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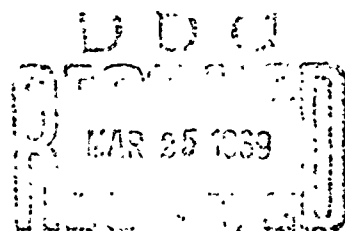
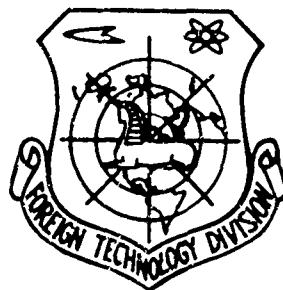
FOREIGN TECHNOLOGY DIVISION



NEW HEAT-RESISTANT MATERIALS FOR WORK IN CONTACT WITH
REFRACTORY METALS

by

A. L. Burykina, O. V. Yevtushenko, et al.



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ABSTRACT

The most promising field for wider application of refractory metals and compounds is their use as protective coatings on metals and various nonmetallic materials. The article reviews results of systematic research to develop a technology for protecting refractory metals with coatings made from refractory compounds (carbides, nitrides, borides) of these metals. The research, conducted at the Institute of the Problems of the Science of Materials AN UkrSSR, included an investigation of the solid phase interaction between refractory compounds, between refractory metals and refractory compounds of these metals, and between refractory metal compounds and graphite. On the basis of the obtained results, an investigation was made and the optimum conditions for vacuum diffusion bonding and brazing TiC, ZrC, NbC, TaC, Mo₂C and WC carbides to Nb, Ta, Mo and W were determined. A satisfactory technology was also developed for coating graphite with TiC, ZrC, NbC, BNC and AlN coatings. In depositing aluminum-carbide and aluminum-nitride coatings, graphite specimens were placed into a graphite container filled with the required powder metal and annealed in a vacuum furnace for 2-3 hr at a temperature 50-100°C higher than the melting temperature of the metal. A homogeneous aluminum nitride layer was obtained in annealing graphite specimens in aluminum powder at 775-1475°K. Dense, strongly adhering titanium-carbide coatings with a microhardness of 144 kg/mm² were obtained with annealing graphite specimens in titanium powder at 1075°K for 2 hr. In a similar manner, zirconium-carbide coatings with a microhardness of 2750 kg/mm², and niobium carbide (Nb₂C) coatings with a

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microhardness of 2380 kg/mm^2 , were obtained in annealing graphite specimens in corresponding metal powders at 2073°K for 2 hr and at 2173°K for 3 hr, respectively. Engineer A. N. Krasnov and Engineer T. V. Dubovic participated in the work. Orig. art. has: 3 figures and 8 tables.

NEW HEAT-RESISTANT MATERIALS FOR WORK IN CONTACT WITH REFRACTORY METALS

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The development of modern technology is associated with the increased temperature of technological processes; for this reason refractory metals and their compounds have wider and wider use [16].

A highly promissive area for the use of refractory compounds is as coatings on metals and various nonmetallic materials, for example, graphite, which together with tungsten is considered the most promising high-temperature structural material, provided the problem of protecting it from oxidation and gas erosion can be solved [17, 18].

The quite good development of the technology of creating certain coatings, and also a comprehensive study of their properties, permits a significant expansion of the field of application of refractory compounds in high-temperature engineering.

In the area of refractory compounds the Institute of Problems of the Science of Materials, Academy of Sciences, Ukr. SSR is conducting systematic work in the indicated directions.

Study of the Solid-Phase Interaction of Refractory Compounds with Refractory Metals, Compounds, and Graphite

