in the temperature range 1500-1900°. In this case, because of the diffusion of carbon into solid metal the metallic layer was carbidized, whereupon the composition and properties of the formed carbides depended upon temperature and time of homogenizing. This is especially noticeable in titanium carbide which has a wide homogeneity region.

Thus, as a result of annealing the graphite sample with the layer of metallic titanium at a temperature of 1500° for 1 h, titanium carbide is formed with a 4.301 Å lattice spacing and a 2813 ± 120 kg/mm^2 microhardness (Fig. 1a, b). According to data on the dependence of the lattice spacing of TiC on carbon content [9], this corresponds to titanium carbide with approximately 11 wt. % carbon. Chemical analysis confirmed these findings. An increase in annealing time leads to growth in the width of the carbide layer until the metal is completely uncarbidized. Subsequently the carbide will be saturated with carbon, drawing closer to becoming stoichiometric in composition. However, this process is more gradual than the formation of the carbide, since it is limited by the diffusion rate of carbon through the lattice of carbide, while during the formation of the carbide the carbon diffuses through the lattice of titanium. A rise in homogenizing temperature shows more substantially on the composition of the formed carbide. Thus, an increase in annealing temperature by 200° leads to the formation of titanium carbide with a 4.321 Å lattice spacing and a 16.9 wt. % carbon content. As a result of annealing at a temperature of 1700°, there is success in obtaining titanium carbide with a composition close to being stoichiometric (Fig. 1c; see Table also).

Fig. 1. Microstructure of titanium carbide coatings on graphite, ×70. a) Without homogenizing; b) Annealing at a temperature of 1500° for 1 h; c) Annealing at a temperature of 1800° for 2 h. 1 – Graphite; 2 – Titanium; 3 – Solid solution of carbon in titanium; 4 – Titanium carbide.

A mode of annealing was similarly established at which zirconium carbide coating had a composition close to being stoichiometric (see Table).

The time necessary to transform the metallic layer into a carbide for each annealing temperature can be calculated on the strength of layer thickness and data on the diffusion of carbon into the metal [10].

With the application of niobium carbide to the graphite, two phases were detected already during the first stage: niobium

Characteristics of coatings made from titanium, zirconium, niobium carbides on graphite as a function of homogenizing temperature.

Карбид (1)	Температура отжига, °C (2)	Период решетки, Å (3)	Микротвердость, кг/мм² (4)	Содержание углерода, вес. % (5)
TiC	1500	4.301	2813±120	11.0
	1600	4.312	2903±175	16.9
	1700	4.319	3144±215	20.0
ZrC	1600	4.645	2400±117	8.0
	1700	4.666	2630±190	9.8
	(6) 1800	4.688	2750±115	11.8
Nb_2C	Без отжига.	—	2263±120	—
	1700	—	2260±100	—
	1800	—	2221±120	—
	(6) 1900	—	2380±120	—
(7) Твердый раствор углерода в ниобии.	Без отжига.	—	282±30	—
	1700	—	350±50	—
	1800	—	400±50	—

KEY: (1) Carbide; (2) Annealing temperature;°C; (3) Lattice spacing; (4) Microhardness, kg/mm^2; (5) Carbon content, wt. %; (6) Without annealing; (7) Solid solution of carbon in niobium.

carbide Nb_2C with a 2263 kg/mm^2 microhardness and a solid solution of carbon in niobium with a 282 kg/mm^2 microhardness (Fig. 2). Homogenizing at a temperature of 1700-1900° leads to the gradual transformation of the solid solution into a carbide and also to an increase in carbon concentration in the remaining layer of the solid solution. In this case the clear boundary between the initially formed niobium carbide and the carbide which came about as a result of homogenizing is retained. This is apparently connected with the different mechanisms of their formation. The "initial" carbide will arise as a result of the interaction of liquid niobium with carbon; the "secondary" – as a result of the diffusion of carbon through the lattice of carbide into the solid solution; at the same time not only the migration of the carbide-solid solution boundary is observed, but also the growth of the carbide in the region of solid solution in the form of dendritic formations. When a metallic layer is applied to graphite, unlike titanium and zirconium where only a solid solution is formed, the fact that niobium carbide is formed already during the first stage can be explained in the following manner, Titanium and zirconium have an identical electron configuration of outer valence levels d^2s^2. During the interaction of these metals with carbon, they will tend to form stable d^5-configurations because of the breakdown of the sp^3-configuration of carbon atoms. However, this process requires great energy expenditures in connection with the comparatively low probability of completing the d^2-configuration to d^5. It is not the same with niobium. Niobium in the isolated state has a d^4s^1 construction. Here the probability of forming stable configuration d^5 is substantially higher in connection with the fact that the formation heat of niobium carbide is substantially lower than titanium and zirconium carbides. This also leads to the fact that niobium carbide is formed faster and easier than titanium and zirconium carbides.

