

TEST METHODS AND PROPERTIES OF POWDER METALLURGICAL MATERIALS

REACTION OF BORON CARBIDE WITH TITANIUM UNDER ORDINARY AND PLASMA HEATING CONDITIONS

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Boron carbide, owing to its many attractive properties, including high hardness, good wear resistance, and resistance to chemical attack, is finding extensive application in modern industry both in pure form and as a component of cermets. Alloys based on the diborides of transition metals with additions of iron and boron carbide (5-15 wt.%) are employed as facing materials [1], while boron carbide with 5 wt.% titanium, which, according to [2], is superior in hardness to all other materials based on boron carbide and Groups IV-V metals (0.5-10 wt.% of metal), is used for high-temperature microhardness measurement indenters [3]. Boron carbide with an addition of a refractory metal such as titanium may also be assumed to have potential as a wear-resistant facing material suitable for application by gasothermic spraying methods. During the gasothermic deposition of such a composite its components may react with each other, with the formation of titanium carboborides, which surpass in mechanical properties both titanium carbide and titanium boride. It is reported [4] that the lowest values of coefficient of friction and the least wear in this system are exhibited by alloys of eutectic composition.

To find the optimum coating composition and deposition parameters, a study was made, using the methods of thermodynamic, differential thermal, and x-ray phase analysis and microhardness measurement, of the reaction of boron carbide with titanium.

Data on the reactions in the ternary system Ti-B-C and an isothermal section through the system at 1400°C (Fig. 1) are given in [5]. The system contains no ternary compounds, the borides TiB and TiB₂ being in direct equilibrium with TiC. The quasibinary section TiB₂-B₄C is characterized by the formation, at 1900°C, of a simple eutectic containing 70 mole% B₄C [6]. In the quasibinary section TiC_x-TiB₂ a eutectic forms, depending on the composition of the carbide, at 2520 (TiC_{0.95}) or 2380°C (TiC_{0.68}) [7].

The reaction of boron carbide with titanium was studied by the DTA (differential thermal analysis) method, as described in [8], at temperatures of up to 2200°C. Powder mixtures of three compositions were employed (Table 1). The powders were thoroughly mixed under alcohol and then pressed under a pressure of 50 kgf/cm² into 8-mm-diameter, 10-mm-high cylindrical specimens. Heating and cooling during DTA were performed, using hafnium oxide crucibles, at a constant rate of 80 deg C/min in a "v.ch." ("high-purity") grade helium atmosphere (under a pressure of 0.5 atm).

Thermodynamic calculations showed that in the temperature range investigated all the three reactions listed in Table 1 are possible (Table 2, $\Delta Z_T^0 < 0$), the least probable being the formation of titanium carbide and boron, and the most probable, the formation of titanium boride and carbon; the greatest thermal effect per unit amount of mixture accompanies the formation of a mixture of titanium carbide and titanium boride (Table 1).

DTA curves obtained for the mixtures investigated are shown in Fig. 2. The temperatures corresponding to the first exothermic peaks for mixtures 1, 2, and 3 were found to be very close: 1440, 1475, and 1490°C, respectively. The greatest peak height was recorded for composition No. 3, calculated to give a mixture of titanium diboride and titanium carbide, and the smallest for composition No. 1, calculated to yield titanium carbide and free boron. Thus, there is a qualitative correlation between the height of the peak on a DTA curve and the magnitude of the thermal effect of a reaction per 1 kg of mixture (Table 1).

The endothermic effects observed on the DTA curves at 1800-1820°C were caused by a polymorphic transition in the material of the crucible. At still higher temperatures each of the three DTA curves shows a weak exothermic effect indicative of a slow rate of reaction in the concluding stage. It is interesting to note that the DTA curves exhibit no thermal effects attributable to the melting of titanium (1670°C).