Works [19, 20] studied the behavior during heating in a vacuum ($5 \cdot 10^{-2}$ mm hg) of the powdered carbides: TiC, ZrC, HfC, NbC, TaC, Mo₂C, WC; nitrides: TiN, ZrN; borides: TiB₂, ZrB₂, TaB₂, Mo₂B₅, W₂B₅; and hot-extruded oxides: BeO, MgO, ZrO₂, ThO₂ in contact with solid refractory metals: Nb, Ta, Mo, V. The interaction was studied of oxygen-free refractory compounds - carbides: TiC, ZrC, HfC, NbC, TaC, Mo₂C, and WC and nitrides: TiN, ZrN; borides: TiB₂, ZrB₂ with oxides MgO and ZrO [21], and also carbides: TiC, ZrC, HfC, NbC, TaC, Mo₂C and WC; borides: Mo₂B₅, W₂B₅, TiB₂, ZrB₂, HfB₂, NbB₂, TaB₂ with graphite [22]. The interaction was studied of silicon carbide in contact with refractory metals: Nb, Ta, Mo, W and oxides: BeO, MgO, Al₂O₃, ZrO₂, ThO₂ and the interaction of TiB₂, TiC, TiN with Ti, Zr, V, Nb, Ta, Mo, W.

By metallographical analysis of the zones of contact after heating it was established that, depending on the nature of the components, the temperature and the time (duration) of the test at the contact boundary of the refractory metals, there occur intermediate phases: chemical compounds or solid solutions, having high microhardness (from 1000 up to 4000 kgf/mm²).

Identification of the phases formed was carried out by the microhardness method [19-22] or by the microhardness method in combination with x-ray phase analysis. However, in a number of situations it was not possible to draw a simple conclusion as to the nature of the intermediate phases formed.

The typical structure of several contact boundaries of two refractory materials after heating is shown in Fig. I.13:

a - microstructure of the boundary of HfC-Nb after heating at a temperature of 2273°K for a period of five hours. The forming phase in the form of a wide layer adjoins the metal and penetrates into the sample along the grain boundaries. Microhardness of the phase at a load of 50 gf is 4250 ± 350 kgf/mm², which corresponds to the microhardness of solid solution HfC-NbC;

b - microstructure of the ZrO_2 -SiC boundary after heating at a temperature of 2073°K for a period of two hours. On the surface of the oxide there forms a layer of gray color with metallic lustre and microhardness of $2160 \pm 150 \text{ kgf/mm}^2$. According to x-ray analysis the new phase is a zirconium carbide with a small content of carbon (~5% by weight).

With the increase of interaction temperature, the carbon content in the zirconium carbide in contact with the silicon carbide is reduced to a zirconium carbide with a composition close to stoichiometric.

The temperatures at the beginning of the reactions for analysed compositions are given in Tables I.17-I.20.

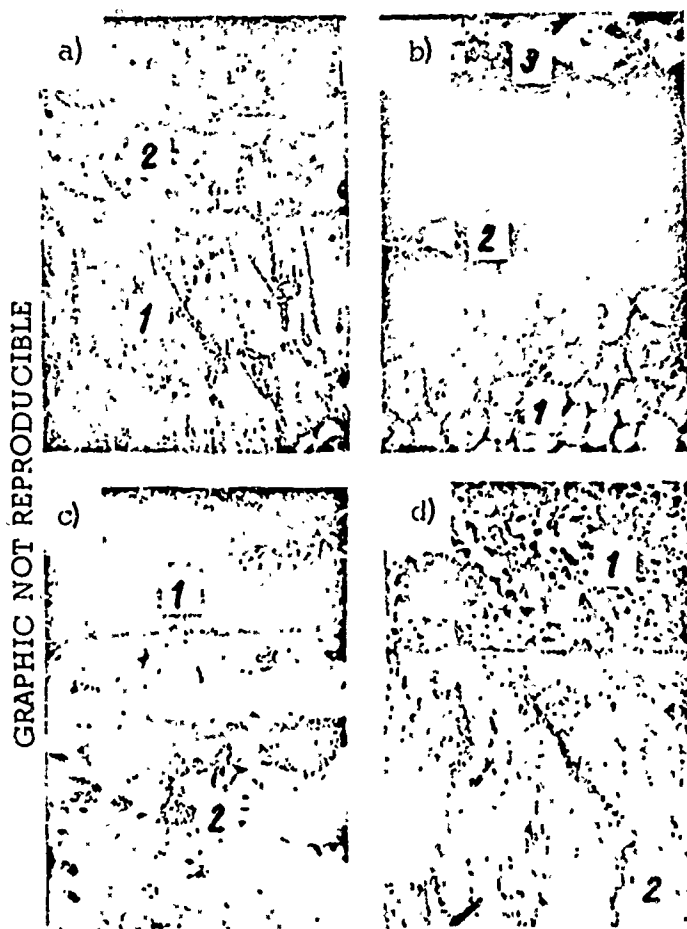


Fig. 1.13. Microstructure of contact boundaries of refractory materials at high temperatures in a vacuum:

a) HfC (powder) Nb after heating at 2273°K for 5 hours (1 - Nb,

2 - new phase - solid solution HfC-NbC); b) ZrO_2 -SiC (powder) after heating at a temperature of 2073°K for 2 hours (1 - ZrO_2 , 2 - new phase ZrC, 3 - SiC); c) WC-Mo after diffusion welding under the conditions: 2273°K, 10 min, 0.5 kgf/mm² (1 - WC, 2 - new phase, Mo₂C and WC); d) NbC-Mo after diffusion welding under the conditions: 2073°K, 10 min, 0.5 kgf/mm² (1 - NbC, 2 - Mo). Magnification 200×.

TABLE I.17. Starting temperatures of weld junction formation of carbides with metals, in °K.

Metal	Carbides					
	TiC	ZrC	NbC	TaC	Mo ₂ C	WC
Nb	---	1673	1573	1473	---	---
Ta	---	2173	1973	2173	---	---
Mo	1873	1573	1873	1673	1573	1873
W	---	2073	2073	2273	1673	1773

TABLE I.18. Temperatures at the beginning of reaction between the metals, graphite, and refractory compounds, in °K (duration of contact 5 h).

Compound	Material					
	Nb	Ta	Mo	W	Graphite	
	Temperature at the beginning of the reaction in °K					
Carbides	TiC	1973	2173	2273	2273	2473
	ZrC	1673	2473	2273	2473	2473
	HfC	1673	1673	1773	2273	2473
	NbC	1973	1973	1973	2473	2473
	TaC	1673	2473	2273	2173	2473
	Mo ₂ C	1773	2073	1973	1973	2473
	WC	2173	1973	2273	2273	2473
	SiC	1573**	1473**	1473**	1773**	---
Nitrides	TiN	2073	2273*	2273*	2273	---
	ZrN	2273	2373	2373	2373	---
Borides	TiB ₂	1573**	1873**	1673	2073	2473
	ZrB ₂	1473	1473	1473	1473	2473
	HfB ₂	---	---	---	---	2473
	NbB ₂	---	---	---	---	2473
	TaB ₂	1673**	1673**	1673	1773	2473
	MO ₂ B ₆	1573	1573	1573	1473	2373
	W ₂ B ₆	1673	1673	1573	1673	2473
Oxides	B ₂ O	1973*	1973*	---	1873*	---
	MgO	2173	2073	2273	2273	---
	ZrO ₂	2273	2073	2273	2273	---
	ThO ₂	2373	2373	2373	2373	---

* Time of contact 1 h.
** Time of contact 2 h.

TABLE I.19. Temperatures at the beginning of reaction between the oxides and refractory compounds, in °K (duration of contact 2 h).

Oxides	Compounds											
	TiC	ZrC	HfC	NbC	TaC	Mo ₂ C	WC	SiC	TiN	ZrN	TiB ₂	ZrB ₂
BeO	2073	2273	2473	2073	2273	2074	2273	1973	1573	1673**	1473	1373
MgO	2473	2473	2473	2473	2473	2473	2473	1773	1673**	1473**	1373	1573
Al ₂ O ₃	—	—	—	—	—	—	—	2273	—	—	—	—
ZrO ₂	—	—	—	—	—	—	—	—	—	—	—	—
TiO ₂	—	—	—	—	—	—	—	—	—	—	—	—

* Duration of contact 1 h.
** Duration of contact 5 h.

TABLE I.20. Temperatures at the beginning of reaction, in °K, between the refractory metals in a vacuum of $5 \cdot 10^{-5}$ mm Hg.