Fig. 2. Microstructure of niobium carbide coatings on graphite, ×70. a) Without homogenizing; b) Annealing at a temperature of 1800° for 2 h; c) Annealing at a temperature of 1900° for 2 h. 1 – Graphite; 2 – Solid solution of carbon in niobium; 3, 3' – "initial" and "secondary" niobium carbide.

The table gives the characteristics of coatings made from titanium, zirconium and niobium carbides as a function of homogenizing conditions.

An aluminum nitride coating on graphite was produced by the method of plasma spraying aluminum with the subsequent nitriding of the metallic layer. Spraying the aluminum was done on a UPU-2M standard plasma unit conforming to the wire-exposed anode system. Nitriding was done in a graphite-tube resistance furnace in a nitrogen atmosphere. Aluminum has a comparatively low melting point (660°) and therefore the correct selection of a heating rate during nitriding is important. Heating should be accomplished without sweating the coating since this would lead to a sharp reduction in the specific surface of the layer and therefore to a reduction in its reactivity. In this investigation a heating rate of 9-10 deg/min was accepted, which was recommended earlier in the technique of producing aluminum nitride powder [11]. The samples were placed into the furnace at a temperature of 500°, the maximum nitriding temperature was 1200° and holding was selected depending on the thickness of the applied aluminum layer.

Various temperature conditions for nitriding and charging were investigated for the purpose of obtaining a uniform layer of aluminum nitride through the entire thickness of the coating.

As a result of the investigation it was established that a filling plays a decisive role in the nitriding process. As metallographic and X-ray diffraction analyses showed, nitriding without a filling or in a filling made of boron nitride causes the formation of a very thin surface layer of aluminum nitride (several microns), because a reaction in these cases is prevented by the oxide film which is coated by the aluminum layer. When a cake of boric anhydride with carbon black is used as a filling, the aluminum layer is nitrided completely. This is connected with the destruction of the oxide film due to the action of boric anhydride on it. However, in this case the aluminum nitride layer appears to be the contaminated nitride of boron. When using aluminum powder as a filling it partially cakes, as a result of which the access of nitrogen to the coating is hampered and there is uneven nitriding through the depth of the layer.

The result was good when the coating was nitrided in a filling made of aluminum powder. Powder has a large reaction surface, and since every aluminum particle is coated by the oxide film, the interaction of this layer with aluminum apparently occurs during heating by the reaction

$$Al_2O_3 + Al = 3AlO\uparrow.$$

It is known that vapor pressure is always higher over the surface of particles with a smaller radius of curvature; in this case the smaller the particle the more active the purification of its surface from oxide. Therefore, it is evident that a decisive role in purifying the surface of the coating from oxide film should be played by the powder particles, which easily release oxygen and in turn can take it from the surface of the coating:

$$2Al\ (\text{powder}) + Al_2O_3\ (\text{coating}) = 3AlO\ (\text{powder}) + Al\ (\text{coating}).$$

The purified from oxide aluminum coating is nitrided through the entire thickness:

$$Al + N = AlN.$$

A uniform layer is formed on the surface of the graphite. The layer wholly consists of aluminum nitride (Fig. 3a, b) whose composition is: aluminum – 65.5 wt. %, nitrogen – 34 wt. %; microhardness 1200 ± 50 kg mm^2, porosity 12%.

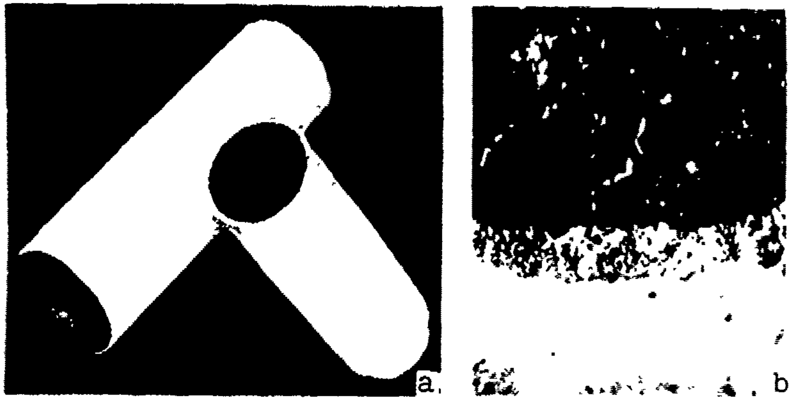

Fig. 3. Exterior view (a) and microstructure of the samples (b, ×100) with an aluminum nitride coating.

The investigation made it possible to develop a technique of applying to graphite coatings made of titanium, zirconium and niobium carbides and aluminum nitride by means of applying to the graphite a metallic layer with subsequent diffusion treatment (carbidizing or nitriding).

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