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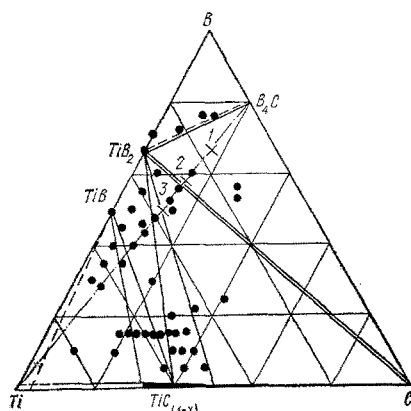


Fig. 1

Fig. 1. Isothermal section through ternary diagram of Ti-B-C system at 1400°C [5].

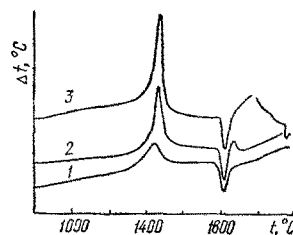


Fig. 2

Fig. 2. Heating thermograms for Ti + B₄C powder mixtures of various compositions (as shown in Table 1).

An x-ray diffraction analysis of specimens after DTA was carried out, using CuK α radiation, by the powder method in a 57-mm-diameter RKD camera. The results of this investigation (Table 3) show that the reaction products obtained during the heating of all three mixtures to 1600°C contained, in addition to the main phases - TiC and TiB₂, small amounts of boron carbide. This analysis, like DTA, revealed no titanium, but traces of the boride TiB were detected in the specimens. Thus, during continual heating to 1600°C at a rate of 80 deg C/min the reactions in the Ti-B₄C mixtures investigated proceeded almost identically, failing, under these conditions, to reach completion. Completion of the reactions was observed when the end heating temperature was raised to 2200°C (Table 3), but agreement of the composition of reaction products with a calculated composition was found only with mixture No. 3.

After DTA the specimens were porous (Fig. 3a), and consequently microhardness H μ measurements could be made only in certain areas. A specimen of composition No. 3 after heating to 1600°C was found to have light-colored, gray, and dark-gray areas, with microhardnesses of 1700 \pm 100, 3300 \pm 200, and 5100 \pm 300 kgf/mm², respectively. These values of H μ are close to the reference-book microhardness values of the following phases: TiC_{1-x} (1930-3170 kgf/mm²), TiB₂ (3370-3480 kgf/mm²), and B₄C (4950 kgf/mm²) [9].

Heating to 2200°C brought about only a negligible fall in the porosity of specimens, but changed the microhardness of their phase constituents. In the two-phase specimen of composition No. 3 (Fig. 3c) it raised the microhardness of the carbide grains to 1800 \pm 100 kgf/mm² and lowered that of the boride grains to 2600 \pm 100 kgf/mm².

Comparing the results of these metallographic examinations, x-ray phase analysis, and DTA, it can be concluded that in the Ti-B₄C system an active reaction commences at 1300°C. The reaction proceeds in the solid phase, and is accompanied by appreciable heat evolution, the amount of heat evolved depending, other things being equal, on the composition of the mixture. However, as the reaction gives rise to considerable volume changes (the decrease in volume during the formation of a TiC + TiB₂ mixture from Ti + B₄C amounts to about 10%), the reactants quickly become separated not only by reaction products but also by a continuous zone of porosity (Fig. 3d). Under these conditions the rate of reaction (as can be seen from DTA curves) sharply falls.

A study was made of the kinetics of contact reaction between dense titanium and boron carbide powder in a vacuum corresponding to 10⁻⁴ torr at temperatures in the range 1100-1300°C. The reaction resulted in the formation on the titanium surface of a TiB₂ layer (microhardness 2000 \pm 200 kgf/mm²), whose thickness grew as a function of time according to the parabolic law $y^n = 2K\tau$ (Fig. 4a). The exponent in the equation of the parabola was found to be equal to less than 2 (1.5 \geq n \geq 1.8), which was due to the formation of porous reaction products. The effective energy of activation of the reaction, determined from Fig. 4b, proved to be equal to 23,800 \pm 200 cal/mole.