Metals	Compounds											
	TiB ₂		TiC				TIN					
Me powder	Me solid	Me powder	Me solid	Me powder	Me solid	Me powder	Me solid	Me powder	Me solid	Me powder	Me solid	
def. powder	TiB ₂ powder	def. powder	TiC powder	def. powder	TiC solid	def. powder	TiC solid	def. powder	TIN powder	def. powder	TIN solid	
Ti	1173	1273	1373	1373 (1 h)	1473	1573 (3 h)	1573	1273	1273	1273	1273	
Zr	1173	1273	1373	1573 (1 h)	1473	1573 (3 h)	1573	1273	1273	1273	1273	
V	1573	1773	1873	1873	1873	1873	1873	1573	1573	1573	1673	
Nb	1573	1773	2073	1973	2173	2173	2073	1673	1673	1673	1873	
Ta	1773	1773	2173	2173	2273	2273	2173	2173	2173	2173	2173	
Mo	1573	1873	1973	1973	2073	2073	1973	2273	2273	2273	2373 (TIN evaporated)	
V	2073	2173	2173	2173	2573	2573	2573	2173	2173	2173	2737 (TIN evaporated)	

Температура начала реакции, °K

Diffusion Welding and Brazing of Refractory Compounds with Refractory Metals

The most promising method of joining refractory materials is vacuum diffusion welding. Fusion welding in the given situation turns out to be unacceptable because of technical difficulties (high melting point) as well as because of the insufficient heat stability of these materials. For selection of diffusion welding conditions the results on research of solid-phase interaction in a vacuum can be used. However, in a number of instances the temperatures at the beginning of the reaction and the nature of the interaction of the refractory materials during diffusion welding are different from those observed in those situations where one or both of the components are taken in powder form.

According to the method described in work [23], the conditions of vacuum diffusion welding of the carbides TiC, ZrC, NbC, TaC, Mo₂C, WC with the refractory metals Nb, Ta, Mo, W were studied. The research took place in the temperature range 1473-2273°K. Holding at a given temperature was 5-15 min, pressure - 0.5-1.5 kgf/mm². The quality of the weld junctions was checked by metallographic analysis. With the purpose of explaining the nature of the phases formed during welding, the microhardness of the substances was changed in the zone of contact.

The temperatures at which the weld junction of the carbides with metals starts to be formed are given in Table I.17.

As follows from Table I.17, the starting temperatures of formation of the weld junction differ significantly from the beginning temperature of the reaction of solid metals with powdered refractory compounds (Table I.20).

During metallographic research it was established that with increasing temperature, the quality of the weld junction for all compositions became better. At the contact boundary there occur most often solid solutions of carbon in metal or solid solutions of carbides (Fig. I.13 c,d). The composition of the solid solutions

depends on the welding temperature; during this the formation of carbides or their solid solutions is preceded, as a rule, by the formation of a solid solution of carbon in metal at lower temperatures. The characteristic of the weld junction during optimal welding conditions is given in Table I.21.

For compounds of materials not forming a chemical bond, the diffusion welding method in the form used by us for carbides is inapplicable. For example, the diffusion welding method cannot be used to weld boron nitride and carbonitride with refractory metals Nb, Ta, Mo, W, since these materials do not interact with each other in a solid state.

For compounds of materials not forming a chemical bond, it is necessary to introduce an intermediary body - a "binder" - mutually soluble with these materials. For compounds of boron nitride and carbonitride with refractory metals a method of brazing was developed using, as the brazing material, refractory compounds that are chemically active relative to these materials.

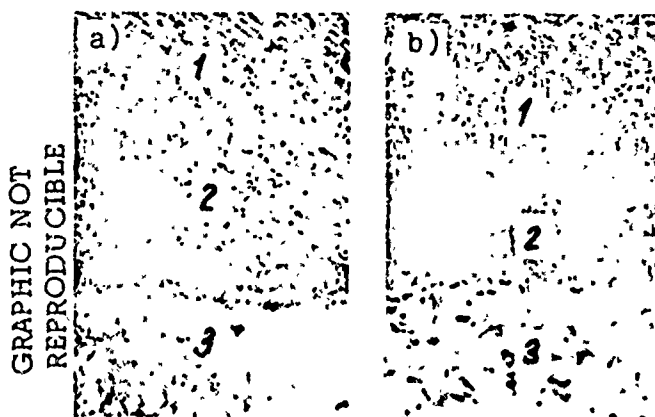


Fig. 1.14. Microstructure of junctions of refractory materials: a) BN-Ta (1 - BN, 2 - braze, 3 - Ta); b) BNC-Mo (1 - BNC, 2 - braze, 3 - Mo). Magnification 100x.