TABLE 1. Thermal Effects of Reactions in Ti-B₄C System

No.	Reaction	Ti content of mixture			Thermal effect $-\Delta H_0^{298}$			
		wt. %	at. %	vol. %	Ti, kcal/mole	B ₄ C, kcal/mole	Mixture	
							kcal/mole	kcal/cm ³
1	Ti+B ₄ C=TiC+4B	46,6	17,0	40,5	30,2	30,2	292,7	1,14
2	Ti+1/2B ₄ C=TiB ₂ +1/2C	63,4	28,6	57,4	59,9	119,9	793,8	3,24
3	Ti+1/3B ₄ C=2/3TiB ₂ +1/3TiC	72,2	37,6	66,8	54,6	163,8	823,5	3,44

TABLE 2. Calculated Values of Isobaric-Isothermal Potentials of Reactions in Ti-B₄C System

ΔZ_T , kcal/mole, at T, °K, of			
500	1000	1500	2000
-28,80	-27,33	-25,10	-19,52
-56,20	-56,50	-55,75	-51,89
-53,10	-51,50	-50,90	-46,60

TABLE 3. Results of X-Ray Phase Analysis of Specimens after DTA

DTA to 1600°C		DTA to 2200°C	
TiC _{1-x} , TiB ₂ , B ₄ C, TiB	TiC _{1-x} , TiB ₂ , TiB (traces)		
TiC _{1-x} , TiB ₂ , B ₄ C, TiB	TiB ₂ , TiC _{1-x} (traces)		
TiC _{1-x} , TiB ₂ , B ₄ C, TiB	TiB ₂ , TiC _{1-x}		

To obtain plasma-sprayed coatings from a Ti-B₄C composite, mixture No. 3, calculated to give TiC + TiB₂, was employed. Powders for spraying were prepared by the following methods:

- 1) rolling* of batches of the starting mixture into strips, followed by comminution and the separation of the required fraction;
- 2) rolling and sintering of batches of the starting mixture, followed by comminution and the separation of the required fraction; the sintering temperature was lower than the initial active reaction temperature, which ensured that coarse conglomerates from the mixture components were obtained, but did not allow the exothermic reaction to occur;
- 3) cladding† of boron carbide particles with a fine titanium powder by means of phenol binders. In this case deposition was performed on basis plates preheated to 900-1000°C. Basis plates of St. 45, 1Kh18N10T, and Kh23N18 steels‡ were used.

The microstructures of the plasma-sprayed coatings are shown in Fig. 5. X-ray phase analyses showed that in the first two cases the plasma coatings contained three phases - TiC_{1-x}, TiB₂, and B₄C, although, judging by the intensity of x-ray lines, the amount of boron carbide in the plasma-sprayed coatings was much higher compared with the DTA specimens. Unlike the DTA specimens, the coatings were comparatively dense. When the presintered powder was used in spray deposition, the coatings adhered particularly strongly to the basis plates. In the third case (deposition of the clad powder onto preheated basis plates) fine-grained coatings with a typical eutectic structure were obtained, containing, according to x-ray phase analysis data, only two phases - TiB₂ and TiC_{1-x}. The presence of titanium carbide of nonstoichiometric composition in the coatings was due to a partial burning out of carbon during deposition in air.

Specimens with plasma-sprayed coatings were studied with a Cameca electron probe microanalyzer. The results obtained, together with data yielded by x-ray diffraction analysis, made it possible to ascertain the phase composition of individual structural constituents. In the three-phase coatings (Fig. 5a and b) the light-colored grains contained titanium and carbon (Fig. 6, phase 2); the gray grains, titanium and boron (phase 3); and the dark-gray grains, boron and carbon (phase 1). Thus, these structural constituents were grains of

*Powder rolling was performed at the Institute of Materials Science, Academy of Sciences of the Ukrainian SSR, under the supervision of O. A. Katrus.