The braze was in the form of finely dispersed powder or pellets with a thickness of up to 2 mm. Brazing took place in an induction furnace in an argon atmosphere at temperatures of 2073-2573°K. The quality of the joint was checked by metallographic analysis. The

results of the research are given in Table I.22, the photographs of the weld microstructure - in Fig. I.14 a, b. As follows from the table, the best refractory brazes turned out to be disilicide of molybdenum and zirconium.

TABLE I.21. Characteristics of weld junctions of carbides with metals during optimal welding conditions.

Welded materials	Temperature, °K	P. Pressure, kg/cm ²	Time, min.	Forming phase (mole composition in %)	Characteristics of weld zone
TiC—Mo	1973	0,5	10	Mo ₂ C	Narrow dense band of the new phase
TiC—W	—	Did not succeed in bonding			—
ZrC—Nb	1873	1,5	10	NbC	Dense band of the new phase with 20-30 mm width
ZrC—Ta	2273	0,5	10	TaC+20 ZrC	Dense band of the new phase with 40 μ width
ZrC—Mo	1773	1,5	10	Solid solution Mo—C	Sharp nonporous boundary
ZrC—W	2073	1,5	10	Solid solution W—C	Porous junction zone
NbC—Nb	1873	0,5	10	Nb ₂ C	Porous band of the new phase with 40 μ width
NbC—Ta	2073	0,5	10	NbC+40 TaC	Dense narrow band of the new phase
NbC—Mo	2073	0,5	10	Solid solution Mo—C	Sharp nonporous boundary
NbC—W	2073	0,5	10	NbC+30 WC	Porous band of the new phase with a 30 μ width
TaC—Nb	1473	0,5	10	Solid solution NbC	Porous junction
TaC—Ta	2173	0,5	10	Ta ₂ C	Dense band of new phase with irregular width
TaC—Mo	1873	0,5	10	Ta—Mo—C	Narrow dense band of the new phase
TaC—W	2273	0,5	10	Ta—WC	Wide dense band of carbide TaC
Mo ₂ C—Mo	1673	0,5	10	Solid solution Mo ₂ C—Mo	Sharp nonporous boundary
Mo ₂ C—W	1773	0,5	10	Solid solution W—C	Porous junction
WC—Mo	2123	0,5	10	Mo—WC, Mo ₂ C	Wide two-phase band
WC—W	2173	0,5	10	N ₂ C—WC	Porous band of the new phase with a 700-800 μ width

Welded materials	Temperature, °K	Pressure, kgf/mm ²	Time, min.	Forming phase (mole composition in %)	Characteristics of weld zone
TiC—TiC	2173	0,5	10	TiC	Location practically indiscernible
Mo ₂ C—Mo ₂ C	1973	0,5	10	Mo ₂ C	Location practically indiscernible
WC—WC	2273	0,5	30	WC	Porous junction

TABLE I.22. Means of brazing boron nitride and carbonitride with refractory metals.

Composition	brazing materials	Temperature of brazing, °K	Junction characteristic
BN—Nb	MoSi ₂ Zr	2323	Junction stable No junction
		2173	
BN—Ta	Zr MoSi ₂	2173	Junction stable No junction
		2323	
BN—Mo	MoSi ₂	2323	Junction stable
BN—W	MoSi ₂	2323	Junction stable
BNC—Nb	Ti VC ₂ ScN MoSi ₂ Sc ₂ O ₃	2073	Junction stable, but Ti interacts with BNC, forming TiN No junction Junction stable, but Nb partially dissolves in ScN Junction stable Junction unstable
		2373	
		2373	
		2323	
BNC—Ta	Zr MoSi ₂	2173	Junction unstable No junction
		2273	
BNC—Mo	ScN MoSi ₂ Sc ₂ O ₃	2373	Junction stable, but Mo interacts with ScN Junction stable Junction unstable
		2323	
		2373	
BNC—W	Zr LaC ₂ MoSi ₂	2573	Junction stable Junction stable Junction stable
		2373	
		2303	

Diffusion Coatings of Refractory Compounds on Graphite

The possibility of practical utilization of graphite in high-temperature processes is highly restricted because of the strong oxidation, erosion and burn-up in gas flows and interaction with carbide-forming metals. Along with this, protection of the graphite

from oxidation, burn-up, and interaction with the metals is an important scientific-technical problem. Promising materials for application of coatings can be refractory compounds, primarily carbides, nitrides, borides, and silicides of metals and their alloys. Apart from protection from oxidation, refractory-compound coatings possessing hardness and wear-stability permit increasing the mechanical properties of the graphite.

We investigated the conditions of applying coatings of titanium, zirconium and niobium carbides, boron carbonitride, and aluminum nitride onto graphite.

The process of coating carbides and aluminum nitrides consists of two consecutive stages.

1. Vacuum coating of the metallic layer from the liquid phase.
2. Diffusion annealing - carbidization (nitration) of the metallic layer.

The samples were placed in a graphite holder, covered with the powdered metal and heated in a vacuum furnace to temperatures 50-100°C higher than the melting point of the metal. The metal layer can also be deposited by another method, in particular, by plasma spray-coating, permitting coating of an article of large dimensions. When applying AlN coatings to graphite the method of plasma spray-coating of the metallic layer was utilized.*

Diffusion annealing of graphite specimens with metallic coatings took place in a vacuum resistance furnace with a graphite heater at a temperature range 1773-2173°K. Thanks to carbon diffusion in the solid metal, carbidization of the metallic layer took place, the composition and properties of the formed carbides being dependent

*Engineers A. N. Krasnova and T. V. Dubovik helped to develop aluminum nitride coatings on graphite.

on the temperature and time of diffusion annealing (Fig. I.15 a, b, c). This is particularly noticeable for titanium carbide which has a wide region of homogeneity. We experimentally established the conditions of annealing during which the carbide coatings had compositions close to stoichiometric. For each annealing temperature it is possible to calculate the time required for changing the metallic layer into carbide, proceeding from the thickness of the layer and data also on the carbon diffusion in metal [24]. In Table I.23 are given the optimal conditions of producing titanium-, zirconium- and niobium-carbide coatings on the graphite.

For depositing the aluminum nitride layer on the graphite, diffusion annealing was carried out in a nitrogen environment in a graphite-tube resistance furnace.

Various conditions of nitration and charging were tested. A uniform layer of aluminum nitride was obtained during nitration in aluminum-powder charging in the temperature range 773-1473°K; heating was carried out at a rate of 10 deg/min, holding at maximum temperature was selected depending on the annealing temperature.

Boron carbonitride was deposited on graphite by means of baking, in a nitrogen medium, of the charge layer calculated to produce boron carbonitride. For this, the charge, mixed in the binder (solution of nitrocellulose in acetone), was deposited on the graphite specimens, which then were dried and placed in a graphite holder with a covering made of a cake of boric acid with carbon black. Baking took place in a graphite-pipe resistance furnace at a temperature of 2373°K and a time of 1-3 h (dependent on the deposited layer). The coating received had good cohesion with the graphite backing and a uniform composition throughout the layer.

TABLE I.23. Characteristic of carbide coatings at optimal conditions of diffusion annealing.

Carbide	Anneal in; time	Temperature, °K	Lattice constant to X	Micro-hardness kgf/mm ²	Carbon content % by weight
TiC	2	1973	4,319	3144	20,0
ZrC	2	2073	4,688	2750	11,8
Nb ₅ C	3	2173	3,18 : 5,00	2360	11,2



Fig. I.15. Microstructure of titanium carbide coatings on graphite: a) without diffusion annealing (from top to bottom - titanium layer, graphite layer); b) annealing at 1273°K for a period of 1 h (upper layer - solid solution of carbon in titanium, in the middle - titanium carbide, below - graphite); c) annealing at 1773°K for a period of 2 h (from top to bottom - titanium carbide, graphite). Magnification 200×.

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