†The cladding of powder was performed by Yu. A. Sidorenko and V. R. Kalinovskii at the Belorussian Institute for the Mechanization of Agriculture.

‡0.45% C, Ti-stabilized 18% Cr-10% Ni, and 23% Cr-18% Ni grades, respectively - Translator.

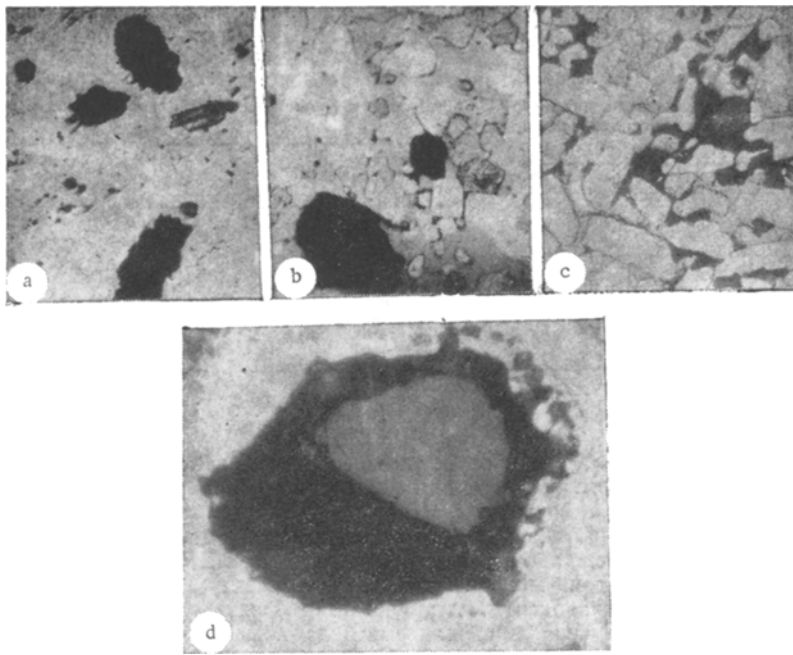


Fig. 3. Microstructures of products of reaction between boron carbide and titanium (mixture No. 3): a) 1600°C, × 500; b) 1600°C, × 1500; c) 2200°C, × 200; d) 1600°C, × 1500. Microsections: a, d) unetched; b, c) etched with HF + 2HNO₃ + 2HCl + 4H₂O mixture.

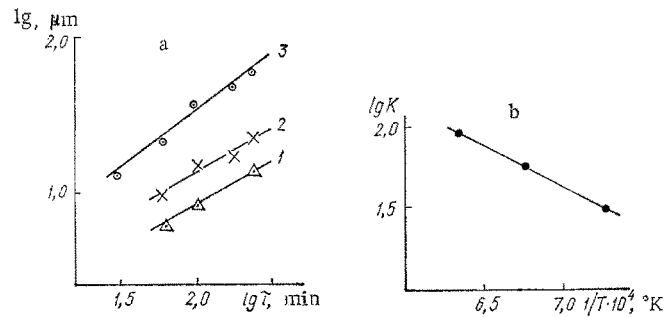


Fig. 4. Variation of constant of reaction between boron carbide and titanium in vacuum with time (a) at temperatures of 1100 (1), 1200 (2), and 1300°C (3) and with temperature (b).

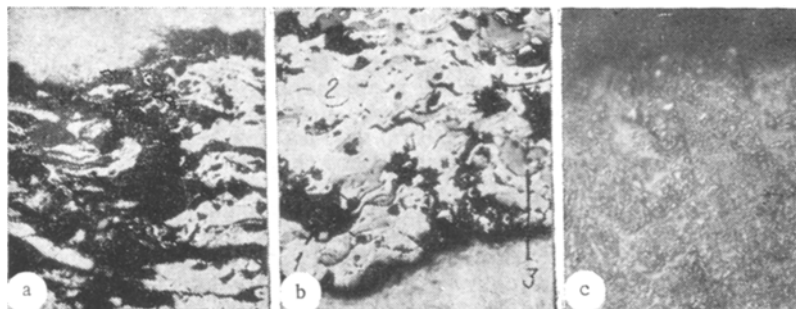


Fig. 5. Microstructures of plasma-sprayed Ti + B₄C composite coatings: a) from rolled powder, × 320; b) from rolled and sintered powder, × 320; c) from clad powder, × 500. Unetched microsections. Phases in Fig. 5b: 1) B₄C; 2) TiC; 3) TiB₂.

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MEASUREMENT OF THE THERMOELECTRIC CHARACTERISTICS OF
MATERIALS BY MEANS OF A SMALL CONTACT
UNDER STEADY-STATE CONDITIONS

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The method of measuring the thermoelectric characteristics of materials by means of a contact of small surface under pulse conditions, developed by M. Cutler [1], is simple and involves no thermal flux measurements. The principle of this method is as follows. When an electric current is passed through a specimen placed between two conducting electrodes having substantially different areas of contact (one is a point electrode, while the other has a relatively large surface), heat due to the Peltier and Joule effects is generated in the specimen in the vicinity of the point contact. The Peltier heat produced on the other contact is distributed over a large surface. The Joule heat, too, is considerable only in the vicinity of the point contact (as a result of a sharp increase in contact electrical resistance due to a compression of current lines). Local heating of a small part of the specimen near the point contact leads to the appearance of a thermoelectric voltage δV between that part and the remainder of the specimen,

$$\delta V = \frac{\alpha}{\rho\kappa} \Pi V \pm \frac{1}{2} \frac{\alpha}{\rho\kappa} V^2, \quad (1)$$

where α is the Seebeck coefficient of the specimen relative to the material of the point electrode; ρ , electrical resistivity of the specimen; κ , thermal conductivity of the specimen; Π , Peltier coefficient, $\Pi = \alpha T$; T , absolute temperature; and V , voltage applied to the contact.

From Eq. (1) it can be seen that the magnitude of the thermoelectric voltage δV is determined by the thermoelectric properties of the specimen, and does not depend on the size and shape of the point contact. This method is suitable for measurements at various temperatures. To allow for radiant heat losses (at temperatures above 1000°K), a correction coefficient is introduced into Eq. (1) [1].

The main disadvantage of Cutler's method is that it cannot be used for measuring the quantities ρ and κ simultaneously but separately. The authors have developed an apparatus (Fig. 1) whose operation is based on a combination of two methods: the usual potentiometric measurement of ρ and α by means of two thermocouple probes attached to specimens and Cutler's method used under steady-state conditions. This has enabled the expensive oscillograph to be replaced with a less costly and more accurate instrument - a potentiometer. Thus, in the course of a single experiment independent measurements are made of three quantities - ρ , α , and $\xi = \alpha/\rho \cdot \kappa$, from which κ can readily be calculated. In the determination of ξ by this method use is made of the point contact theory, a detailed description of which will be found in [1]. The method can be employed for measuring the properties of specimens produced by powder metallurgy techniques, and enables determinations of the above-mentioned properties to be made at various points on a specimen.

The specimen 1, of diameter more than 6 mm and length 10-30 mm, is placed between two conducting electrodes 3 and 4, the former being a point electrode. The design of the point contact drawn on a larger scale is shown in the circle. A 0.2-mm-diameter nickel (N) wire 8 bent into a V is held in a two-channel Alundum tube 6. To prevent deformation of the V-shaped electrode as a result of the softening of nickel at high temperatures, a drop of aluminum nitride mixed into water glass 7 is applied to the end of the Alundum tube so that the tip of the nickel electrode protrudes from the drop by not more than 0.1 mm. One of the leads of the V-shaped electrode is conducting and the other potentiometric. Current supplied to the specimen passes through a switch S_3 from a series circuit consisting of a battery B, a resistance box R, and a milliammeter

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